IFPRI Research Project Brief

Crystal Structure Transformation in Milling

The International Fine Particle Research Institute (IFPRI) wishes to fund a project to develop a molecular understanding of transformations in crystal structure observed during size reduction by milling. Milling is often the final step in production of crystalline powders--used to control the particle size distribution of the product. It is not unusual that milling also causes undesirable structural changes, in the bulk and on the surface of crystals. The mechanism of these transformations is not understood, and it is not possible to predict whether a given crystalline phase will be sensitive to milling or not. This project aims to build a mechanistic understanding of mechanically-induced plastic transformations to provide a basis for prediction of, characterization of, and potentially avoiding surface damage in milling. More specifically, the focus of the project is experimental elucidation of surface damage, localized defects, disorder and/or phase change in a brittle or semi-brittle crystalline structure caused by a mechanical shock from collisional impact relevant to impact milling.

This is an experimental project and should employ advanced imaging and/or spectroscopic tools for characterizing crystal defects (bulk or near-surface), strain, surface damage such step or void creation, polymorphic changes, and disorder. Both crystalline organic and inorganic materials are in scope, however semi-crystalline polymers are out of scope.

IFPRI Research Project "Crystal Structure Transformation in Milling"

Project presented by the MMT team of the University of Lille (France)
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Milling is mainly used to reduce the size of solid particles. However it is also able to modify the properties of materials. Upon milling, compounds (crystal or amorphous) can transform polymorphically to other crystal phases or amorphize. Sometimes a milled compound does not show a perceptible phase transformation. But the modification of its microstructural characters can be at the origin of later unexpected phase transformations.

The investigation of the effects of milling is a major part of the research activity of our team since the 2000s. Our research area is focused on the physical state of molecular materials composed of "small" molecules and/or of biological molecules. We are particularly involved in the investigation of their physical changes under various stresses: temperature, pressure, milling, dehydration. The main goal is to analyse the situations of metastabilities, the glassy states and the phase transformations and out-of-equilibrium evolutions induced by these stresses. As physicists we are interested in understanding the fundamental mechanisms that are at play in these transformations. Our investigations concern both structural modifications and modifications of molecular mobility, as well as thermodynamic impacts. We conduct these investigations from an experimental point of view. To do this the team has a wide range of experimental techniques covering all these analytical aspects.

It has emerged quite recently that process-induced changes of states play a key role in the formulation of pharmaceuticals and food materials, as well as in the field of cosmetics or molecular materials for energy and electronics. For our studies we have therefore chosen to select model compounds, with representative properties, in the vast array of molecular compounds that may have applications in these fields. Our works have direct implication in the control of the formulation and the stability of these materials with direct consequences, in pharmacy for example, on their bioavailability. Our research in this field is carried out in close collaboration with major companies of pharmacy and agribusiness. They are also integrated into European projects, for which we are responsible, bringing together the activities of companies and large academic laboratories in various European countries.

Our research, on the specific field of milling, has resulted in about 70 publications and 10 PhD theses. We have mainly investigated molecular solids which have several important advantages: They are generally easy to amorphize, their glass transition temperatures are close to room temperature they have a rich polymorphism and are very sensitive to milling effects. They show a particular sensitivity to changes in milling intensity and milling temperature. The latter are very easy to control since they are located in the vicinity of room temperature. Molecular compounds are thus good model system to study the different facets of milling induced transformations in general. We have gained good practice in their response to milling stresses with respect to both amorphization and polymorphic changes. This experience is the basis of the project that we present below.

Administrative situation

The MMT team (Molecular and Therapeutic Materials: 12 permanent researchers, 3 engineers, 6 PhD students presently) is one of the 6 teams of the UMET laboratory of Lille university (France) (UMET: Materials and Transformations Unit: 80 permanent researchers, 40 engineers, 60 PhD students)). UMET is associated to the French national research centre (CNRS).The project will be carried out under the responsibilities of Dr. Jean-François Willart and Pr. Marc Descamps. 2 PhD students will be allocated to the project.

Web page: http://umet.univ-lille1.fr/MMT/index.php?&lang=en

Available Analytical Equipments

In the team: 2 powder X-ray diffractometers. 8 DSC and modulated DSC. 2 TGA. 2 microcalorimeters, 1 Broadband thermodielectric spectrometer, 2 Raman spectrometers (T and P variable. Micro Raman). Solution calorimetry. Thermomicroscopy. Specific equipments to control aging.

+ access to all facilities of the laboratory: TEM, MEB, NMR (solid and liquid), Infra red, Mass spectrometer etc...

The team frequently uses synchrotron and neutron facilities ILL, ESRF, Soleil...

Amorphization/milling relationship

Main problems to solve

Amorphous or defective crystal? Milling a compound can cause its amorphization. There are situations where this is indisputable because of the presence of a glass transition. But it is often difficult to distinguish a true amorphous state from a highly defective crystalline state. This sometimes leads to denying the possibility of amorphizing a compound by milling. It is essential to define analysis strategies to resolve without ambiguity between these two situations.

Nature of the amorphous state: Unlike a polymorphic crystalline variety which is a stable or metastable equilibrium state, a solid amorphous compound, i.e. glassy, is in a state of non-equilibrium which depends on the history of the sample (conditions of preparation, aging etc). Because of this variability of the amorphous state and even the possibility of a polyamorphism, it is essential to find the means to determine the effect of the amorphization by milling on the physical properties of the amorphous end product, in particular its reactivity and its potential for further evolution. It is the same for the modifications induced by milling of an initially amorphous compound. An important point to resolve is to characterize and possibly distinguish the amorphous states (polyamorphism?) resulting from the quenching of a liquid, the application of a high hydrostatic pressure and from milling.

Mechanism of amorphization: The milling causes a modification of the grain sizes, but the process of transformation from crystalline to amorphous state happens inside the grain. The understanding of the amorphization mechanism requires simultaneous investigation of changes in the grain both of its microstructure and on the structural evolutions of ordered and disordered domains that constitute it. One issue is thus the question of whether amorphization is a two-phase process where the amorphous state coexists with a crystalline state residue. The amorphization would then result from an evolution of the proportion of these two phases. The other image would be that of a progressive bulk disorganization of the crystalline state.

Milling characteristics allowing amorphization. The possibility of amorphizing a compound and the kinetics of amorphization depend on the milling conditions and the physical properties of the milled compound. There is a wide variety of possible milling equipments. However, the main relevant parameters are the characteristics of the environment of the sample (temperature, humidity, etc.) and an accurately defined milling intensity. Systematic investigation of theses effects on the nature of the final state are scarce. Our past investigations have shown us that competition between mechanically induced ballistic diffusion effects (athermal) and thermal restoration effects play antagonistic roles. Their competition is undoubtedly paramount in the determination of the final state and the kinetics of the transformation. We have observed therefore that the value of the milling temperature with respect to the glass transition temperature (Tg) is crucial in many cases. We could show that a decrease of the milling temperature yields a higher content of amorphous material, while milling above the Tg favours crystal-to-crystal polymorphic transformations. However, certain compounds can not be amorphized using milling conditions for which amorphization could be expected. It is therefore appropriate to broaden the investigation by integrating these compounds in the cohort of investigated compounds and considering additional effects such as that of elastic constants and nucleation rates. This would help to permit isolation of the disordering phenomenon from its kinetic counterparts.

Some practical details

The Issues briefly underlined above are intimately mixed. To try to solve problems we propose to carry out, on representative compounds, X-ray diffraction structural analyzes, spectroscopic analyzes giving information on the molecular mobility, and calorimetric analyzes giving access to the glass transition and thermodynamic equilibrium level of the phases. If it is useful, additional microscopic analyzes, by SEM and TEM will be done.

The amorphization mechanism will be investigated using both *ex situ* and *in situ*, the latter possibility has been recently developed and uses synchrotron X-ray powder diffraction (at ILL in Grenoble and SOLEIL in Orsay). Diffraction patterns, collected in real time during the milling operation will be analyzed by sequential PDF (pair distribution function) and Rietveld refinements. This allows a simultaneous view of the development of the SRO specific to the amorphous part and to extract crystalline coherent domains attributes (including size as well as stress / strain broadening)

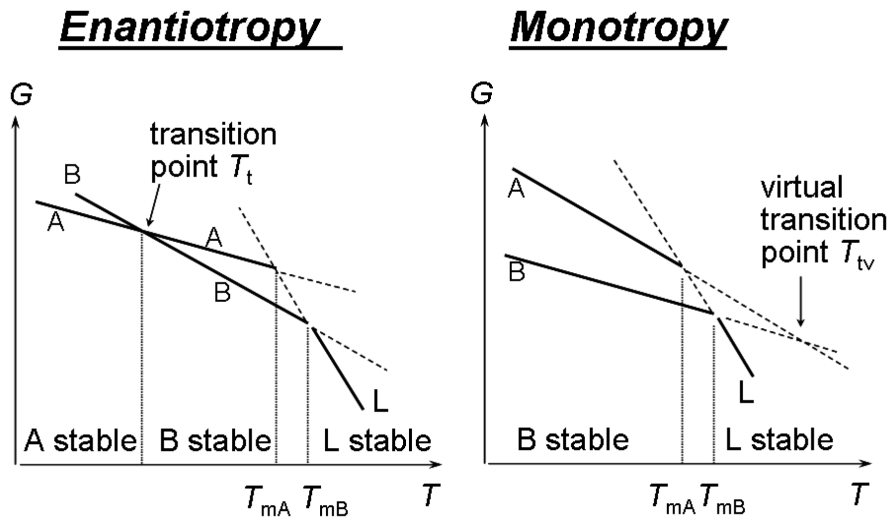
Spectroscopic analyzes will be mainly carried out by dielectric relaxation and Raman scattering. Investigation of the evolution of the relaxations as a function of temperature both above and below the glass transition temperature allows comparing the fragility level of glasses obtained in different ways. It also allows identifying secondary relaxations which reveal the amorphous character when a calorimetric glass transition is not detected. The ability of dielectric relaxation to detect very low amorphous quantities (resulting from jet- milling process in particular) will be tested.

It is possible to follow, by in situ Raman scattering, the effects of the application of a high hydrostatic pressure on a crystal. This will allow comparing the amorphization conditions and the amorphous states (polyamorphism?) that result from the application of a high hydrostatic pressure to those resulting from the application of a shearing during milling.

Calorimetry will be used first to analyze the neighborhood of the glass transition. A fine analysis of the shape of the thermograms provides a great deal of information on the nature of the glass itself. This will determine whether the glass transition (Tg) has similarities to that of a conventionally formed glass. For T <Tg, the presence of an exotherm and a sub-Tg peak reveal the effective formation rate of the amorphized compound whereas an overshoot at Tg is indicative of aging. It gives access to the fictive temperature. This technique will be particularly useful for identifying the potential reactivity level of the amorphous parts and will provide indications on the possibility of manipulating the glassy state by mechanical activation.

Polymorphism/milling relationship

Crystalline polymorphism is the ability for a compound to crystallize in several different forms: same molecule but different crystalline lattices. It may exist intrinsically disordered crystalline polymorphic varieties (such as so called "plastic crystals" or "orientationally disordered crystals". cyclohexane, ethanol or hexagonal ice are examples). But they can always be described by a lattice with long range translational order (LRO), contrary to glasses.
There are two different types of polymorphic behaviors namely monotropic and enantiotropic.



Gibbs free energy as a function of Temperature showing the stability relation between two polymorphs and the liquid phase (L): Enantiotropy (left), Monotropy (right)
Monotropy: One polymorph (B) is stable at all temperatures below the melting point, with other polymorph (A) being metastable. No reversible phase transition between the two forms. Only A --> B can be observed.
Enantiotropy: One polymorph is stable over a temperature range, the other is stable over a different temperature range. Reversible phase transition at T_t

The enantiotropic phase transition at T_t can be a first order transition (with latent heat as in the figure, much more frequent in practice) or second order one (no latent heat, no break in the G(T) diagram, singularity of the specific heat).
To be exhaustive the investigation of the link between milling and polymorphism should consider situations of monotropism and enantiotropism.

Main problems to solve

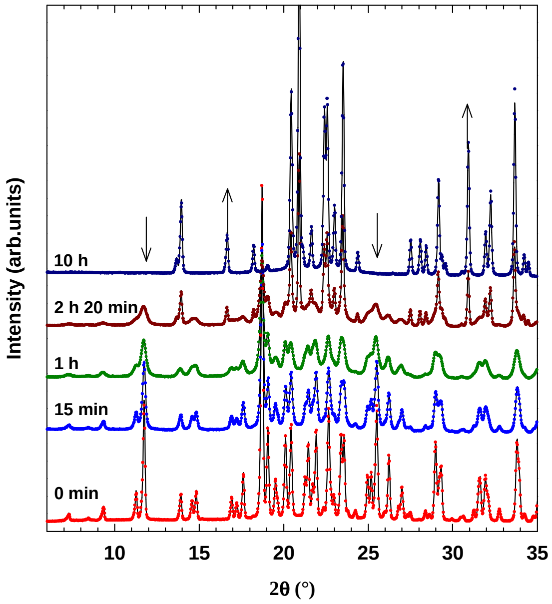
A number of questions are quite similar to those for amorphization. In addition there are situations where the effects are nested. Amorphization and polymorphic transitions between crystalline varieties could be studied profitably on the same compound when possible.
Direction of the transformation: The literature and our own experience show that milling can induce transformations from a stable state to a metastable state. But the opposite situation is also encountered. It is therefore advisable to carry out, on suitably chosen compounds, a systematic investigation of the influence of the milling variables and of the temperature in order to determine if a reversal of behavior can be obtained at some particular value of the milling variables. The role of the

structural proximity of the phases, and their relative densities, should be taken into account. In the case of an enantiotropic situation, the position of the milling temperature with respect to the transition temperature should be considered if this is practically possible.

Influence of the initial state. Uniqueness of the end product? : In the case where a compound has polymorphism and if the different phases can be prepared at the same temperature, it should be determined whether their transformation by milling produces a final state whose nature (single phase or phase mixture) depends only on milling conditions. This study should be expanded to include the glassy state as a starting or finishing variety.

Polymorphic transition or amorphization? : As an extension of the previous question, it would be useful to identify systematic and clear rules concerning the milling variables making it possible to generate phases - or phase mixtures - of different degrees of stability (or/and density).

Crystal to crystal transition mechanism: The transitions between two crystalline forms of the same compound generally involve a drastic change in the crystal lattice (1st order phase transition). In the (very frequent) case of monotropism one can not envisage, by the usual thermal way, transformation of the stable form towards the metastable form. On the other hand, milling very often makes it possible to induce this transition from stable to metastable (example of sorbitol, see figure below). The mechanism of this type of transformation is not understood in detail.



X-Ray diffraction:
Transformation of **sorbitol** during milling from the stable form (red) to the metastable form (Dark blue): the weakening of the Bragg peaks of the stable form is observed, followed by the appearance of the peaks of the metastable form. It may be noted that under milling the crystalline quality of the metastable form improves in the late stage.

The mechanism is not understood.

In a certain number of kinetically favorable cases we have been able to detect the transient development of an amorphous state. It can then be suspected that the transition from the stable crystalline state to the metastable state is mediated by the transient appearance of this amorphous state followed by the recrystallization of the metastable form.

In many cases, as for sorbitol (figure above), such a transient amorphous state is not detectable experimentally under the usual grinding conditions. The question of the mechanism of transformation is therefore totally open:

Two options are a priori possible:

1) *An amorphization* followed by a recrystallization; and, in this case, why recrystallization of a metastable phase? The life time of the amorphous state would become so short that it can not be detected in practice for certain systems and grinding conditions.

2) *A more direct transformation* by which a slip system is activated by shear and provide unit cell distorsions which facilitate the molecular rearrangement and accomplish the interconversion until a stationnary state is reached.

It is also questionable to determine whether the monotropic or enantiotropic nature of the polymorphism, which has a thermodynamic meaning, also has an influence with respect to the transformations induced by grinding.

As for the mecanism of amorphization, an other issue is to determine if the transformation is a two-phase process or results from a progressive bulk disorganization/reorganization of the crystalline state.

Some practical details

The investigation techniques of the polymorphic transitions are largely similar to those specific to amorphization and have been specified above. Moreover, it is clear that an amorphization mechanism can play a transient role in a crystal-to-crystal polymorphic transformation. An amorphization may also compete with a polymorphic transition for some milling conditions.

The first techniques of choice to be used immediately in order to characterize milled samples will be X-ray thermo-diffraction, calorimetry and thermo-Raman scattering. These techniques are available in quantity and quality in the laboratory, and in close proximity to grinding equipments. This allows for parallel investigations without delay. This is an important aspect because of the potential instability of the samples after milling.

X-ray diffraction obviously has a very important role to play in the analysis of structural transformations between crystalline varieties. Investigations will focus on microstructural evolutions by Rietveld refinement of Bragg diffraction lines. This should help to identify the particular roles played by decreases in crystallite sizes at nanoscale and lattice strain increases. It will also be necessary to carry out a meticulous comparison of crystalline structures of the different phases. This should make it possible to determine whether the two forms involved in the transition have a common slip system associated with weak values of the cohesive strength of some crystallographic planes. New in situ monitoring techniques (Simultaneous milling and Synchrotron X-ray diffraction) are expected to improve the perception of transformations and in particular to identify a possible role of an amorphous state or other intermediate crystalline phases.

In general, the possibility of changing the grinding temperature will be very useful to modify the possible lifetimes of intermediate states and increase the possibilities of identifying them. Molecular compounds that are very sensitive to near-ambient temperature variations are particularly interesting from this point of view. The comparison of milling effects for which the shears play an important role to hydrostatic pressure effects that contain no shear components can be followed in detail by Raman scattering because our equipment allows following hydrostatic pressure response up to more of 5GPa.

Kinetics of transformations. After-effects

Kinetics: During milling, the mechanical action is a discontinuous and localized process. A small fraction of the powder is actually processed at each impact. The overall kinetics of a transformation under milling is therefore very dependent on this effect. We have observed that, under milling, amorphization kinetics often have very different behaviors from polymorphic transformation kinetics. We plan to gain a better understanding of this phenomenon, which should help to better understand and control the mechanisms at stake and also to provide predictive tools.

After-effects: Limited millings that do not induce perceptible phase conversions can however have a significant impact on subsequent transformations, especially during heating. For example, a slight grinding of a glass can lead to changes in the nature of the phases which recrystallize. A slight milling of a crystalline phase can induce new kind of phase transformations under heating. Milling thus provides an additional possibility of exploration of physical states that may be useful for screening of polymorphs and their relative stabilities. This effect will be studied during the project.

Milling methods

It is possible to change the impact/shear ratio by changing the type of the instrument or by varying the milling parameters using the same mill (frequency of vibration, rotation rate of the disc, rotation rate of the vial holder etc.). Three mill types with different impact/shear ratios will be used: a Single ball vibration Mill operating at different temperatures, an air Jet Mill, and several Planetary Ball Mills which provide a sizeable shearing contribution. Particular care will be taken to vary and control the surrounding temperature of the mills and the atmosphere inside the milling jars. We will use the possibility of placing the milling instruments in a humidity-controlled cold room where it is also possible to prepare the conditioning of the milled compounds for subsequent analyzes.

Very powerful *in situ* high energy synchrotron powder diffraction during milling is available recently. This new technology should provide very important additional opportunities in the understanding of solid-state processes under milling. We have gained a good experience of this new method for studying both amorphization and transition between crystalline phases. We plan to use it for this project. While powerful, this technology remains underdeveloped. It will be necessary, on the one hand, to contribute to improving the design of containers (X-ray transparent, mechanically durable and thin enough) and, on the other hand, to evaluate the available milling intensities.

It would be interesting to test the response of compounds to millings made in industry (Jet milling in particular) with the help of IFPRI participants.

Compounds to study

To ensure the broadest and most comprehensive investigation, systems will be selected to represent the widest range of responses to milling. As a result of our previous works, we will be able to optimize the choice of representative compounds. In particular it will be taken into account the Tg value of their amorphous form and their ability to develop well-identified surface and volume amorphizations. Carbohydrates, several mono and disaccharides (glucose, trehalose, lactose...) and a lot of pharmaceutical active compounds (indomethacine, carbamazepine, griseofulvine ...) will offer a variety of interesting systems. Saccharides that give hydrates will specifically allow analyzing the effect of moisture content on the amorphization capabilities. Difficult to amorphize compounds will be added to the cohort to clarify the role of elastic constants (e.g. hexamethylenetetramine) or nucleation rate (e.g., caffeine). Polyols (sorbitol, mannitol, arabitol...) have a rich polymorphism and they have glass transition temperatures (Tg) fairly close to room temperature which makes it easy to test the sensitivity of the compounds to the milling temperatures. Caffeine and Chlopropamide will be specifically studied because of their ability to present an enantiotropic phase transition in the solid state.
It will be also possible to consider the study of interesting compounds proposed by members of IFPRI

Brief summary of objectives

- One aim is to clearly define the relative influence of the ballistic (athermal) effects related to mechanical actions on the one hand and the effects of thermal restoration on the other hand for the different types of transformations induced by milling.
- A second aim is to clarify the role of shears and hydrostatic pressure on phase transformations, amorphization capacity and nature of the amorphous state.
- The final goal is to be able to draw a phase diagram which integrates these types of parameters and has a predictive ability.

Many theories compete to describe the physical transformations under milling using arguments founded on thermal equilibrium considerations. They are based on the expression of a "constrained free energy" where the internal energy would be increased by the contribution of stored defects or by the increased effect of surface free energy when nanosizes are reached. However these theories have a lot of shortcomings because transformations under milling do not occur at thermodynamic equilibrium. The proposed experimental study is guided by the fact that it can ultimately help to build a more realistic theoretical approach.

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Crystal Structure Transformation in Milling

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Milling of crystalline materials is a common top-down approach to achieve a desired particle size during industrial processing and development. It is well known that in doing so, a whole range of bulk and surface changes can occur in crystalline solids which can subsequently affect further processes. However, it should be noted that the degree of milling induced changes in crystal lattice is material specific and depends on several processing parameters. Moreover, the driving forces and mechanisms for the transformation of crystalline particles during and post milling are still poorly understood and difficult to predict. This project seeks to develop a scientific understanding of these complex transformation mechanisms and address the key gaps in the existing knowledge.

Overview into current state of art on milling induced transformation

The current state of research on milling of solids revolves around two main aspects namely, particle breakage and induced physicochemical transformation/s. Crystalline solids subjected to mechanical processing, like milling, are expected to generate structural disorder and deformed states. Although a size reduction operation, it can cause a wide range of secondary and sometimes unwanted physicochemical changes in particle properties, in particular, introduction of defects, amorphisation and polymorphic transformations. These changes ensuing bulk and/or surface of the solids. Some of these significant changes in crystalline solids are depicted in Fig. 1.

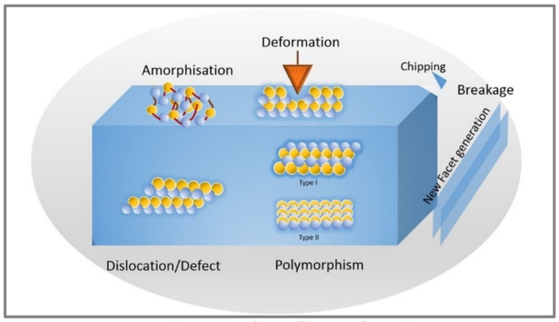

Fig. 1 Types of crystalline transformations

The most commonly observed adjunct change in milled crystalline materials is the occurrence of small degree of amorphisation, especially on the vicinity of the surface stress event [1,2]. Luisi et al. (2012), have also suggested that certain intermediate phases coexist in milled materials instead of two distinct crystalline and amorphous phases [3]. Another phenomenon which has intrigued researchers over the years is the milling prompted polymorphic transformation in the crystalline solids. Descamps and co-workers from their work have reported such polymorphic conversions in a wide variety of crystalline materials [4,5].

In addition, the mechanical stresses imparted could result in abrupt changes in surface textural and energetic properties of particles [6–11]. Often, milled material also has the most active surface, making it more interactive with other surfaces. Further insight provided on such milling induced surface evolution put forward a heterogeneous surface energy landscape that can affect interparticle interaction [12,13].

Although crystalline forms are preferred in industries due to the reasons of stability, it is in common knowledge that mechanical treatments such as milling could result in a stability problem by increasing the level of defects or disorder and phase transformations. Researchers have found that often the solid-state stability appears to correspond to the crystallinity or contrarily, to the extent of disorder in that material [14]. The mechanical treatment exposes the solids to a large variety of perturbations in the physicochemical properties and the associated thermodynamic vulnerability of the activated solids can result in the spontaneous recrystallization with time. Furthermore, altered interfacial interactions (adhesion/cohesion) in milled particles could result in problems like processing delays, increased cost and lower yield.Studies have also proposed that anhydrous forms of crystalline solids are more prone to amorphisation as compared to their hydrate forms [15]. Moreover, scientists have also reported alterations in the magnetic, electrical and electronic properties of inorganic materials like alloys due to high mechanical deformations induced from the milling treatment [16]. Besides, it has been reported that high mechanical stresses could also lead to release of bound water in some cases.

When it comes to the predictive approaches, the majority of research work in milling is focused around utilisation of energy input-size reduction relationship. As a result, early attempts have led to development of several empirical size reduction laws (Rittinger's, Kick's and Bond's law) correlating energy input with the particle size parameters. However, seldom these laws apply well in practical situations. From a molecular perspective, researchers have also tried to explore the use of crystal inter-planar d-spacings and slip-plane interaction energies for predicting and characterising mechanical properties of crystalline solids [9]. Sun and Kiang (2008) proposed that precautions in the selection of appropriate force field must be taken while using attachment energy calculations for identifying the slip planes or cleavage planes in organic crystals on milling [17]. Heng et al. (2006), investigated the milling of paracetamol crystals and observed an increase in the dispersive component of surface energy upon milling. It was argued that upon milling, crystals fracture along the weakest attachment energy planes, which is known to be the most hydrophobic and have high a dispersive component of surface energy [18]. Moreover, the importance of crystal habit and crystal anisotropy in milling and breakage cannot be understated [19].

Overall, it is clear from the literature that not a lot of work has been done on understanding the milling induced changes from surface properties perspective of the milled crystalline solids. Also, there is a vast scope for understanding the localised deformation and the associated residual stresses in different milled crystalline solids from the material properties and processing conditions viewpoint. As far as process optimisation and prediction capabilities with regards to crystal structure transformation in milling are concerned, the present methodologies lack systematic understanding of the process as well as the materials involved. The intrinsic difficulty in predicting the complex nature of the properties of the resulting solids post-milling again lies in uncertainty and poor understanding of mechanisms creating the vast spectrum of crystalline disorders. Thus, it becomes imperative to develop an efficient integrated analysis framework for an in-depth understanding of the properties of disordered crystalline solids.

Current practices in advanced physicochemical characterisation of milled crystalline solids

To discern the milling promoted transformations in crystalline solids, several recent efforts have concentrated on developing methods to follow in situ bulk and surface alterations. Particularly, powder X-ray diffraction (PXRD) is the go-to analytical technique in most studies, when it comes to elucidating crystalline disorder [20]. Once the solid phase and structure identification is established, spectral methods like Fourier transform spectroscopy (FTIR), UV-Vis spectroscopy can be used for further examining the nature of crystalline disorder. Thermal methods also play a significant role in characterising the crystalline transformations and these include differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and hot stage microscopy (HSM). However, these techniques are not always adequate to quantify low levels of disorder or amorphous content and focused predominately on the bulk aspect of the crystalline material. Advanced techniques like solid-state NMR (ssNMR) has shown usefulness for quantitative amorphous characterisation of milled solids. Similarly, Raman spectroscopy, for quantifying the density of lattice defects and identifying the surface amorphous domains, is another potent tool to aid solid state characterisation.

On the other hand, for the characterisation of structural or physical properties, several microscopic and spectroscopic techniques are employed. Thus, imaging techniques like SEM, polarised light microscopy, TEM, usually coupled with other complimentary techniques, are used to elucidate the surface features and damage of milled crystalline materials. Single particle analysis tools such as Atomic Force Microscopy (AFM) are mostly employed for the study of defects in crystalline materials. The technique allows for very accurate studies, both in dry or wet conditions. Besides, optical scanning technique like profilometry can be used to image the surface texture of the milled and deformed surfaces. Likewise, to gain information on the mechanical properties of crystalline particles from their fracture mechanics and breakage behaviour, single particle impact loading tests using nano-indentation technique are frequently performed [21]. However, owing to the anisotropy in crystalline properties, due considerations should be given to the crystallographic structure and crystalline planes during analysis [22]. Another drawback of these analytical tools could be their inability to assess large amount of material, representative of the sample, often leading to bias.

Moreover, adsorption-based techniques, such as inverse gas chromatography (IGC) and dynamic vapour sorption (DVS), appear to have found the potential to provide quantitative data on the number of surface defects present in crystalline materials, along with the surface energies associated with them.

Engineering the analysis for crystalline transformations

Experimental and modelling works done previously have not decoupled the surface effects from the bulk body breakage properly. Moreover, organised study at different length scales and/or in different time domains (eg rates/kinetics vs equilibrium) is missing. Hence, before commencing a systematic investigation to establish facts and reach new conclusions on physico-chemical transformations of milled crystalline materials, it is imperative to break down the overall methodology to the following aspects.

1. Understanding the extent of crystalline transformations

In milling processes of crystalline solids, the disruption or transformation of crystalline structure often leads to varying degrees of disorder. From a practical viewpoint, the different levels of disorders could be classified as below.

- ***Minor disorder***: This disorder includes small perturbation of crystalline order like lattice defects and dislocations, including exposure of new crystalline facets. In one of our earlier works demonstrating the anisotropic properties of milled crystalline materials, Heng et al. (2006), reported that on milling of paracetamol, the dispersive component of surface energy increased with decreasing particle size and it was attributed to the surface energy of the weakest attachment energy plane exposed during milling.
- ***Major disorder***: This degree of disorder corresponds to a marked departure from the existing crystalline order, eg. phase transformation (polymorphism, hydrate formation and amorphisation) of materials. Moreover, it is important to state that both the above degree of disorders and the intermediate states can also occur simultaneously.

2. Decoupling surface and bulk changes

The ability to decouple contributions of surface vs bulk will be key in developing understanding of the respective transformations in milled crystalline solids. Reduction of particle size by milling cause increase in surface area and surface energy of particles, which consequently promotes adhesion of particles. In one of our recently reported works on powder cohesion, we decoupled the effects of milling on surface energy from surface area. Normalisation of surface energy of milled mefenamic acid crystals using silanisation approach was achieved to decouple the surface energy and surface area effects on powder bulk behaviour [23]approach was successful in decoupling the role of surface energy and surface area, other surface alterations like textural changes (roughness and deformation) as well as surface amorphous regions could be targeted. Likewise, the influence of transformational effects in particle shape, crystalline facets, surface chemistry (acid-base properties) could be elucidated.

3. Interplay between environment and multiple length-time scales in crystalline transformations

Milling can cause numerous changes in a crystalline solid, as mentioned previously, and the majority of these begin at the surface, which may later propagate to the bulk of the particle. The length scales and domains over which such order and disorder persist is also important. As it can be conceived, even in amorphous materials, a short-range order exists due to chemical constraints. Milling can thus induce disorder in the crystalline form but induce order in its amorphous form. Also, the surface chemical environment becomes important during milling.

Moreover, the external environment can either assist or resist the process related material transformation. Many of these transformations can result from an interaction of stresses in material and the environment. These effects can be physical, principally irreversible plastic deformation, or chemical such as phase change due to the adsorption of vapours in the disordered domains. In one of our previous works, we reported that milling temperature may affect the particle mechanical properties (elasticity/ brittleness) resulting in significantly higher surface area for cryogenic temperatures compared to room temperature milling conditions (Shah et al., 2015).

Certainly, in order to investigate the milling induced transformations in crystalline solids at different levels, comprehensive strategies to carefully control the disorder and employing suitable technique/s to probe milled solids is needed. Thus, designing the methods and selecting the conditions that create different degrees of disorder and/or in different domains as well as analysing them at this level is important.

Hypothesis and critical unknowns

The abrupt and complex nature of changes in milled solids pose a serious challenge in predicting the outcome from the operation. Thus, it becomes essential to develop a better framework for understanding the bulk and surface transformations in milled crystalline materials from molecular level perspective.

1. Generation of new surfaces

It is observed that milling results in the generation of new surfaces exposing different crystal facets varying in facet specific surface energy, defects, generation of high energy amorphous regions or a combination of any of these. As far as cleavage planes are concerned, it is often argued crystals fracture along weakest attachment energy planes, which are known to be the most hydrophobic. However, the importance of crystal habit and crystal anisotropy in milling and breakage also cannot be understated. ***Unknowns:*** Crystal slip planes, attachment energy predictions, influence of crystal habit, anisotropic mechanical and chemical properties of crystals.

2. Generation of metastable regions

The disorders created due to the mechanically intensive processes like milling provides the required space and energy for solid state transitions. For example, a small amount of amorphous content or surface cracks/defects in the crystalline solid is likely to be exacerbated through processes like milling. At the molecular level however, the mechanisms by which milling creates low levels of amorphicity remains unclear. Investigators believe that molecular level disorder generated during milling is the main source of free energy storage, considered as a driving force for phase transition to amorphous nature. Recently, researchers have also indicated that the milling prompted transition from crystalline to partial amorphous nature could occur through intermediate crystalline mesophases [24]. The presence of such metastable regions often prompts stability issues and pose a concern post milling operations. ***Unknowns*****:** Critical material attributes, methods applied and extrinsic conditions that create localised disorder/s or damage. Sensitivity of tools and techniques to capture these alterations.

3. Non-equilibrium nature of materials/ Dynamic behaviour of processed materials

Milling induces an extensive disruption of the local arrangement of the molecules and different levels of energy are transferred to the particle in the impaction processes. These changes beginning at the surfaces, often in the form of lattice defects, then propagate or migrate to the bulk of the particle. The molecular level changes occurring are exhibited as a form of relaxation behaviour and thermodynamically speaking, the system fluctuates from moment to moment. Moreover, materials can transform or heal over a period post milling, sometimes aided by external environmental conditions. Such dynamic behaviour, in the form of disordering and reordering of materials over a period of time or due to extrinsic factors, involves complex mechanisms and pose a great challenge for the study and understanding of processed solids. ***Unknowns:*** How these materials evolve and transform? The rate of transformation or time dependent changes. Difficulty in predicting change, e.g., size, phase change etc.

Research Objectives: The overall research objectives of this project are i) to develop an integrated framework for identifying and characterising the nature of disorder in milled crystalline solids, ii) to gain a mechanistic understanding of the molecular level events initiating the transformations for predicting the outcome of milling operation and iii) to investigate the non-equilibrium/dynamic nature of processed materials.

Project Planning (Work packages)

WP1: Identification of materials

Selection of possible crystalline materials will be done following consultation with IFPRI members covering the industries of interest. The materials will be screened for different particulate attributes like crystalline habit or shape, size (particle or granule), chemistry (organic or inorganic), susceptibility for polymorphic transition and tensile properties (elasticity and plasticity) etc. The idea is to undertake comprehensive characterisation of the feed materials (pre-milling) in order to tease out the differences in these samples post-milling.

WP2: Processing of the selected materials

Keeping in mind the objectives of this work, considerable efforts will be invested in pre-processing or pre-treatment of crystalline materials. This preparative component of the work will include selection of specific feed material and impact mills like ball mill or fluid energy mill to introduce controlled disorders caused by the mechanical shocks of the collisional impact. The sample preparation process will be optimised by modulating different material and process parameters like particle size, shape, energy input and time of milling as well as through external processing conditions like temperature and humidity. Also, commonly known empirical models will be used to examine the performance of the operation and for generalizability of these findings to a range of conditions used in other mills.

WP3: Analysis of the type and extent of milling induced transformations

An extensive study on the complex nature of surface and sub-surface properties of the crystalline solids post milling operation is planned. In this multi-tier evaluation proposed (Fig.2), the first step would involve crystal structure determination using microscopy and diffraction techniques. Microscopy (optical and electron) will be used for crystal habit, size and surface texture investigation and PXRD for crystalline nature, degree of crystallinity, polymorph identification and stability analysis. Moreover, these techniques will thus provide the first hint about the type/s of crystalline disorder. The next step will involve understanding the nature of crystalline disorders like defects, polymorphic form, amorphisation, dehydration or hydrate formation. This will be done employing a combination of different spectroscopic techniques like IR, Raman and ssNMR alongside the thermal methods like DSC and TGA. For comprehensive elucidation, the third-tier of analysis (depicted in Fig. 2) will predominantly focus on surface properties and damage caused in milled crystalline solids, which will be covered under WP4.

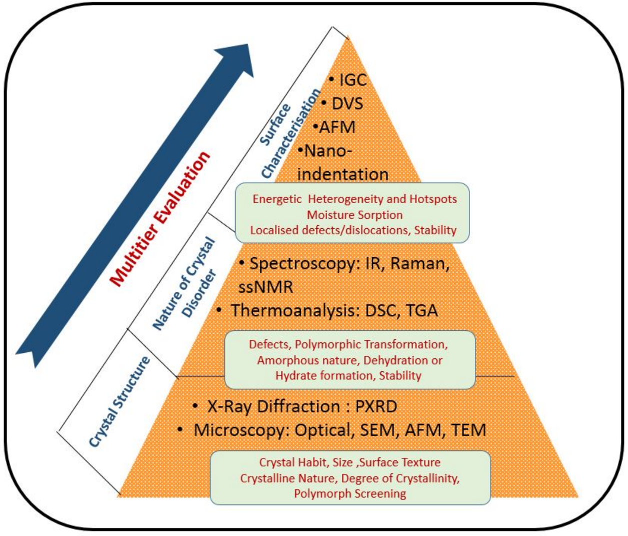

Fig. 2. Multitier approach for evaluation

WP4: Characterisation of mechanically induced surface changes

As mentioned earlier, this WP primarily focuses on the milling induced surface transformations in selected crystalline materials. In addition to the conventional analytical techniques several advanced probing tools will be employed to investigate the surface properties of milled solids.

- Surface energy evolution: Inverse Gas chromatography (IGC) to characterise energetic hotspots and heterogeneity of the damaged/disordered surfaces. These hotspots might be a consequence of crystalline disorders, like localised defects, phase change and surface stress. Finite dilution IGC (FDIGC) approach will provide the heterogeneity of the processed surfaces alongside the acid-base properties from the exposed chemical moieties which will be determined using polar probes. Measurements on milled samples with normalised surface energies, achieved through surface modification, will uncover the localised energetic domains generated.
- Surface amorphous regions: Dynamic Vapour Sorption (DVS), in combination with in-situ Raman spectroscopy and/or AFM morphological imaging, will be used to identify the surface amorphous domains. (Note: Both IGC and DVS tools will enable us to analyse the representative sample of the large population of particles produced after milling.)
- Facet specific studies: To study the deformation characteristics of crystalline material, nano-indentation experiments on different facets of single crystals will be performed. Similarly, these facets will also be probed for regions of localised density of defects or dislocations using AFM.

Some of the data generated and information gained in WP3 and WP4 will be incorporated in the subsequent WP's to facilitate design of experiments (DOE).

WP5: Investigating dynamic behaviour of thermodynamically activated solids

This work package will primarily focus on the time dependent evolution of milled materials with the influence of environmental conditions on its behaviour. The fresh surfaces of the milled solids will be exposed to varying moisture and temperature conditions to examine critical conditions for dynamic behaviour like spontaneous annealing or recrystallisation of the surfaces. To achieve dynamic measurements, multiple samples will be exposed to the pre-set conditions and analysis will be done at different time points in order to establish repeatability and accuracy of measurements. Investigations will be performed on multiple samples under both accelerated (ramped) and long-term (sustained) conditions. In addition to such continuous conditioning profiles, inspections under cyclic conditions of temperature and humidity are planned.

WP6: Studying influence of processing conditions

The milling experiments will be performed at ambient and cryo conditions, to compare the effect of processing temperatures on the nature of crystalline transformations. Additionally, experiments under humid conditions or in presence of other grinding media are also planned with selected crystalline materials. Subsequently, whenever relevant, studies with varying processing parameters like feed rate, mass of feed, milling time and milling speed will be covered.

Existing programs and infrastructure to leverage impact

The work packages are proposed for a dedicated PhD student in Years 1-3 with a second PhD student in Years 4-6 (see Appendix for Work Plan). This project will be leveraged with the following existing projects and PhD studentships at Imperial College London (ICL).

- EPSRC funded project (EP/N025261/1) *Virtual Formulation Laboratory (VFL)* for prediction and optimisation of manufacturability of advanced solids-based formulations. The project involves a dedicated post-doctoral research associate (PDRA) at Imperial College London and 4 additional PDRAs based at University of Leicester, University of Leeds and University of Greenwich.
- Two EPSRC iCASE Studentships with two pharmaceutical companies looking at the manufacturability of powders focusing on the powder surface properties related to the mixing and sticking of pharmaceutical solids.

Our laboratory at ICL has a well- established infrastructure and proven track record of research in the area of surface chemistry, particle engineering and interfacial phenomena. Research activities include studying the influence of particle engineering operations like milling, crystallisation on surface properties of solids, employ modelling tools for the predictions and control of these operations and the development of inverse gas chromatographic techniques to determine surface energy characteristics of powders.

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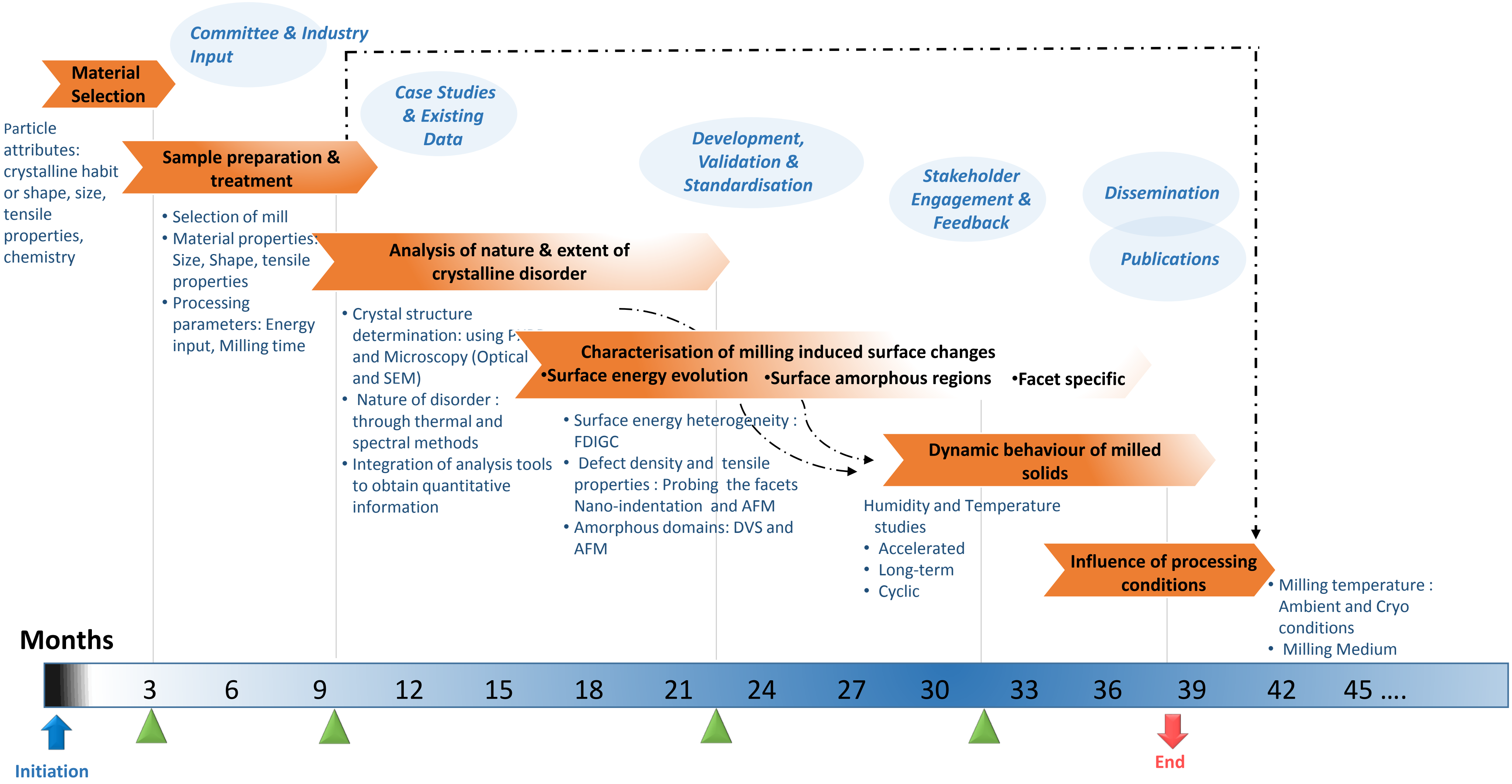
Proposed Workplan



Committee & Industry Input

Material Selection

Particle attributes: crystalline habit or shape, size, tensile properties, chemistry

Sample preparation & treatment

- Selection of mill
- Material properties: Size, Shape, tensile properties
- Processing parameters: Energy input, Milling time

Case Studies & Existing Data

Analysis of nature & extent of crystalline disorder

- Crystal structure determination: using P and Microscopy (Optical and SEM)
- Nature of disorder : through thermal and spectral methods
- Integration of analysis tools to obtain quantitative information

Development, Validation & Standardisation

Characterisation of milling induced surface changes

•Surface energy evolution •Surface amorphous regions •Facet specific

- Surface energy heterogeneity : FDIGC
- Defect density and tensile properties : Probing the facets Nano-indentation and AFM
- Amorphous domains: DVS and AFM

Stakeholder Engagement & Feedback

Dynamic behaviour of milled solids

Humidity and Temperature studies

- Accelerated
- Long-term
- Cyclic

Dissemination

Publications

Influence of processing conditions

- Milling temperature : Ambient and Cryo conditions
- Milling Medium

IFPRI Research Project Brief

Mechanism of Formation and Growth of Powder Layers on Process Equipment Surfaces at low Stresses

The International Fine Particle Research Institute (IFPRI) wishes to fund a project to elucidate the mechanism(s) of initiation and growth of powder layers on surfaces of process equipment under low compressive or shear stress. This project is motivated by a common process issue in powder processing, sometimes called "make-up": the formation of thick, immobile layers of powder adhering to walls and internals of equipment such as chutes, silos, pneumatic conveying lines, dryers, mixers, and furnaces. The main objectives of the project are to understand the mechanisms for "nucleation" of a thin powder layer and its growth or death with attention to environmental conditions, surface properties, and mechanical stresses at the surface. It is expected that the project will have a major experimental component involving the development of appropriate experiments with well-characterized and controlled flow and environmental variables.

Investigation of environmental variables (humidity, temperature), wall properties (roughness, hardness, surface chemistry), particle properties (morphology, mechanical properties, surface properties), surface interactions (dispersive, hydrophilic/hydrophobic, electrostatic) are all potentially in scope. Static systems (i.e. caking of powders) and layer formation at high stresses (i.e. in die compaction or extrusion) are out of scope. While the use of highly idealized particles like glass ballotini may provide useful insight into mechanisms, we request that such idealized experiments be balanced with experiments using more realistic (but still potentially simplified) powders.

IFPRI Research Proposal

Understanding formation and growth mechanism of thick powder layers on process surfaces

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Summary

Deposition of powders on the surface of process equipment (process surface) is very common phenomena across industries. While at the initial stage of the layer formation is due to very loosely adhered particles on the process surface, under the influence of the prevailing environmental and process condition, the layer becomes thick and immobile which creates problems in chutes, silos, pneumatic conveying lines, milling machines, dryers, mixers, furnaces etc. Though the phenomena is very well known across industries, there exists lack of scientific knowledge to understand the formation mechanisms of the thin powder layer (“nucleation”) and its growth or death under various process and environmental conditions In this proposal, it is proposed to explore the undelaying scientific knowledge which dictates the formation and growth of the undesired powder layers which creates severe problems in the powder handling industries.

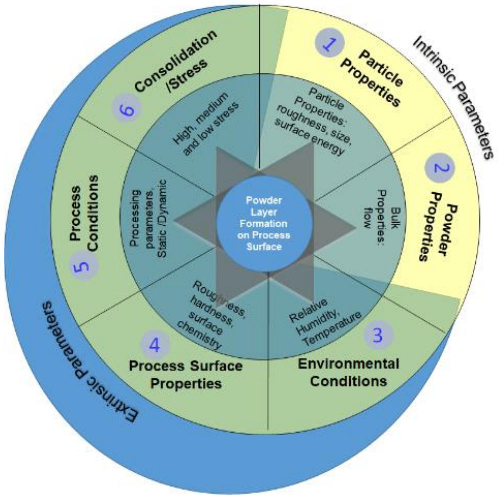

Figure 1: Powder 'horoscope'

The study aims to correlate various particle properties (1) and powder bulk properties (2) under different environmental conditions (3) and their interaction with equipment surface (4) during various processes (5) of different consolidations (6). The effort will establish the formation and growth kinetics of powder layer on the equipment surface. The work will help the powder industries to identify the critical parameters in the powder ‘*horoscope*’ (shown in Figure 1) and predict the powder layer formation on processing equipment at the different process and environmental condition. The study has also an enormous implication to solar energy industries where dust deposition on the solar panel reduces significant energy production. The results of the study will help industries to take appropriate cleaning strategy to reduce particle deposition on the process equipment as well as solar panels.

1. Background of the proposed research

Powders form an important component in various industries like pharmaceutical, cement, food, minerals, fertilizers, paints, dyes, catalysts, additive manufacturing industries etc. Majority of these industries process different fine powders which often belong to group C powder (Geldart, 1973). The various unit operations in the powder industries are mixing, agglomeration, drying, comminution, fluidization, granulation, separation etc. along with its storage (silos, cans, bags) and transport (feeders, hoppers, conveyors). The powder processing through process equipment results deposition of fine particles on the equipment surface (process surface) due to strong adhesion between process surface and particle surface under the prevailing consolidation, process and environment conditions (categories here as extrinsic parameter such as RH, T, consolidation or stress, static or dynamic condition etc.). These adhered particles on the process surface grow over time (Figure 2) and create the problem in powder operation.

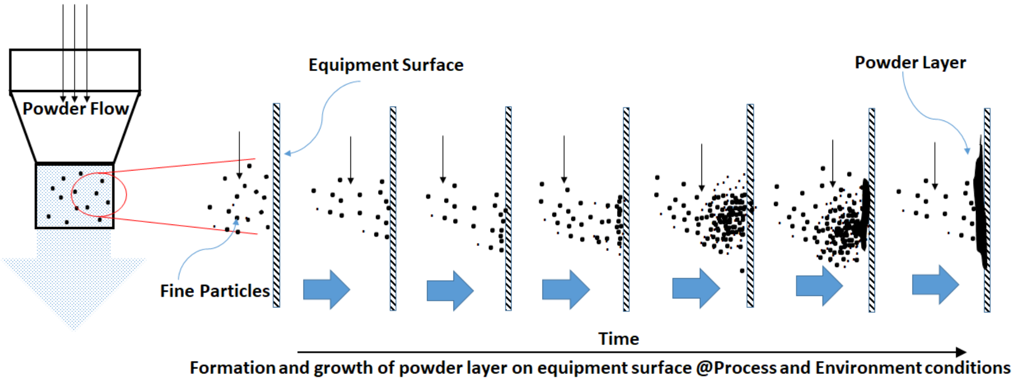

Figure 2: Schematic of powder layer formation (probable mechanism)

The phenomena influence by various physicochemical properties of particles (such as particle size and its distribution, shape, surface area, density, surface roughness, surface chemical groups, surface charge and surface energy) and bulk powders (flow, compressibility, packing) (Ghoroi et al., 2013; Shah et al. 2017) which are categories here as intrinsic parameters. Both intrinsic and extrinsic parameters (detail parameters of powder horoscope shown in Figure 3) influence the inter-particle interaction forces which ultimately affects the adhesion or sticking property of the particles among themselves (form the agglomerates) and on the process surface as shown in Figure 2. The inter-particle interaction forces like van der Waals forces, electrostatic force, capillary force and solid bridge force affect the powder bulk properties like powder flow, compaction and particle interaction with process surface. Though the attractive inter-particle interaction is desired for specific application such as granulation, roll compaction, the coating of particle, it is undesirable during handling or processing of highly cohesive powders which causes unwanted processing problems and losses such as powder build-up on the process surface, loss of powders, product quality. Though there are few studies on particle properties to bulk powder properties (two intrinsic properties: Region 1→ Region 2 in the powder horoscope) (Shah et al. 2017), but their influence on powder layer formation on process surface is mostly unavailable in the literature.

In addition to the inter-particle forces between particles, there are also different stresses involved namely, tensile stress (pulling force), compressive stress (pushing force) and shear stress (force acting parallel to the motion) during powder handling and processing operations. Friction could become dominant inter-particle interaction in powder flow, especially in dry conditions (Castellanos, 2005) referred as dry friction (coefficient of friction, µ). Sometimes, this friction also generate the stick-slip type of friction which is highly undesirable phenomena in many powder handling industries (Roberts and Wensrich, 2002).

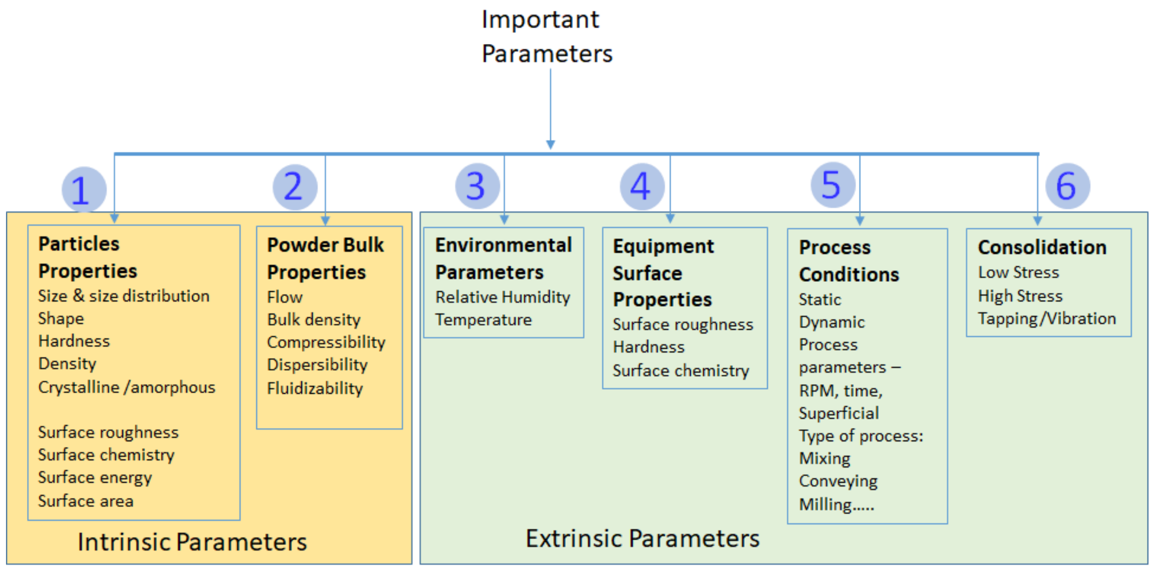

Figure 3: Details parameters which influences the powder layer formation in process surface

The extrinsic properties such as atmospheric humidity greatly affect powder materials due to the presence of unbound moisture, which is available for chemical or physical interactions (Karde & Ghoroi 2015; Bravo-Osuna et al., 2007; Faqih et al., 2007; Zografi G., 1988). Moreover, these interactions are also influenced by the frictional force between particles and between particles and contacting equipment surface. Presence of humidity, temperature, stress and the type of the process increases the interactions which are undesirable during transport, storage and in the feed systems. Humidity can also influence the van der Waals forces. Coelho and Harnby (Coelho and Harnby, 1978) found that the van der Waals forces are strengthened by adsorbed moisture because the added thickness of moisture layer decreases inter-particle distance by increasing the apparent diameter of the particle. It is well known that at the higher relative humidity (RH), capillary forces may contribute largely to the inter-particle adhesion forces. However, the actual impact of humidity on adhesion may depend on number of factors like particle size, shape, roughness, material properties like elasticity modulus, hardness along with packing or consolidation state of powders and surface properties of the process surface (Butt, 2008; Cleaver and Tyrrell, 2004; Farshchi-tabrizi et al., 2006; Paajanen et al., 2006). Also, the electrostatic interactions decrease in presence of moisture due to the dissipation of charges through conductive properties of water molecules. In some cases, the moisture adsorbed on the surface could lead to increase in flowability owing to the lubrication effect of the moisture film and as a consequent reduction in inter-particle friction and mechanical interlocking (Coelho and Harnby, 1978; Crouter and Briens, 2014). The resultant effect may be either an increase in the inter-particle capillary force at high humidity conditions or increase in other forces such as friction, van der Waals and electrostatic at low humidity (Emery et al., 2009; Rowley and Mackin, 2003), all of which could create complications in powder processing or handling. However, not much work is there on particles interactions on process surfaces under these external variables.

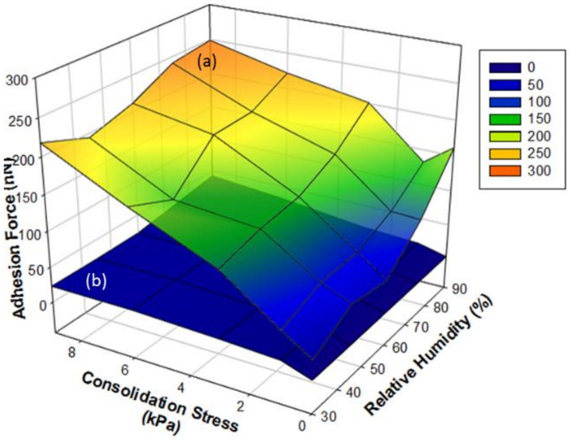

Figure 4. 3D plot depicting experimental inter-particle adhesion forces under varying humidity and consolidation for (a) as received or uncoated and (b) nano-silica coated corn starch powders

In addition, the compressive stresses in powder bed influence powder behavior to a great extent (Valverde et al., 1998), especially in cases when the powder is stored in silos, hoppers etc. These compressive forces developed during storage, handling or processing are an important consideration while determining particle adhesion. Depending upon the industrial processes involved, these compressive stresses exerted could vary from very high (during compaction) to lower values (during mixing, separation, dispersion, fluidization). Further, the introduction of humidity could make the situation much more complex. As such, the typical effect of humidity on powder bulk behavior is familiar to powder flow community (Crouter and Briens, 2014; Emery et al., 2009; Mollan and Celik, 1995). However, a combined effect of humidity and applied consolidation on powder behavior under different temperature is not studied well. In such cases, the estimation of total adhesion forces in powders exposed to different RH conditions at varying compressive stresses can provide a much better understanding of powder flow for different applications and its interaction with process surface. Our recent investigation of humidity influenced frictional behavior of corn starch powder under varying consolidation stress and its effect on the bulk behavior within the relative humidity conditions ≤60% (Karde & Ghoroi 2015) indicates that for as received powders at low consolidation stress, the contribution from the inter-particle capillary forces is greater to the total adhesion forces (Figure 4). However, at higher consolidation load, other contact forces become dominant. Humidity and consolidation induced contact deformation in particles led to increasing in total inter-particle adhesion forces. From our preceding work, it is clear that the powders display (corn starch as model powder) a tendency of exhibiting increased cohesivity owing the unusual frictional behaviour at lower RH conditions. However, detail understanding requires comprehensive investigation on the subject. In fact, literature on the powder layer formation on process surface is not there.

2. Motivation

The fine powder deposition on the process equipment is very common phenomena observed in the powder-based manufacturing process. This is mainly due to sticking of particles on the process surface under process and environmental condition. The phenomena results powder build up, powder loss and also influences the product quality. Moreover, it has a huge implication in the solar energy production. Deposition of dust particle can contribute about 17 to 25% energy production (Mike & Ghoroi 2017 et al. 2017) which can cost India 1 billion USD per annum for projected 100 GW solar plan by 2022. Though powder deposition on the surface is very critical across industries, there exists scientific knowledge gap in the powder community except for few studies on fine particles adhesion on electronics (Ranade 1987). The proposal is intended to study this important issue and generate scientific knowledge on formation mechanism and growth kinetics of powder layer on the process surface.

The research questions

- What are the critical parameters responsible for powder adherence and powder layer formation?
- How does the powder layer grows over process surface?
- What are the parameters which help to destroy or grow the layer?
- What is the correlation among different parameters which dictate the nucleation and growth mechanism of the powder layer growth?
- How to validate the plant scale powder layer from the laboratory scale study?
- Does the mechanism is true for all the particles? What is the influence on particle size and their surface characteristics?
- What mush it (powder layering) is influenced by extrinsic parameters?

3. Objectives

- Identify the critical parameters for powder layer formation (nucleation) and growth
- Establish mechanism of the layer deposition
- Establish model that will predict the powder layer formation irrespective of the scale
- Training to students and personnel from industry through labs, course and workshop

4. Methodology

Understanding powder behavior involves large number particle and powder properties which makes it difficult to analyze the powder system. In fact, unlike their counterpart (fluid system), the powder system is inherently complex. The proposed research is plan to investigate the different interactions using powder ‘horoscope’ involving various binary, ternary and quaternary interactions among six groups of parameters described through six specific regions (particle, powder, environment, process surface, process conditions and nature of consolidation in Figure 1. For example, particle interaction with process surface (wall) can be explore by studying the various parameters of region 1 (R1) and region 4 (R4) in the powder horoscope. Thus, a few binary and ternary interaction studies are planned (as in the Table 1). Similarly, several binary, ternary and quaternary interactions are planned for the project to understand the powder layer formation and growth mechanism.

Table 1: Various interactions among different components in the powder horoscope

No	Symbol	Interactions	Different phenomena study based on the different regions of powder horoscope
		Binary interactions between two different regions in the powder horoscope	
1	A-14	R1 – R4	Particle – wall interactions: particle parameters vs. process surface parameters
2	A-25	R2 – R5	Powder behavior under process conditions: Mixing, fluidiation, milling etc.
3	A-36X	R3 – R6	Environmental conditions on consolidation / stress
4	B-12	R1 – R2	Particle properties to powder properties
5	B-23	R2 – R3	Powder properties under environment conditions
6	B-34X	R3 – R4	Influence of environment on process surface
7	B-45X	R4 – R5	Process condition on equipment surface parameters
8	B-56X	R5 – R6	Process condition and consolidation / stress
		Ternary interactions among three different regions in the powder horoscope	
9	C-135	R1 – R3 – R5	Particle behavior under process conditions at various environmental condition
10	C-246	R2 – R4 – R6	Powder bulk properties at different consolidation under process surfaces
11	D-123	R1 – R2 – R3	Particle and powder properties on environmental conditions
12	D-234	R2 – R3 – R4	Powder bulk interaction with process surface under environmental conditions
13	D-345X	R3 – R4 – R5	Process condition on process surface under environmental condition
14	D-456X	R4 – R5 – R6	Process condition on process surface at different consolidation
15	E-612	R6 – R1 – R2	Particle properties when powder under consolidation
16	E-561	R5 – R6 – R1	Particle properties under consolidation at various process conditions
		Quaternary interactions among four different regions in the powder horoscope	
17	F-1345	R1-R3-R4-R5	Particles under different environmental conditions, process surfaces and process conditions
18	F-2456	R2-R4-R5-R6	Powder bevahior in different processes involving different surfaces and consolidations
19	F-3561	R3-R5-R6-R1	Particle in different process condition and consolidation under different environment condition
20	F-4612	R4-R6-R1-R2	In presence process surface how particles and powder behaves under consolidation
21	F5123	R5-R1-R2-R3	In process condition how particle behaves under different environment conditions
22	F-6234	R6-R2-R3-R4	Under consolidation how powder behaves in contact with process surfaces under different environmental conditions

The symbol end with ‘X’ (A-36X, B-34X, B-45X, B-56X, D-345X, D-456X) corresponds to the interaction where either particles (R1) or powders (R2) is not there. So they will not be considered for this study. However, their influence and information are important in other aspects of scientific investigation.

5. Scope and experimental plan

- Time scale of the study: 3 years
- Model powders: one hydrophobic, one hydrophilic, one spherical and one cylindrical shaped particle
- Size range: 5 microns to <120 microns powders
- Models process surface – Stainless Steel, rubber, plastic and glass surface
- Environmental conditions: RH variation from 30 to 90% and temperature variation from 10^0C to 65^0C
- Consolidation: zero to 15 kPa
- Process conditions: Some of the experiments to be considered in static condition (storage vessel) and some are in dynamic condition (mixing, conveying, milling)

- Parametric variations to be studied: as per the table 1 for each type of powder and each type of process surface at several environment conditions and consolidations.
- Some experiments will be carried out to study the importance of various extrinsic parameters on powder layer formation. Similarly some experiments will be planned to understand the correlation among intrinsic parameters only (particle to bulk scale relation: R1 & R2). Results from both the type of experiments will be compared to find any parametric correlation with the various extrinsic and intrinsic parameters.
- While thickness of the powder layer measurement will be planned for experiments in V-blender, ball mill, fluid energy mill and the turbula mixture in the lab in the room condition at different time of the year to capture the various environmental conditions, there will be dedicated experiments in the fabricated instrument to measure the powder layer deposition on the hopper, conveyor belt and storage device under controlled environment as shown in the schematic experimental setup in the figure 5.
- All the data will be compiled to generate the mechanism of the powder layer formation and growth kinetics for different powder for different process and environment conditions.
- Some of the experimental finding will be compared with the plant data available from Indian industries or industry members from IFPRI

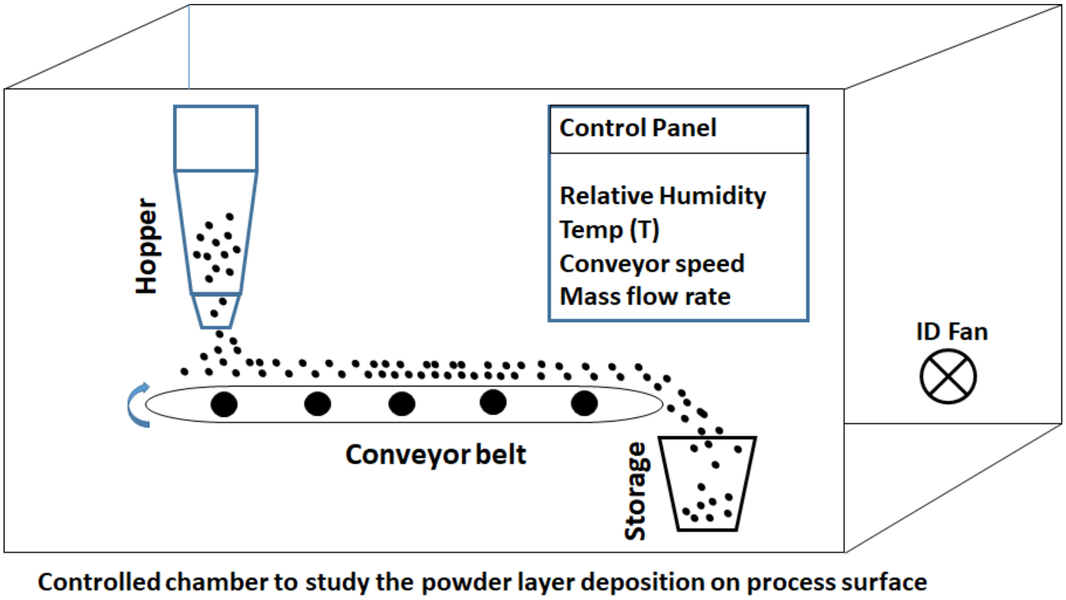

Figure 5: Controlled experiments to study the powder layer deposition in hopper, conveyer belt and the storage vessel.

6. Timeline and Experimental plan

No	WP	6	12	18	24	30	36
1	WP1	▨					
2	WP2	▨					
3	WP3	▨	▨				
4	WP4	▨	▨				
5	WP5	▨	▨				
6	WP6		▨	▨			
7	WP7		▨	▨			
8	WP8		▨	▨	▨	▨	
9	WP9			▨	▨	▨	
10	WP10				▨	▨	
11	WP11					▨	▨
12	WP12					▨	▨
13	WP13						▨
14	WP14						▨

Table 2: Description of the work packages (WP)

No	**WP**	**Description of the various work packages**
1	WP1	Hiring Manpower
2	WP2	Literature
3	WP3	Procuring instruments
4	WP4	Detail physicochemical characterization of the model particles, powders and process surfaces at room condition
5	WP5	Detail physicochemical characterization of the model powders and process surfaces at controlled environment (3 RH and 3 temperatures covering Indian whether conditions)
6	WP6	Measuring particle – process surface interactions in terms of friction coefficient, sticking coefficient, adhesion force measurement
7	WP7	Powder processing in flow through hopper, different mixing, milling devices in the lab and measure the deposited powder layer thickness measurement for given room RH and T
8	WP8	Study the interactions as per Table 1
9	WP9	Experimental set up fabrication and conducting studies in the fabricated instruments and layer thickness determination
10	WP10	Analyse growth kinetics of powder layer formation in different experiments

11	WP11	Correlate growth kinetics of powder layer with the powder and particle properties and other extrinsic variables
12	WP12	Formulate prediction tool for powder layer formation
13	WP13	Making reports of the research findings, publications
14	WP14	Knowledge dissemination to Indian industries and academia through joint workshop of IITGN & IFPRI

7. **Yearly milestone** (An outline of what will be accomplished in each of the three years)

Year 1

- Complete recruitment of the manpower, install the instrument
- Complete details characterization of particle, powder and process surfaces under different process and environment conditions

Year 2

- Complete the fabricate of the experimental set up and perform half of the intended experiments
- Complete the study of various binary, ternary and quaternary interactions described in table 1
- Complete the experiments on flow through hopper, different mixing, milling devices in the lab and measure the deposited powder layer thickness for given room RH and T
- Complete the interactions as per Table 1

Year 3

- Complete the controlled experiments in the fabricated experimental set up
- Complete the analyse of all the data
- Establish the formation mechanism and growth kinetics
- Complete the report and workshop for dissemination of the knowledge

8. **Critical unknowns that may influence the direction/outcome of the project):**

    i. Not getting proper manpower in time
    ii. Getting multiple verities of industrial powders in time
    iii. Attrition of trained manpower
    iv. Instrument breakdown

9. Budget

Table 1: Budget in ***USD for three years***

	Items	Year 1	Year 2	Year 3	Total
A	**Equipment/Fabrication**	32,394	7,042	0	39,437
B	**Consumables**	2,817	2,817	2,817	8,451
C	**Salary**	13,183	13,183	13,183	39,549
D	**Travel**	4,225	4,225	4,225	12,676
E	**Workshop**	0	0	4,225	4,225
F	**Total (A+B+C+D+E)**	52,620	27,268	24,451	104,338
G	**Overhead (20% of F)**	10,524	5,454	4,890	20,868
	Total (E+F)	**63,144**	**32,721**	**29,341**	**125,206**

Total budget USD 125, 206 (Year 1 USD 63,144, Year 2 USD 32,721 and Year 3 USD 29,341)

10. How this project could leverage into existing programs

In spite of production of large quantities of fine and ultra-fine powders in industries and well know handling problem across industries, science and engineering of handling this class of materials are often ignored or underestimated. In fact, the subject is seldom taught in University curriculum except for very few Universities in the world. Even a passing reference to this important subject remains unheard during the whole span of undergraduate /postgraduate education. Powder processing industries are mostly dependent on the experience of the workforce who learn the art by handling fine powder in day-to-day plant operations. The Legacy continues without much progress in fundamental understanding in the area. To fill this gap, research on fine powder got some momentum around the world in the last few decades. Along with the IFPRI's initiative and Engineering Research Center for Particle Science and Technology by NSF at University of Florida (1994), the National Special Super Fine Powder Engineering Research Center of China is more recent initiative of China in 2005. However, in India, it is yet to be appreciated. India being a major producer of pharmaceutical powders and prominent player in food, cosmetic and fine chemicals etc, this becomes more important. Presently there is no dedicated research lab in the country in this area. A basic understanding of science and engineering of fine powders can minimize several problems in many industries and help the industry to improve existing operations and quality of product. Thus, there is a gap in the country for proper education, training and research on Fine Powder which is prerequisite for further advancement of powder handling industries. Keeping this in mind, we have created a state-of-art Fine Powder Research Lab which is providing related education, training and research in India.

As we are located in country's industrial hub, there is enormous opportunity to connect our research with industry. Along with the planned research, training through workshops/symposiums, summer research and short term research program is very much active. About 15 students from other Universities trained in our lab on fine powder research. Also, we have introduced a course on "Particulate Solid Processing & Surface Engineering" for senior undergraduate and postgraduate students at IITGN. The course have considerable theoretical component and extensive hands on experience on handling fine powders in the lab scale. Several IITGN students have benefited from the course. In addition, we have managed to write several research proposals for funding and attracted 7 PhD students and 7 M.Tech students along with several Junior Research Fellows (JRF) to work on various aspects of particles and powders. During the last few years, we have also established several industrial collaborations.

Major research focus in our research group is on understanding fine and cohesive dry powder (Geldart's Group C) and its behavior in static and dynamic conditions; Influence of humidity on powder flow; Surface engineering of fine particle (using nano-particle, plasma processing, lithography & chemical methods) for improved dry powder processing – mainly improving flow & packing; surface wetting and super-hydrophobic/ Hydrophilic powders etc.

These ongoing activities in our research group is very much in-line with the proposed project and the initiatives of IFPRI to spread the powder research. The proposed project has direct bearing to strengthen our existing program (both to strengthen the research and curriculum) on fine particles and powders. In addition, through the proposed project, our research group and IFPRI together can arrange knowledge sharing sessions for Indian academics and industries which will be a huge benefit to fine powder research in India.

11. IFPRI members support the program through following provisions

In the proposed project from IFPRI can help us to strengthen our effort on Fine Particle Research in India. There are multiple ways where IFPRI can help us where Indian scientists and engineers can be benefited. Also, IFPRI members can explore the various powder based Indian industries such as pharmaceuticals, food, cement, cosmetics etc. Thus, there are mutual benefit to float the proposed project in IIT Gandhinagar. It is more so because IITGN is strategically located in the Industrial hub of India. In the vicinity of IITGN, there are several clusters of industries which are handling fine powders in day-to-day basis. IFPRI members can help us by

a. Providing model powders
b. Training on few unknown test methods which can be extended to industry person
c. Sharing their experience to students
d. Sharing the experience to other Indian academics and Industries through workshop and hands-on-training
e. Establishing the relationship with Indian Industries and encourage them to contribute in IFPRI

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Research project proposal for the IFPRI theme:

MECHANISM OF FORMATION AND GROWTH OF POWDER LAYERS ON PROCESS EQUIPMENT SURFACES AT LOW STRESSES

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Outline of the problem

Several papers and books in the literature deal with the adhesion of single particles on walls. Mostly, the effect of particle and surface roughness is highlighted and the action of the different kinds of interparticles forces is described. Instead, the build-up (make up) of powder layers on the equipment surface during operation at ambient temperature is not described nor quantified in the literature with the exception of dedicated patents [1] and of the vast literature on slag accumulation phenomena in combustors and gasifiers (e.g. [2])

Considering flow within containers, in granular mechanics it is generally assumed that the wall friction, at equal system conditions, is lower than the internal friction. This is reasonable considering the microscopic interactions that can be assumed at the wall and within the material. In fact, in process and storage equipment, it is reasonable to assume that the wall roughness is generally lower than the roughness of particle-particle contacts in an internal shear plane and that the number of particle to wall contacts per unit surface is generally lower than the number of particle-particle contacts in an internal shear plane. The first effect is dominating in case of prevailing frictional interactions between particles and between particles and wall. The second effect is dominating in the case of cohesive forces between particles and adhesive forces between particles and wall. Therefore, the occurrence of the formation of a stationary layer during powder shear, whatever its thickness, can only be associated to increased particle-particle cohesive and particle-wall adhesive forces in the layers close to the surface.

More complex phenomena take place in particle layer build up in dilute systems, in which the interaction between particles and wall occur with particles hitting the wall. The nucleation of a static particle layer on the wall depends on the possibility that the elastic energy accumulated by the particles hitting the wall is not able to produce the work necessary to win the adhesion forces between the particles and the wall at the rebound. The buildup of layers is related to the rate of accumulation of new adhering particles (on the wall or on the particle layer already formed) and the tendency of the hitting particles to remove the adhering particles.

From the description above, it is clear that the experimental set up, useful to measure the initiation and the accumulation of a particle layer on the walls of a container with a dense particulate system, cannot be the same of the experimental setup to be used to measure the nucleation of a layer of particles and its growth in a dilute system, in which many other phenomena than powder shear occur. Nevertheless, experiments in powder shear may provide useful information on the interparticle forces acting in particulate system that can be used to understand the behavior of dilute systems. For this reason, first we will focus our attention on the layer formation in dense powder shearing during this proposed project. The study of the formation of a static layer in pieces of equipment with particles travelling in dilute systems could be addressed later in a possible extension of the present project.

Several system conditions can determine a local increase of interparticle cohesive forces, which can justify the formation of a static layer of particles on the wall of a container hosting a powder. These may be local changes of air relative humidity, for example due to lower temperatures at the wall, which can determine local capillary condensation of water. With hydrophilic materials, local changes of air humidity can induce the soaking and consequent softening of some of the particles phases that, by deformation, may increase the contact areas between particles and between particle and wall and, consequently, also the interparticle forces. Even worse effects can be observed with temperature fluctuations at the wall that can determine caking phenomena due to the precipitation of solids in the capillary bridges of changing volume or the hardening of material at contacts. Temperature increases at the wall can also determine a local variation of van der Waals interactions. In this case, the principal effect of temperature is related to the change of particle hardness. In fact, at higher temperatures hardness decreases and determines larger contact areas between particles and, consequently, larger contact forces. More significant can be the effect of temperature increase at the wall when it determines the partial melting of particulates or the fusion of low melting phases in the particulate systems. In this case, capillary forces set up determining a significant increase of interparticle cohesion.

Scope of the project

Scope of the project is the understanding of 1) the changes of interparticle forces at the wall that can determine the formation of a static powder layer in shear flow occurring at low but quantified compressive stresses and 2) of the conditions leading to the growth of a static layer of particles during powder shear.

In this project, the temperature will be used to change the intensity of interparticle forces and to determine the formation of a static particle layer on a wall. The study will include the use polymeric particulates and the investigated temperatures will be in the range ranges between 100 and 300 °C. Experiments with sub millimeter particulates made of polymer, carried out below the polymer melting temperatures, will describe the temperature effects on van der Waals interactions due to changes in the material hardness and thus in the particle contact area. The effect of temperature on the flow properties of these systems will be studied with the help of a High Temperature Annular Shear Cell (HT-ASC) [3] developed at the University of Salerno (UNISA). To characterize the effect of temperature on the powder properties, the cell will be used according to the established procedure in which the sample is uniformly heated up to the desired temperature of the shear test. Furthermore, the apparatus, will be modified in order to dynamically study the temperature profile condition that can lead to the formation of a static layer on a wall sample on which model shear conditions are realized.

Experimental set up

The High Temperature - Annular Shear Cell (HT-ASC)[3] developed at UNISA operates on the same workbench of the original manual tester developed by Schulze for shear test at room temperature. Figure1a shows a schematic of the HT-ASC. It consists of a bottom aluminum annular trough containing the powder sample and an aluminum and steel annular lid placed on the top of the sample like the original cell in the Schulze tester. As for the original shear cell, the lid is fixed at a crossbeam connected by two tie-rods to two load beams. These allow measuring the shear force acting on the shear plane developed inside the powder sample

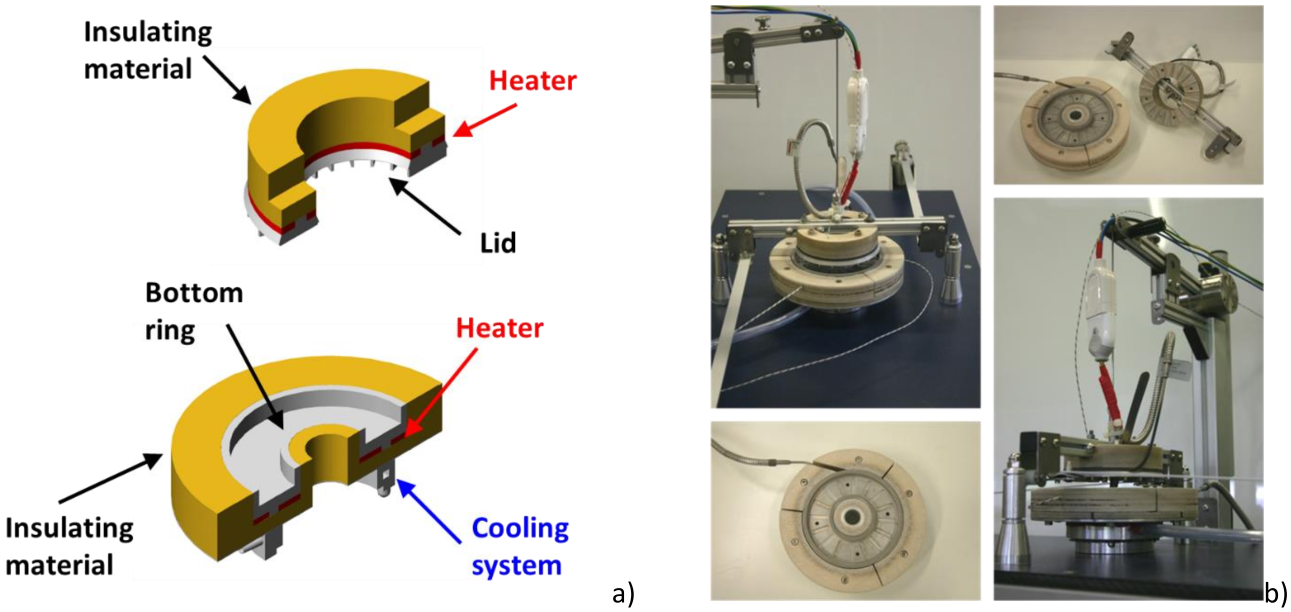


Figure 1 Schematic of the High Temperature - Annular Shear Cell (HT-ASC) (a) and its operation on the Schulze RST (b)

by the rotation of the bottom ring relative to the lid for a specified normal load, exerted by weight pieces placed on a hanger connected to the crossbeam.

Electric heaters were introduced below the cell bottom and on the lid to heat the cell and the powder sample contained in it. In order to reduce the heat flux from the external surface of the cell and then to minimize the temperature gradient within the sample and, for safe operation of the cell, a covering insulating material was placed around the trough of the cell and above the lid. A cooling system was designed and built to cool the cell base where it is in contact with the gears of the rotation mechanism of the tester. Some pictures of the HT-ASC operating on the Schulze workbench are reported in Figure1b. The material used for the construction of the HT-ASC allows a safe operation of the system up to 500°C.

A temperature control system was developed to achieve the set temperature in the powder sample. It consists of three J thermocouples measuring the temperature at three different depths of the sample connected to a data acquisition board. A dedicated software was developed to read the three temperatures and regulate the heating power in order to keep the temperature as uniform as possible. In particular, the procedure acquires and digitizes the three temperature values. The top and bottom temperature, T_{UP} and T_{DOWN}, are compared with the set-point temperature, which can be the same or different for the two separate PID software loops that are used to control separately the heating power on the lid and on the trough.

Materials

As above mentioned, two different cuts of model particulate solids and a further real powder will be used in the experiments.

The first particulate material made of sub-millimetric polymeric particles (100-600µm) will be used below the melting temperature for experiments in which the presence of van der Waals forces only will be assumed so that the effect of temperature on the interparticle forces could be governed by changes of the material hardness [4,5].

The second material will be a mixture of a ceramic non-porous particulate (e.g. sand) in the sub-millimetric range (300-1000 µm) and of a micrometric polymeric powder (1-30 µm). It will be used in temperature ranges including the melting temperature of the polymer. The presence of a molten phase will introduce strong changes in the interparticle forces [6].

The real industrial powder will be chosen with the help of the IFPRI members and possibly provided by them on the basis of their experience of materials showing the formation of static layers in conditions accessible with the proposed experimental set up

Procedures and required changes to the set up

Shear experiments will be carried out in two different modes: with uniform temperature and with a temperature gradient.

The uniform temperature mode will be used for the measurement of internal powder properties and wall friction with temperature as a system parameter. In this mode the set point values of the temperature control loops on the lid and at the bottom heater will be the same. The internal flow properties and the wall friction will be measured with the usual procedures applied to the ring shear testers [7] after the uniform temperature in the system is reached and verified by reading same temperature at the three thermocouples. The trough of the cell will be adapted in order to carry out wall shear experiments at high temperature.

The temperature gradient mode of use of the shear cell will be adopted in a separate set of measurements focused on the dynamics of growth of the static particle layer. In these experiments, the cell will be used with the heated lid hosting a wall coupon. The temperature at the lid will be increased gradually up to a level at which the shear strength at the lid wall is higher than the internal shear strength at the vanes tip. The schematic situation is reported in Figure2 showing that, at the beginning of the heating process, when the temperature is uniform, the internal shear strength at the vanes s_i is larger than the shear strength at the wall s_w (Figure2a and b). Therefore, the shear plane is at the wall. Instead, when the temperature profile is such that the internal strength at the vanes s_i is smaller than the strength at the wall s_w (Figure2c), the shear occurs at the vane tip.

In order to carry out experiments with a temperature profile in the sample, the existing cell will have to be modified as it is shown in Figure3. The cell lid will have to be adapted to hold an annular wall coupon in contact with the heated surface. The cell base will require a number of more significant changes. First, vanes will be placed at the cell bottom. Then the trough side walls, presently made with the same material of the bottom wall, will be made of fused silica (quartz). The lower thermal conductivity of the wall will avoid thermal bridges between parts of the powder samples at different temperatures. Furthermore, fused silica, that can withstand temperatures up to 1500°C, is transparent in the visible and near infra-red (NIR) range and, therefore, can be used in conjunction with a NIR camera to read the material temperature[8]. The NIR camera fixed on the rotating base will be calibrated to measure the temperature profile. Images sequences taken in the visible range will be used with a Particle Image Velocimetry (PIV) procedure to derive the particle movements behind the wall. Since the camera is moving with the base, particles adhering on the heated wall surface fixed on the lid will be seen as in movement.

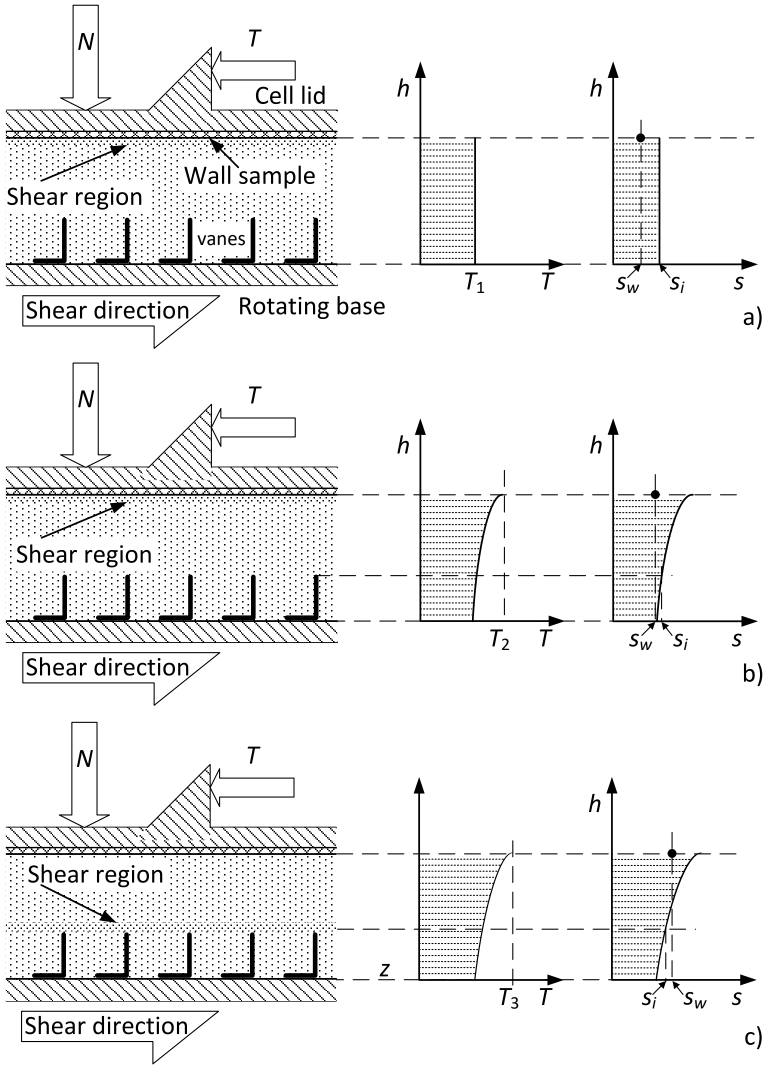


Figure 2 Evolution of the shear cell experiment at variable temperature gradient ($T_1<T_2<T_3$): a) initial condition with uniform temperature; b) Start of the heating process; c) final stage of the heating process. In a) and b) the internal strength at the vanes s_i is larger than the material adhesion s_w and the shear occurs at the wall. In c) the internal strength at the vanes s_i is smaller than the material adhesion s_w and the shear occurs at the vane height.

The outcome of the experiments with the new cell will be the time evolution of the temperature profile in the powder sample in the shear cell and of the presence of a static shear layer by applying a temperature gradient. The main variables that will be investigated are the extremes of the temperature gradients, the normal force applied in the shear experiments and the surface quality of the wall sample. With the second model system also the mixture composition, i.e. the amount of liquid bridges, formed will be investigated. These results will be compared with the theory hypothesized above and reported in Figure 2. In order to verify the theory, the internal and wall strength as a function of the temperature, previously measured with the conventional HT-ASC, will be needed. The measured powder shear properties at changing temperature will be used to derive the necessary information.

Project time deployment and expected outcome

The time distribution of the activities in the project is shown in the Gantt chart reported in Figure 4.

At the end of year 1, the experimental procedure will be completely defined with the construction of the new apparatus, its functionality testing and some first exploratory measurements of the first particulate to be investigated. In fact, by that time this material will be also completely characterized for internal and wall shear at relevant temperatures. Some preliminary results on the applicability of the theoretical framework will be also available.

At the end of year 2, the complete thermal flow characterization (internal and wall shear) of both model materials will be accomplished and tested for the static layer formation.

At the end of the last year (year 3), the complete thermal flow characterization (internal and wall shear) of the real material chosen for the experiments will be accomplished and tested for the static layer formation. The results will be completely analyzed and the theoretical framework confirmed.

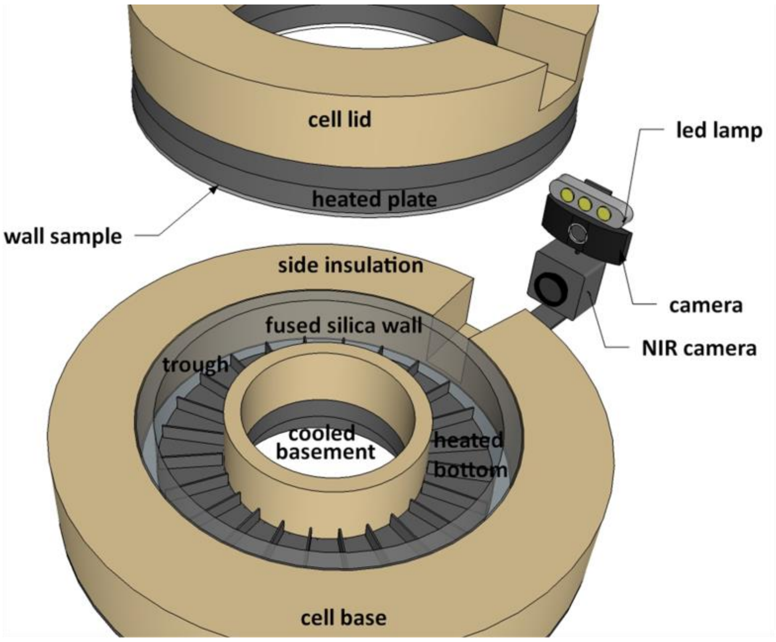
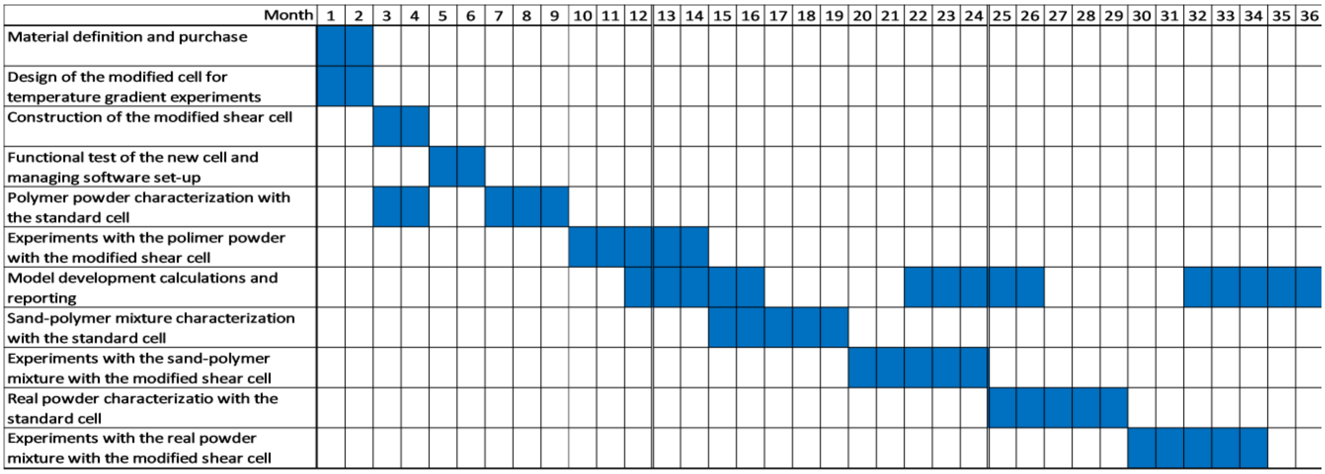


Figure 3 Modified set up of the shear cell base for experiments with a vertical temperature gradient.

Project leverage into other research activities at UNISA

The project will rely on the continuing research activities on the effect of temperature on powder flow properties and the project could not take the present configuration without the vast research activity carried out on the topic. In the next years the study of the thermal effect on the powder flow properties will focus mainly on topics related to the distribution of powders in Selective Laser Sintering (SLS), an additive manufacturing techniques which alternates the addition of powder layer and selective sintering of the particle in the layer, in order to obtain three dimensional objects. One of the main issues in this field is related to the characterization of powders to understand if these are suitable for the SLS process with respect to the possibility to obtain with powders a layer of good quality layer. At UNISA a PhD student is presently working on this topic and some of his materials are polymeric powders. The experience we are gaining with this project will help us in the right choice of the model material.

In 2019 other two PhD projects on topics related to SLS will start at UNISA. Both these PhD projects are part of Mathegram an Innovative Training Network financed by the EU Commission within the MSCA-ITN program with highly competitive calls. Mathegram is lead by prof Charley Wu at University of Surrey and involves 5 universities, 4 public research centers and 6 major research centers of major companies in Europe. One of the 2 PhDs project at UNISA is related to the flowability of SLS powders, among the other things, will study if



Month	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
Material definition and purchase	■	■																																		
Design of the modified cell for temperature gradient experiments	■	■																																		
Construction of the modified shear cell			■	■																																
Functional test of the new cell and managing software set-up					■	■																														
Polymer powder characterization with the standard cell			■	■			■	■	■																											
Experiments with the polimer powder with the modified shear cell										■	■	■	■	■																						
Model development calculations and reporting												■	■	■	■	■						■	■	■	■	■						■	■	■	■	■
Sand-polymer mixture characterization with the standard cell															■	■	■	■	■																	
Experiments with the sand-polymer mixture with the modified shear cell																				■	■	■	■	■												
Real powder characterizatio with the standard cell																									■	■	■	■	■							
Experiments with the real powder mixture with the modified shear cell																														■	■	■	■	■		

Figure 4 Gantt of the project

it is possible to use a light compaction of the powders in the layer preparation for the SLS. One of the instrument that can be applied is the forward rolling of a cylinder. The effective possibility to use it is related to the circumstance that the forward rolling cylinder does not detach in its trailing section material from the layer spread, due to the adhesion of part of the layer to the cylinder. This phenomenon occurs when the adhesion force of the compressed powder on the cylinder surface is larger than the internal resistance of the compressed layer, a situation very similar to that to be studied in the project related to the present proposal to IFPRI. Therefore, the understanding on the phenomenon occurring at the SLS roller will help in the right interpretation of the IFPRI project. Also, the experimental set up developed for the PhD project, a roller operating at controlled temperature, may constitute a valid alternative to the experimental set up proposed here, in case something is not working properly.

The second PhD project at UNISA within Mathegram will be on the heat transfer during the laser sintering action in the SLS project. The plan is to use a dedicated set up in which a layer of particles is placed on a fused silica glass and the heat transfer is measured by looking at the evolution of the temperature distribution of the powder above the glass. The similarity with the experimental set up considered for this project is clearly evident as well as the benefit that will derive from similar experimental experience in both projects.

Critical unknowns and get around solutions

The most critical issues of the proposed project are related to the effective functionality of the new cell that will be designed for in which a temperature profile is applied. Problems may arise for the following reason:

1) The apparatus is not sufficiently transparent to visualize the flow in presence of liquid bridges due to sticking of liquid on the cell wall. This problem can be overcome either changing the materials to be investigated or with the design of a different cell, not transparent but with an appropriately designed sensor highlighting the presence of shearing material at different heights. A temperature probe will be required to measure the temperature profile
2) The new apparatus is not able to visualize the position of the shear plane due to important sidewall interactions. In this case different apparatus derived from the one used to study SLS layer deposition will be used to apply compression on the powder over a heated layer and to study its resistance to scratching actions.

Support from IFPRI members

As above mentioned, the real industrial powder will be chosen with the help of the of the IFPRI members.

It would be advisable that they could also provided a material that, on the basis of their experience, has showing the formation of static layers in conditions that can be explored with the proposed experimental set up.

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IFPRI Research Project Brief

Model-Assisted Design of Granular Products

The International Fine Particle Research Institute (IFPRI) wishes to fund a project to develop a framework for model-assisted design of structured granular products. In a wide spectrum of industries, from commodities to consumer products, fine chemicals to pharmaceuticals there is a strong push towards efficient development of granular products with prespecified functional properties. Instead of relying on repeating cycles of small-scale formulation experiments and functional testing, efficient product design requires development of linked models of the formulation process and product performance. For granular products, these models are necessarily multi-dimensional in particle properties, because product performance depends on more than simply particle size. Process and product models must include multiple properties, for example porosity, pore size, distribution of components (e.g. binder, active ingredients), etc.

The objective of this project is to develop multi-dimensional process models of binder agglomeration that have as their output the appropriate particle properties (likely distributed) that are linked to associated product models to predict product performance. We constrain the project scope to high-shear and/or fluid bed granulation, however the choice of formulation(s) and modeling approach(es) are open. The project has the following components:

1. Identify the best modelling methodologies for high-shear and fluid-bed granulation processes and granulated product modelling
2. Identify the best modelling framework
3. Identify the best solution strategy
4. Build models & validate against experiments

This should be done in the context that the modeling framework and the specific models be deployable to industry.

Model-Assisted Design of Granular products for High Shear and Fluid Bed Wet Granulation

Principal Investigator (PI): Rohit Ramachandran

1. Executive Summary

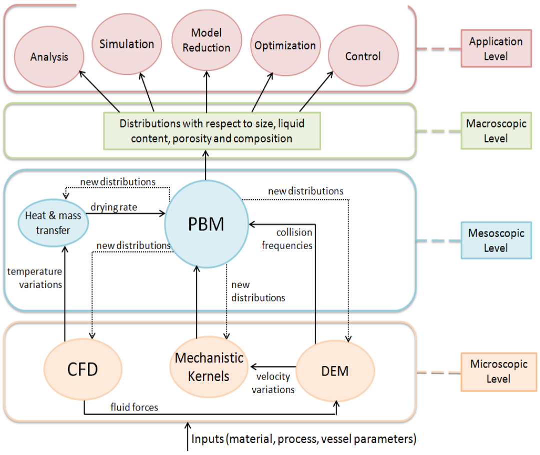
The overall aim of this proposal is to develop validated and predictive process and product models for high-shear granulation (HSG) and fluid-bed granulation (FBG) for both batch and continuous process configurations. The models will be multi-scale and multi-dimensional and will be able to describe the dynamics and evolution of important granule properties as a function of key process parameters, formulation/material properties and design attributes. The granule properties we propose to describe are distributions w.r.t. to 1. particle size, 2. liquid/binder, 3. porosity and 4. active ingredient (active). Efficient numerical and model reduction strategies will be implemented to ensure that these complex process models are able to be accurate/predictive while being computationally efficient for practical implementation and use. In terms of primary mechanisms and basic mathematical structure, the different HSG and FBG configurations are similar. To capture secondary mechanistic features and differences, particle/granule-scale experiments will be performed to ensure accurate sub-physics are captured. To test the robustness and predictive capabilities of models and kernels, DOEs will be performed for a range of diverse formulations at lab-scale. A scale-up methodology will also be proposed and implemented to ensure that key granule properties can be predicted from lab-to-pilot-to-manufacturing scale.

2. Proposed Approach

The following sub-sections describe the details of the proposed approach undertaken in this proposal. The work proposed leverages and builds upon the PI's previous/current work in the same area as can be evidenced by his numerous publications in the areas of 1) multi-scale model development, 2) mechanistic kernel development, 3) experimental studies and particle/granule-scale analyses, 4) computationally efficient numerical solution, model reduction and high-performance computing. See link for papers published by the PI (http://www.pslrutgers.com/publications).

2.1 Identification of best modeling methodologies and framework

Fig 1: multi-scale framework



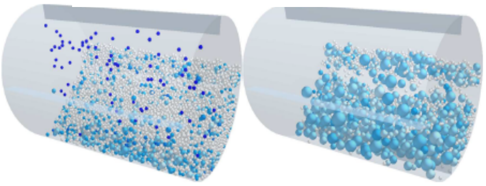
There exist several modeling methodologies in the literature to describe the different aspects of the multi-scale dynamics of granulation processes spanning from the micro- to meso- to macro-scale and its relation to product performance. These range from population balance models (PBM), discrete element method models (DEM), volume of fluid methods (VoF), computational fluid dynamics models (CFD), residence time distribution models (RTD) and reduced order models (ROM) such as Artificial Neural Networks (ANN) or partial least squares (PLS). However, much of the work in the literature has focused on only particle size as the sole indicator of product performance with limited extensions to other performance indicators. In cases where more than one property has been described, models have often been limited to either being (semi)-empirical, with the need for significant experimental effort for model calibration that then translates to limited ranges of predictions. Often, there has also been a lack of rigorous coupling between model forms to enable effective predictive capabilities as a function of key process, formulation and design inputs. To this effect, we propose a flexible multi-scale model framework (**Figure 1**) to capture the effect of critical inputs (process, formulation, design) on key granule properties (distributions w.r.t. to size, liquid/binder, porosity and active). The basis of the framework will be the multi-dimensional PBM (**Figure 2**) which in its full form will consist of four internal coordinates to describe two solid components (e.g. for active, excipient), one liquid component (for liquid/binder) and one gas component (for porosity). The rate terms that will be described are layering, liquid distribution, consolidation, nucleation, aggregation and breakage. Based on this framework, we will first elucidate the integrated model for the batch HSG process. We expect this to be a coupled compartment-based PBM-DEM model where the DEM incorporates the equipment geometry, initial particle size distribution and formulation properties and provides as output micro-scale information such as collision properties (e.g. particle-particle, liquid-particle), shear forces, bulk particle velocities and heterogeneities w.r.t to velocity, and liquid distribution (**Figure 3**). In **Figure 3**, it can be seen that between the two sub-figures, as time progresses, there is homogenizing (and growth) of liquid (dark blue) and particles (grey) to form light blue larger particles. Much of this and related information will be received by the PBM along with other kernel inputs to describe the evolution of the distributed properties for the identified compartment(s). Depending on the sensitivity of the micro-scale properties, PBM outputs can be periodically coupled back into the DEM for updated propagation of dynamics. For the continuous HSG, we expect to utilize the same framework with the addition of inflow and outflow terms in the PBM as well as the axial velocity term whose information will be obtained from the DEM. For batch FBG, we will utilize this developed model in addition to the incorporation of CFD, to determine the effect of the fluid flow term on DEM as well as the micro-scale information previously identified. An energy balance term to account for heat/mass transfer will also be incorporated into the PBM to account for simultaneous heat exchange, drying and (re)-wetting. Inflow, outflow terms will then be added along with axial, radial velocity terms for the continuous FBG. It should be noted that the incorporation of DEM and CFD is important in the model formulation. For instance, in the calculation of aggregation rates; PBM and related criteria (e.g. Stokes criteria) is able to provide information on the collision efficiency but not on the collision frequency. Therefore, a multi-scale model formulation is needed to capture the essential physics-based dynamics.

$$\overbrace{\frac{\partial F(s_1,s_2,l,g,t)}{\partial t}}^{Temporal} + \overbrace{\frac{\partial}{\partial g}\left[F(s_1,s_2,l,g)\frac{dg}{dt}\right]}^{consolidation} + \overbrace{\frac{\partial}{\partial s_1}\left[F(s_1,s_2,l,g)\frac{ds_1}{dt}\right] + \frac{\partial}{\partial s_2}\left[F(s_1,s_2,l,g)\frac{ds_2}{dt}\right]}^{layering} +$$

Fig 2: PBM formulation

$$\overbrace{\frac{\partial}{\partial l}\left[F(s_1,s_2,l,g)\frac{dl}{dt}\right]}^{drying/rewetting} = R_{nuc}(s_1,s_2,l,g) + R_{agg}(s_1,s_2,l,g) + R_{break}(s_1,s_2,l,g)$$

Fig 3: DEM analysis of liquid distribution



2.2 Identification of critical inputs, granulation regimes, kernels and sub-models

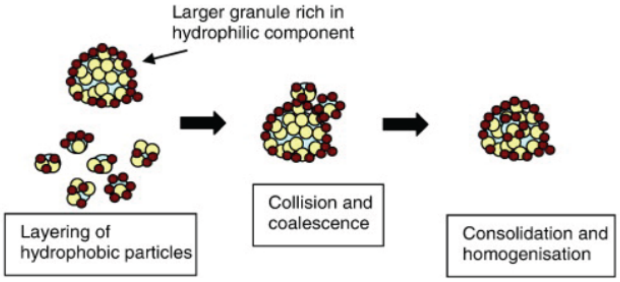


Fig 4: proposed growth scheme (Hounslow, Salman et al. 2013)

The above section (#2.1) represents the proposed model framework for batch and continuous HSG and FBG processes. In this section, we propose to develop the knowledge to distinguish between the mechanistic details and secondary features of HSG and FBG so that only the necessary and applicable physics are implemented into the model framework. We will first perform a risk and criticality analyses to ensure key process inputs, formulation properties and design/equipment attributes are captured in model formulations for both HSG and FBG. This will be performed via a combination of literature review, prior knowledge from the PI's research and interaction/consultation with IFPRI member companies and other companies in the PI's network. For instance, for batch HSG, this could translate to: 1. Process parameters (e.g. L/S ratio, liquid addition time, impeller speed, wet massing time), 2. formulation properties (e.g. system viscosity, solubility and hydrophobicity and 3. design attributes (e.g. vessel and impeller geometry and material type). The next step will be to identify formulation specific regimes and its boundaries for HSG and FBG. This is because, even for the same formulation and similar process parameters, a different balance of rate processes could exist between a HSG and FBG system due to differences in shear rates, differences in particle/droplet size ratio etc. As an example, in the case of a formulation with differing contact angles, where the liquid droplet is larger than the primary particle (e.g. in HSG), the literature postulates that the hydrophilic component is preferentially nucleated while the hydrophobic component remains mostly unnucleated. This in turn leads to initial aggregation whereby the granule is rich in the hydrophilic component where layering then takes place via the adhering of hydrophobic particles onto the granule (**Figure 4**). This is followed by further aggregation and consolidation to eventually form homogeneous granules. Similar theory, postulations and/or studies exit for different formulation scenarios and granulation systems (e.g. FBG, TSG, drum etc.)

We will first study and discern these differences via regime map approaches (nucleation, growth, peak flow stress vs. capillary number). Subsequently, for the same granulation process, we will study regime differences and boundaries for a variety of selected formulation types (see #2.4) to understand mechanistic differences between formulation characteristics. While the regime map approaches provide a reasonable static understanding of these mechanistic differences, additional effort is required to understand the time-dependencies of these mechanisms and eventually translate them to mathematical kernels (rate equations) for the purpose of model-based simulation and analyses. Via dynamic image analyses and quantification of particle microstructure (initial result obtained in **Figure 5**), we will begin to understand not only the time dependency of different granule mechanisms but also their magnitude as a function of process parameters, formulation properties and granulation type. Via this integrated approach, we can articulate the important rate processes in the PBM for both HSG and FBG and also deconvolute their coupled effects during the granulation process. This can then be further broken down to be formulation type specific. We will limit our analyses to develop mechanistic understanding for layering and aggregation. This is primarily because layering is not well described in the literature but is evidently important to account for when certain formulation types are used. Aggregation, while prominent in the literature is often developed as a generic sub-model with missing physics and is not suitable for certain granulation types and/or formulation characteristics. Nucleation has been previously studied in the literature by several groups (Litster, Hapgood, Poon, Emady, Smith etc.) and we will leverage much of that work into this proposal. Breakage on the other hand can be extremely complex to understand and for the purpose of this proposal, we will use a previously developed mechanistic kernel (Ramachandran et al. 2009 in http://www.pslrutgers.com/publications) developed by the PI that is able to sufficiently describe breakage kinetics as a function of key process, formulation and design properties. Consolidation and liquid addition/distribution are described via standard rate equations that have proven to work well. Moreover, much of their mechanistic details will come from the DEM simulations and not from their explicit kernel forms.

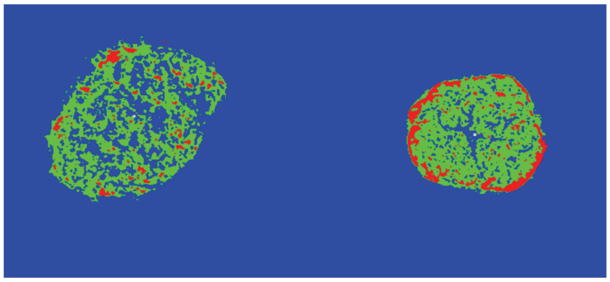


Fig 5: Left: uniform distribution via aggregation.
Right: one component in the periphery via layering

The next step is to translate the developed mechanistic aggregation and layering knowledge into granulation kernels (rate equations). The kernels essentially form the sub-models that are incorporated into the PBM to be able to fully describe granule properties as a function of its inputs. We envision that the process of layering is similar in both HSG and FBG. Finer particles layer on larger granules primarily as a result of capillary forces and to a lesser degree solid cohesion. We will perform a DEM based analysis to model these effects and to understand how layering arises as a result of these forces for different formulation properties. Qualitative comparisons will be made with actual images obtained from granules. Layering correlations will be formulated to be able to describe the layering kinetics as a function of critical inputs. The process of aggregation is inherently different for HSG and FBG processes. In FBG, the liquid droplet is smaller than the primary particle and much of the literature on aggregation is suited for this application. This is essentially based on the Stokes' criteria (e.g. Type 1, Type 2 and rebound) first postulated by the groups of Ennis, Litster and Liu. Criteria has also been established (Stepanek, Hapgood) where aggregation is seen as a function of collision efficiency and frequency where efficiency is a function of surface coverage and liquid layer thickness and is governed first by a successful contact of a dry particle on wet area followed by the balance of kinetic energy and viscous forces to determine a successful aggregation event. Much of this previous work and theory can be leveraged in our proposal to develop FBG specific aggregation kernels for bi-component systems with further considerations to hydrophobicity, viscosity and solubility. For HSG, where the liquid droplet is larger than the primary particle, there exists much less theory compared to the case for FBG. Mostly, two different growth behavior types are explained by the Stokes deformation number which attempts to separate the induction growth regime from the steady growth regime. While this provides qualitative understanding of the evolution of aggregation, there is limited quantitative detail in terms of robust rate equations. Furthermore, much of the existing high shear aggregation kernels are limited in terms of incorporating salient process and formulation inputs and cannot account for multiple components and/or formulation differences in terms of solubility, viscosity and hydrophobicity. Via a combination of regime map approaches and granule-scale experimental analyses we will begin to formulate rate equations for aggregation as applicable to HSG. This will elucidate the dependency of the aggregation rate on key process inputs and formulation properties. We will then perform small-scale DEM simulations to understand the effect of forces (e.g. viscous, capillary, cohesive) as a function of deformable area and contact angle to determine the strength of liquid bridges. This will enable us to formulate constitutive rate equations specific for high shear systems.

At the end of this task, we envision a robust and flexible model framework that is able to incorporate the necessary physics and mechanisms specific to HSG and FBG as a function of different formulation types, to predict key distributions of multiple important granule properties.

2.3 Identification of an efficient solution strategy

The work proposed in sections 2.1 and 2.2 while leading to a more accurate and physics-based model that is much needed to describe granule dynamics, can also lead to computationally intensive simulations. This is mainly due to the large processing requirements for the DEM and CFD models and to a lesser extent the numerical solution of the multi-dimensional PBM. We propose a multi-pronged approach to ensure these simulations are computationally efficient and this is also based on the PI's on-going work in this area. Firstly, the PBM to describe size, liquid content, porosity and active content need not be formulated as a full 4-dimensional problem. This is because much of the experimental data is inherently lumped when measured. For instance, although particle size is generally reported as a function of mass frequency vs. size, other attributes such as porosity (bulk density), active content and liquid content are measured as an average value across different size classes. Therefore, this enables us to re-formulate the 4-D PBM as a 1-D distributed PBM w.r.t to size with lumped equations for other attributes as a function of size. In previous work, we have shown such an approach to be computationally efficient while minimizing loss of accuracy. We also propose the use of reduced order models (e.g. ANN) to replace portions of DEM and CFD calculations. This is because, we have shown in previous work that we are able to utilize DEM and CFD to perform a small but important portion of the micro-scale calculations needed for the PBM, rather than using DEM and CFD to perform the entire simulation. This enables the efficient isolation of the CFD and DEM and with off-line training of the ANN, the ANN is able to fully replace these intensive models and maintain accuracy of information passed to the PBM. We will also utilize our previous work and knowledge on efficient numerical solutions and parameter estimation methods to ensure accurate and computationally efficient model calibration and validation.

2.4 Design of experiments, material property identification, model calibration, experimental validation

In combination with PI's ongoing work and member company input, we will formulate optimal design of experiments for testing of our models and methods. The primary focus will be on varying the formulation space for a system with two solid components. The formulation space we expect to take into consideration is hydrophobicity (i.e. components with similar contact angles and differing contact angles), viscosity (e.g. different binder grades) and solubility (both solid components insoluble, one component soluble). Other formulation characteristics (e.g. drug loading) can be designed into the experiment as required. We will work with the member companies to arrive at the right material selection which can incorporate pharmaceutical, non-pharmaceutical or model compounds. The secondary focus will be on varying the process parameter space and similar to above, we will work with the companies to identify and vary parameters of interest. We envision much of the experimental work to be performed at Rutgers with some experiments at member companies depending on interest. For selected formulations, material property testing, and calibration of model inputs (e.g. those in DEM) will be subsequently performed. In terms of output properties, we will measure size distributions, liquid content, porosity (also bulk density) and active content. The PI has access to key facilities required for these testing methods. As needed, additional tests can be performed in member companies. The models built for HSG and FBG will be tested against these lab-scale data. We envision that some level of iterations and kernel/model update will be needed to ensure experimental sensitivities are captured and that experimental data is validated. Statistical metrics will be used to quantify parameter confidence intervals and ranges of validity.

2.5 Scale-up methodology

Specifically, for batch HSG and FBG, we propose a scale-up methodology to be able to identify optimal operating conditions so as to achieve similar granule properties across scale. Currently for scale-up prediction, dimensional groups (e.g. constant tip speed, constant Froude number) are used with limited success. Even in the successful cases, this can result in additional tedious trial and error experimentation and/or the matching of only one granule attribute (e.g. d_{50}) with mis-match in other attributes such as porosity or content uniformity. The dimensionless number and scale-up approaches currently existing in literature capture only some of these rate mechanisms. In order to develop a holistic scale-up approach it is required to have a more mechanistic framework where each of these rate mechanisms could be evaluated and correlated with different scales of operation. For instance, recent work has shown that for a HSG process, when a constant Froude number was used to determine optimal conditions at the next scale, this shifted the growth regime toward ‘nucleation only’ resulting in weaker and more porous granules. We will use a combination of dimensional groups, regime maps and model-based analyses to design scale up criteria. First, the dimensional group will provide a starting point for operating conditions. Subsequent regime map analyses will be used to fine-tune these conditions to ensure similar regimes are captured across scales. This will then be the next starting point for the model-based analyses which also captures the associated equipment differences. We will then use the model to optimize the set of operating conditions to ensure granule properties across scales match. The coupled model can also be used to maintain shear rates and hydrodynamics across scales that otherwise dimensional groups and regime maps cannot account for, but nevertheless are important to match up across scales. This integrated approach will be first tested from lab to pilot scale and subsequently from pilot to manufacturing. With sufficient training and model updates, we envision a scenario where only one manufacturing scale data set would be needed with other scenarios being able to be predicted from the scale-up methodology. We will work with member companies to identify scales of interest. Data at pilot and/or manufacturing scale would be requested from member companies.

3. Identification of critical unknowns and effect on project direction/outcome

We do not anticipate any critical unknowns that would adversely affect project direction/outcome. One potential unknown could be the timely availability of granulation data at larger-scales for the different formulation types (e.g. manufacturing scale). However, there is sufficient time for planning to ensure this is minimized. Another unknown could be re-prioritization of some of the tasks (based on member company input) which perhaps would change the order of which the outcomes are achieved.

4. Project timeline

Year 1 will focus on developing and identifying the integrated process modeling frameworks for 1. Batch HSG, 2. Continuous HSG, 3. Batch FBG and 4. Continuous FBG. We will also develop and implement efficient numerical solution and model reduction techniques to ensure these integrated models have the right balance between capturing accurate physics and being computationally efficient. DOEs will be performed for batch HSG and FBG for the baseline formulation. Model and experimental risk and sensitivity analyses will also be performed to ensure key experimental trends and sensitivities are captured and that critical formulation, process and design parameters are reflected in model formulations. We will also establish the design space and important boundaries to understand which regimes/kernels are important for different granulation processes and formulations. Experimental validation as benchmarking will be performed using the baseline formulation for batch HSG and FBG. **Year 2** will focus on developing/updating granulation kernels (from the literature and from PI's previous work) to reflect specific granulation and formulation types. Additional DOEs will be performed as a function of formulation type (e.g. soluble, insoluble, hydrophilic, hydrophobic). Particle/granule-scale experiments will also be performed to extract physics and knowledge for kernel development. Experimental validation and model/kernel iteration/update (as needed) for different formulations will be performed for batch HSG and FBG. **Year 3** will focus on batch scale-up of HSG and FBG and extensions to continuous HSG and FBG. For continuous granulation, DOEs will be performed for the different formulations and used for experimental validation. We expect much of the previously built knowledge to be transferrable but with still some additional process/model development. We will also develop the methodology to predict granule properties at scale-up conditions. DOE and data will be requested from companies for the different formulation types for the purpose of experimental validation. Although some of the tasks are sequential and iterative, several tasks are mutually exclusive and can be re-ordered (e.g. starting with which formulation types and with which granulation processes) based on priority, as determined by IFPRI member companies.

5. Synergy between proposed project and existing research programs in my group

The PI and his team are working on research programs that were/are funded by both federal/non-profit (e.g. NSF, DOE, U.S. FDA, NIPTE) and industrial (e.g. BMS, BASF, Evonik, Syngenta, Janssen, GSK, CNH Industrial, Handok Pharmaceuticals, Bosch) sources (http://www.pslrutgers.com/partners) in three specific areas that are highly synergistic to this proposed IFPRI project (http://www.pslrutgers.com/research-areas). These are 1. Multi-scale model development and validation of granulation processes, 2. Development of efficient numerical techniques and high-performance computing strategies and 3. Experimental studies and analysis of particle/granule microstructure. These areas form a solid foundation for the work proposed in the current IFPRI proposal and the PI has been working in these areas for more than 10 years and published more than 80 journal papers (http://www.pslrutgers.com/publications) in the areas of batch and continuous wet granulation (high-shear, fluid-bed and twin-screw), multi-scale modeling, numerical solution, granulation kernel development, experimental analyses, etc. Furthermore, continued research activities from existing projects add further value to the IFPRI project. Similarly, new learnings and findings from the IFPRI proposal will strengthen the PI's existing projects.

6. Interaction framework with IFPRI members and technology transfer

The PI and his team have substantial experience working with industry either individually or through consortiums such as the Rutgers Pharmaceutical Engineering Research Center (www.csops.org) and Rutgers Catalyst Manufacturing consortium (https://cbe.rutgers.edu/catalyst-manufacturing-center). In a similar capacity, we envision working closely with IFPRI members/companies via the following ways: 1. Receiving additional non-proprietary materials/formulations for testing, 2. Using different test methods available to the company(ies), 3. Updating project direction through industrial member guidance and mentorship, 4. Receiving data at different granulator scales and 5. Technology transfer. We expect to successfully transfer technology developed and know-how via the following methods: 1. Documentation of all codes (e.g. Matlab, EDEM, Fluent), test methods and protocols. 2. GUI development for code (E.g. Excel-based interface) for ease-of-use. 3. Periodic training at Rutgers and/or IFPRI meeting(s), 4. Hosting company personnel from member companies at Rutgers. As required, we will work closely with IFPRI members to continuously improve ways to collaborate and to transfer technology/know-how to ensure maximum benefit.

Linking Process and Product models for Wet Granulation: A Compartmentalised PBM-CFD-DEM model framework for Fluidised Bed Spray Granulation

Rachel Smith
The University of Sheffield

Executive Summary

Computational models for wet granulation processes are increasingly being used to model industrial processes. We would like to be able to link process with product performance, however there is a mismatch between the outputs of process models (typically size, sometimes composition) and the inputs for product models (often agglomerate shape and structure, e.g. porosity and pore size distribution). We aim to bridge this gap, by building a wet granulation model framework which outputs agglomerate structure, in addition to size and composition (see Figure 1). In this project, we will:

1. Develop a hybrid model framework for wet granulation which outputs information important for product models.
2. Validate this model experimentally.
3. Provide explicit guidance for future model builders, through the publication of a review paper on linking process and product models for wet granulation.

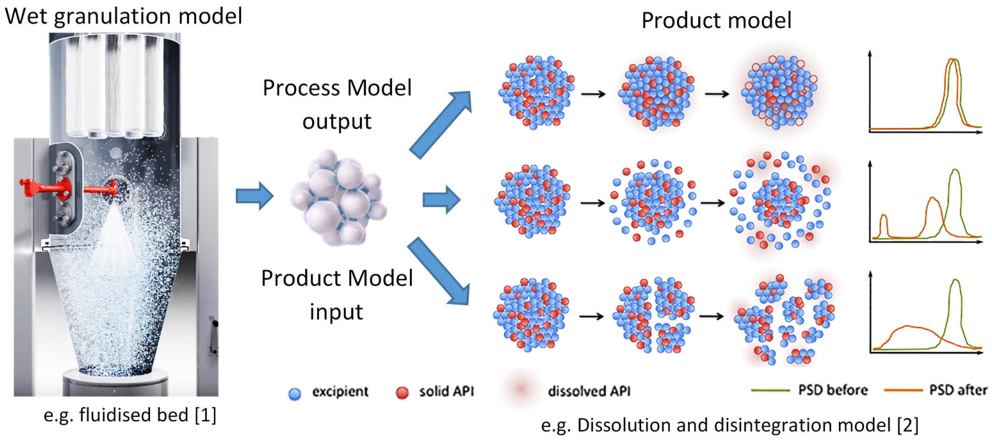


Figure 1: Schematic showing the linking of Process and Product Models

Introduction and Background

Wet granulation is a process used across a large range of industries. In particular, it is an integral operation in the pharmaceutical, food, minerals processing, consumer products and agrichemical industries. Over the past decades, huge strides have been made towards greater understanding of granulation processes, building micro-level understanding [3], regime maps [4, 5], process models [6-9], and product models [10-14].

Within a wet granulation process, particle and fluid interactions are occurring in multiple phases, and across multiple length scales. We have mechanistic models of many of these interactions, and there is great opportunity to apply these mechanistic models alongside modern computational techniques, to aid the design of granulation processes.

In granulation modelling, by far the most common dimension or parameter to be tracked is agglomerate size. However, agglomerate size is not the only input for product performance models. Many other parameters are important for these models, including agglomerate porosity and pore size distribution, wetting characteristics, morphology, and component content and distribution. To successfully link process models with product performance models, it is essential that the process model predicts the essential parameters for these performance models. In the future the linking of these process and product models, likely combined with the use of inverse methods, will enable genuine product driven process design and scale-up.

Modelling approach options

There are several key modelling approaches available to help predict granulation. Each have strengths and weaknesses, and critically, each have some very significant limitations. In this section, a brief overview is given of 3 common techniques: Population Balance Models (PBM), Computational Fluid Dynamics (CFD), and Discrete Element Modelling (DEM).

PBM: Population Balance Models are an excellent tool for process level modelling of granulation. The use of compartmentalised PBM has further enhanced the applicability of this method. However, PBM is restricted by the kernels used within it (often at least partially empirical), by the complicated solution methods required for multi-dimensional models, and by the limitations of the dimensions (or properties) which can be modelled. These limitations have constrained the applicability of PBM for some industrial problems, and using these tools for reliable design and scale-up remains a huge challenge.

CFD: The hydrodynamic behavior of particulate processes involving multiphase flows can be captured by using CFD processes. These include Eulerian-Eulerian (EE) methods (based on two fluid theory) or Eulerian-Lagrangian (EL) approaches. In EE both particle-phase and carrier-phase are considered as a continuum, and their flow field is represented in an Eulerian reference frame. In contrast, EL approaches include a number of models in which the particle phase is considered as a discretely dispersed phase referenced in a Lagrangian frame, and the carrier phase is represented to be a continuum and its flow field is formulated in Eulerian frame.

DEM: Discrete Element Modelling (DEM) is an explicit numerical method that models the interactions of all particles in a domain. The particles are rigid but are subject to local deformation in places of contact and the resulting forces from particle overlaps are calculated. The motion of the particles is modelled on a particle-by-particle basis, which makes the method computationally intensive, and traditionally this has a large impact on the number of particles that can be feasibly simulated. However, advances in computational capacity have made DEM simulations in the order of hundreds of thousands to several millions of particles commonplace. DEM has been used extensively, both on its own and coupled with CFD. Particle positions are known with time, and when coupled with CFD, the particle motion can be influenced by fluid flow.

Comparison of Techniques: It is clear that each of these methods has a series of benefits, drawbacks, and limitations, some of which are summarised in Table 1. These limitations have been identified by several researchers [15-17], who have coupled various models together to enhance the model output, while minimising numerical complexity and computational resource. Many of these models have been successfully used to describe wet granulation, however they lack the modelling of the key particle structure information required to feed into product performance models.

Table 1 – Strengths and Limitations of Particulate Computation Modelling Techniques

Technique	**Strengths**	**Weaknesses/Limitations**
PBM	1. Computationally inexpensive 2. Compartmentally divides the particles into classes – distributed parameters 3. Ability to use mechanistically based rate process kernels	1. Kernels are often mainly empirically 2. Many parameters need to be estimated, some without physical explanation 3. Unable to provide particle dynamics
DEM	1. Tracks particle dynamics based on physical models 2. Important particle dynamics information such as collision frequency 3. Captures the effect of geometry and its influence on particles	1. Computationally expensive 2. Complex criteria required to define particle evolution 3. Difficult to measure parameters required for the contact model, and to calibrate 4. Difficult to apply to full industrial systems
CFD	1. Detailed insight into flow behavior of multiphase systems 2. Computationally efficient in comparison to DEM 3. User friendly for industrial applications	1. Unable to provide collision frequencies and collision forces in a particulate flow 2. Unable to provide changes to particle size and structure in a particulate flow

Aims and Objectives

The aim of this research project is to create an industrially applicable modelling framework for a wet granulation process, and to use this framework to model a fluidised bed spray granulation (FBG) process as a case study. The model will produce the outputs required for product performance models, with a particular focus on agglomerate structure (e.g. pore size, distribution of components). This will be achieved by meeting the following objectives:

1. Development of a 3-way coupled PBM-CFD-DEM for a fluidised bed spray granulation process
2. Development and implementation of a strategy for minimising the required data sets for experimental parameter estimation and model validation.
3. Completion of a comprehensive validation strategy. This will involve the separate validation of individual PBM compartments, the DEM model and CFD, to increase confidence in the model.
4. A proposal submitted to the EPSRC for complementary project funding, to leverage this work, and increase project positive outcomes.

Research Approach

Fluidised bed wet granulation has been chosen as the model system for this project. With current techniques and computing power, it is an almost impossible task to implement a model where “everything” is known and spatially and temporally resolved, and which is able to be solved *a priori*. However, it is achievable to produce a hybrid model which uses mechanistic models for the various rate processes which occur in the bed, and which outputs essential information for product models.

While the product models can vary widely, depending on the intended product use, across the board agglomerate structure is an essential component to product performance. There is evidence that the structure of agglomerates affect strength [14, 18], tabletability/compactability [12, 13], and dissolution and disintegration [10, 19]. Most models which successfully link with product performance models must include some information on agglomerate structure. For example, the recent agglomerate breakage model developed by Dosta and co-workers [14] presented DEM models for agglomerate breakage, and demonstrated that granule strength was highly dependent on the intra-granule distribution of components. There is potential for the results from this model (i.e. DEM generated structures) to feed directly into product models like this one.

A model fitting this description requires the thoughtful development of a model framework. ***In this project, I propose we exploit each of the models for what they are good at, and avoid pushing them beyond their limits of usefulness.***

The first step in defining the modelling framework is to examine the granulator specifications and geometry, the probable rate processes occurring in the granulation, and the required outputs from the model. In the case of lab scale and manufacturing scale fluidised bed processes, granulators vary in dimension considerably. However, even lab scale fluidised bed granulators generally contain numbers of particles which are several orders of magnitude larger than can be comfortably modelled in a coupled CFD/DEM process.

FBG has complex and competing rate processes, which are difficult to model. However, fluidised bed granulators can be conceptually split into different geometric zones, in which different physical processes are occurring. This situation is ideal for compartmentalised PBM, as the geometric space can be separated into linked, simultaneously solved population balances, each containing only the required kernels to describe the dominant physical and chemical processes which are occurring in that volume, and has been demonstrated as a successful technique in the literature (e.g. [20-23]).

Figure 2 shows a conceptual model for a FBG process. It is proposed to split the fluidised bed into 2 PBM compartments: a spraying and layering compartment, and a bed compartment. The relevant rate processes are also summarised in the diagram. Selection and development of new mechanistic kernels for FBG is already occurring at The University of Sheffield as part of a current project, and this proposed project will build upon this work.

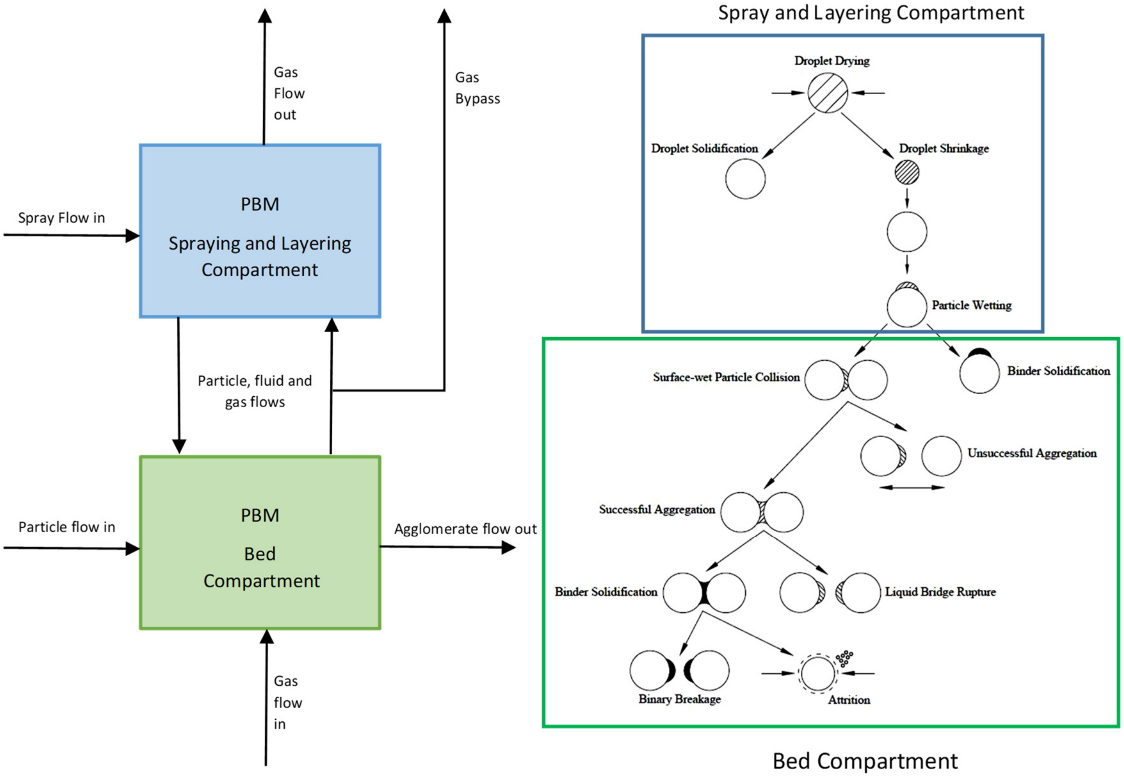


Figure 2: Proposed PBM Compartment Framework, and accompanying key mechanisms

A mechanistically based population balance with potential to be adapted for use in this PBM has recently been developed at the University of Sheffield. As an example of the mechanistic approach, an agglomeration kernel has been written which employs the particle coating number Φ_p [24] and Stokes criterion [3]. Figure 3 gives a conceptual view of the possible outcomes from different particle interaction scenarios. This kernel uses the particle coating number (Eq. 1) to calculate the fraction coating of the particle, F, with liquid (Eq. 2). Agglomeration success is then determined by the likelihood of liquid at the interface, and the Stokes criterion. If the viscous Stokes number St_v (Eq. 3) is smaller than the critical Stokes number St_v^* (Eq. 4), agglomeration will be successful. However, if St_v is larger than St_v^*, agglomeration will not be successful.

$$\Phi_p = \frac{6\, X_{LS} a_d}{\pi d_d^3 \rho_d A_{SA}} \qquad \text{Eq.1 [24]}$$

where Φ_p is the particle coating number, X_{LS} is the liquid-solid mass fraction, a_d is the footprint area of a single droplet, d_d is the volume equivalent spherical diameter of the droplet, ρ_d is the liquid density and A_{SA} is the specific surface area of the particle.

$$F = 1 - \exp\left(-\Phi_p\right) \qquad \text{Eq. 2 [24]}$$

$$St_v = \frac{8\, \rho d_p U_o}{18\mu} \qquad \text{Eq. 3 [3]}$$

where ρ is the granule density, d_p is the surface average particle diameter, U_o is the initial relative granule collisional velocity and μ is the liquid viscosity.

$$St_v^* = \left(1 + \frac{1}{e}\right) \ln\left(\frac{h}{h_a}\right) \qquad \text{Eq.4 [3]}$$

where e is the coefficient of restitution, h is the thickness of the liquid surface layer and h_a is the characteristic height of surface asperities.

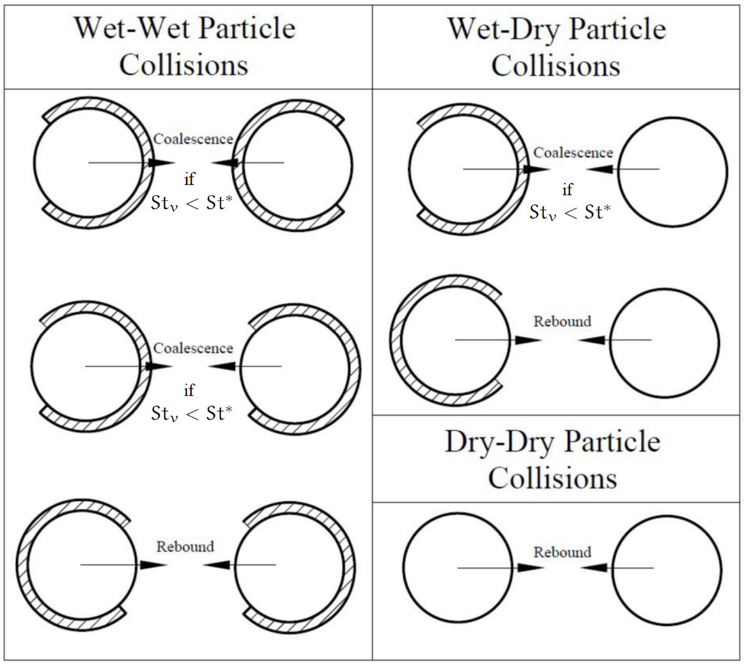


Figure 3: Potential Outcomes from Particle Collisions

Compartmentalised population balance models require key inputs which can be difficult to provide. In addition to a large list of material properties, many of which can be measured, calculated or approximated, there is key information about particle flows, occupancy, and velocities which are difficult to predict. To provide some of this information, we propose to link the compartmentalised PBM to a Eulerian-Lagrangian model for FBG, using Multiphase Particle-in-Cell (MP-PIC) [25]. This method has been shown to be accurate and reliable in simulating flows in fluidised beds, and is significantly faster to solve than CFD-DEM simulations.

This MP-PIC model will provide key information on the size of the fluidised bed compartments, and also provide mass flows into each of the compartments. It is expected that ANSYS Fluent will be used.

Small “Unit Cell” DEM/CFD models will be developed to provide agglomerate structure. As discussed earlier, DEM/CFD is extremely expensive to run. However work at Sheffield is ongoing into the use of these Unit Cell simulations, which are used to simulate very small volumes of a process unit ([26, 27]). By using DEM/CFD, intra-granule particle arrangements can be modelled, and these structures can be analysed to provide information such as void size distribution, overall porosity, and intra- and inter- granule distribution of components. Alternatively, the structures generated using DEM could be inputted directly into product models (e.g. [12-14]). There is also excellent potential to use this technique to input information into the PBM (e.g. collision frequencies and forces). It is expected that the DEM/CFD Unit Cell simulations will be modelled using EDEM and ANSYS Fluent.

The design of these small scale DEM/CFD simulations requires careful thought, and many options remain for the coupling of the models. Coming to these decisions will form part of the initial model design phase. A high-level schematic of the proposed modelling strategy is shown in Figure 4.

Model validation is always an essential and challenging element of model development, and in the case of combined models such as this, robust and careful validation becomes even more difficult and important. A clear model validation strategy will be developed as part of this project. Many options for experimental validation exist. We expect to develop small scale “smart” experiments to individually test the two PBM compartment models, the DEM/CFD simulations, and the MP-PIC CFD simulations, in addition to running lab scale fluidised bed experiments. Available agglomerate characterization techniques include particle size measurement (laser diffraction, sieving), optical microscopy, image analysis techniques, SEM with EDS, and micro CT (voxel size ~1 µm). We also have PIV available, to characterise fluidised bed flow and validate MP-PIC. Particular attention must be paid to validating particle structure outputs.

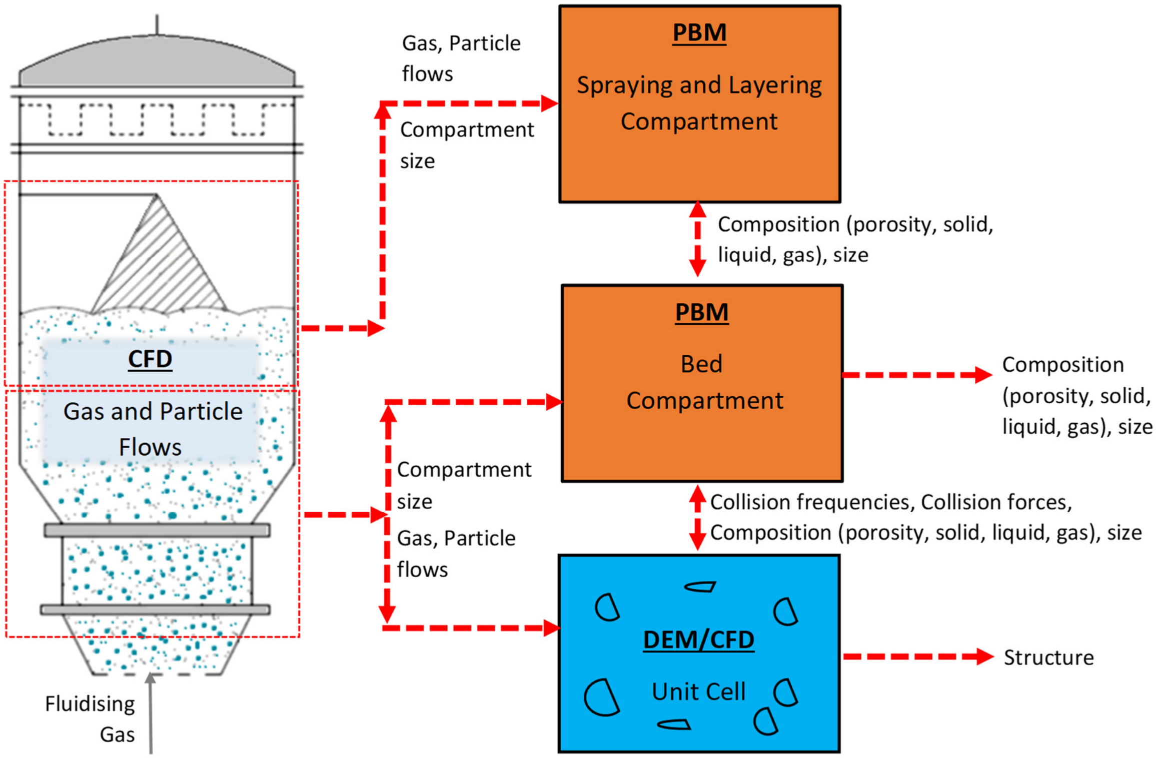


Figure 4: Preliminary high-level model coupling structure

Workplan, Deliverables and Milestones

This is an extremely challenging problem, which requires an integrated modelling approach. This project can be split into a series of individual tasks, as described below:

Tasks:
T1 – Literature review. A comprehensive literature review will be conducted, and will form the basis for the review paper (see milestone M1)
T2 – Overall model structure and coupling development
T3 – Population Balance Development – Spray and Layering Compartment
T4 – Population Balance Development – Bed Compartment
T5 – Fluidised Bed CFD Simulations
T6 – Fluidised Bed Flow Validation
T7 – Experimental Validation - Spray and Layering Compartment
T8 – Unit Cell DEM Development – Bed Compartment
T9 – Experimental Validation - Bed Compartment
T10 – Hybrid PBM-DEM-CFD Simulations
T11 – Hybrid PBM-DEM-CFD Experimental Validation
T12 – Model modification and testing of predictive capability

Milestones:
M1: Submission of a grant proposal for complementary funding from the EPSRC (Manufacturing the Future Theme, Responsive Mode).
M2: Submission of Computational Modelling in Wet Granulation Review Paper. This paper will contain a comprehensive review of the available computation tools for wet granulation, and will provide guidance on model development, with an emphasis on developing links between process and product models.
M3: Annual Report 1
M4: Annual Report 2
M5: Final Report 3

Leverage Existing Programmes and Facilities

There are several current and former projects within the Particle Technology Group which will be useful in this project. In particular, we have an ongoing project on PBM of fluidised bed granulation, which will significantly aid this work. We also have a project on the coupling of PBM (gPROMS) with DEM (EDEM) for a twin screw granulator. Additionally, we are currently conducting Unit Cell DEM simulations of granule breakage in particle flows, and this experience directly applicable to the Unit Cell DEM simulations proposed here.

We have a broad range of experimental and state of the art characterisation equipment, including 3 fluidised beds of varying scales. Of particular importance is the recent purchase of an Oxford Laser VisiSizer N60V System, which is able to measure drop size and drop velocities for liquid sprays.

This is an ambitious project. To support the project and improve the outcomes, I propose to leverage some current postdocs' expertise for this project. Dr. Omid Tash is currently working on PBM, and has significant experience experience in CFD. Omid will overee the MP-PIC development, and integration with PBM. Dr Li Ge Wang is a DEM expert, and is working on the PBM/DEM model for twin screw granulators, in addition to the current Unit Cell development. Li Ge will provide advice on the new Unit Cell DEM development, and on the interface with PBM.

While this project is achievable within the financial constraints, it could benefit from additional, complementary project funding. A key milestone for this project is the submission of a proposal for EPSRC funding, focused on the development of process models which are able to link with product models.

Opportunities for Collaboration with IFPRI Partners

There is excellent potential to work with IFPRI partners on this project. I have had discussions with Nestle and Roche in particular, and there are very good opportunities to work with these companies, and other IFPRI partners. Potential avenues include supplying materials of interest, potentially hosting the PhD student to conduct experimental validation experiments, or opportunities to work with the industrial modelling teams.

Our research group already has active research collaboration with several IFPRI partners (e.g. Roche, Syngenta, Lilly, Roche, P&G, PSE), working on projects ranging from studentships to the large consortium CMAC Future Continuous Manufacturing Hub. This project creates excellent opportunities to strengthen these links, and develop new ones.

Resources

The project budget is $38k/yr for 3 years. This will be primarily used to fund a PhD Student at The University of Sheffield. Using a conservative exchange rate of GBP £0.73 per USD, PhD tuition fees amount to approximately $6200/year, and a typical PhD student stipend is $20600/year. This comes to a total of $26800/year. $2000 will be budgeted for travel to the annual IFPRI meetings. The remaining $9200 per year will be spent on laboratory consumables and software licenses.

To support this project, a fraction of Dr Omid Tash's time will be devoted to the project (funded from other sources), to help ensure the project success. In addition to my normal involvement, I am expecting to take a semester sabbatical in Autumn 2019, and I intend to make this project the focus of my sabbatical leave. This will provide an excellent opportunity to make an accelerated start to the research.

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Project Gantt Chart

	Timescale (months)																																			
Task	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	21	32	33	34	35	36
T1 – Literature review	■	■	■	■	■	■																														
T2 – Overall model structure and coupling development				■	■	■	■	■	■																											
T3 – PBM Development - Spray and Layering Compartment							■	■	■	■	■	■																								
T4 – PBM Development – Bed Compartment									■	■	■	■	■	■																						
T5 – Fluidised Bed CFD Simulations											■	■	■	■	■	■	■	■	■	■																
T6 – Fluidised Bed Flow Validation (PIV)																■	■	■	■	■																
T7 – Experimental Validation - Spray and Layering Compartment													■	■	■																					
T8 – Unit Cell DEM Development – Bed Compartment															■	■	■	■	■	■	■	■														
T9 – Experimental Validation - Bed Compartment																					■	■	■													
T10 – Hybrid PBM-DEM-CFD Simulations																								■	■	■	■	■	■	■	■	■				
T11 – Hybrid PBM-DEM-CFD Experimental Validation																											■	■	■	■	■	■				
T12 – Model modification and testing of predictive capability																															■	■	■	■	■	■
Milestones	M1								M2			M3												M4												M5

IFPRI Research Project Brief

Precision powder feeding: Theoretical understanding and predictive model to link material properties to performance of twin screw feeders

The International Fine Particle Research Institute (IFPRI) wishes to fund a project to develop a theoretical understanding and predictive model for twin screw feeder performance. The project should encompass both theoretical and/or computational model development and validation. The model should predict feeder performance – mean mass flow rate and variability – and consider:

- The dependence of feeder performance on measurable powder properties and feeder geometry and configuration
- Powder density and other variations at the feeder inlet, e.g. due to hopper refill events
- Normal and shear stresses and powder densification in the screws (i.e. evolution of material state in the feeder),
- Predict cleaving/tensile breakage of consolidated powder at feeder outlet.

The model should identify and include critical material properties that impact feeder performance and identify any relevant scaling of the controlling physics across feeders of varying sizes (i.e. screw auger diameter) operating near the lower mass flow rate limit (i.e. slow screw auger rotation speeds), thus forming the basis for scaling to larger feeders. Ideally, the model will be amenable to use in a real-time feeder control scheme in the future.

Finally, the model should be tested/broken/validated with experiments with diverse powders. Of particular interest are “difficult” powders, i.e. fine, cohesive, and aeratable. Diverse mechanical properties should be examined, for example brittle, ductile, and elastoplastic materials. IFPRI members may be able to provide materials on interest and access to feeders of different scales and design.

Exclusive use of multi-variate approaches (e.g. PLS) is out of scope, as are multi-component systems, systems with significant particle damage during feeding, liquid pastes, and extrusion.

Modelling powder flow through screw feeders

Proposal submitted to IFPRI by
Prabhu R. Nott, Indian Institute of Science

Summary: This proposal outlines a study aimed at developing a theoretical model for understanding and predicting flow in twin screw feeders, with the aim of linking feeder performance to the powder properties, feeder geometry and dimensions, and operating conditions. We aim to start with non-cohesive powders, and progressively build in cohesion and other features to address industrially relevant powders. The predictions of the model will be tested against experimental measurements of the mean flow rate, the stress and bulk density at the casing measured by flush mounted sensors, and the velocity profile at the free surface measured by video imaging. DEM simulations will be used to validate and refine the theoretical studies, and guide experimental measurements.

1 Background

To my knowledge, no previous study has conducted a detailed theoretical analysis of the flow of powders in screw feeders using a continuum mechanical model. The reason for this is that constitutive models for powder flow are still in the stage of development, and model validation is typically attempted in simple shear flows, where the problem solution and experimental validation are easier. The flow in screw feeders is complex and three-dimensional, and developing an undertanding is as much a challenging scientific problem as it is of practical importance to industry. Despite the challenges, I believe my group is in a position to make a concerted attempt at tackling the problem, as we have experience in understanding reasonably complex flows. Section §1.1 describes some of our recent work, illustrating how a synergistic combination of theory, experiments and DEM simulations has helped us gain a fundamental understanding of an important aspect of non-cohesive powder flow, and resulted in the formulation of a new constitutive model. The features of this model, which we will use in this study, are then explained in §1.2.

1.1 Our recent work: A puzzling phenomenon in powder rheology, its resolution, and a theoretical understanding.

Motivated by predictions of one of our earlier theories for dense, slow flow of powders [1], we conducted experimental rheometry of non-cohesive powders [2, 3], wherein a custom-built cylindrical Couette device and sensitive 3-axis force sensors were used to measure the stress as a function of position along the outer cylinder (Fig. 1a). We made the surprising observation that when the powder is sheared, the vertical shear stress σ_{rz} at the outer cylinder changes sign, and the radial normal stress rises exponentially with depth (Fig. 1b). The findings were puzzling because they are contrary to previous measurements [4] and the predictions of plastic and visco-plastic theories [1, 3], which show a liquid-like linear rise of the normal stress with depth. To investigate this further, we used a combination of DEM simulations and high-speed video imaging of the free surface [5] and uncovered a remarkable secondary flow, in the form of a single toroidal vortex that spans the entire Couette cell and whose sense is anti-centrifugal. Further, we showed that the vortex is driven

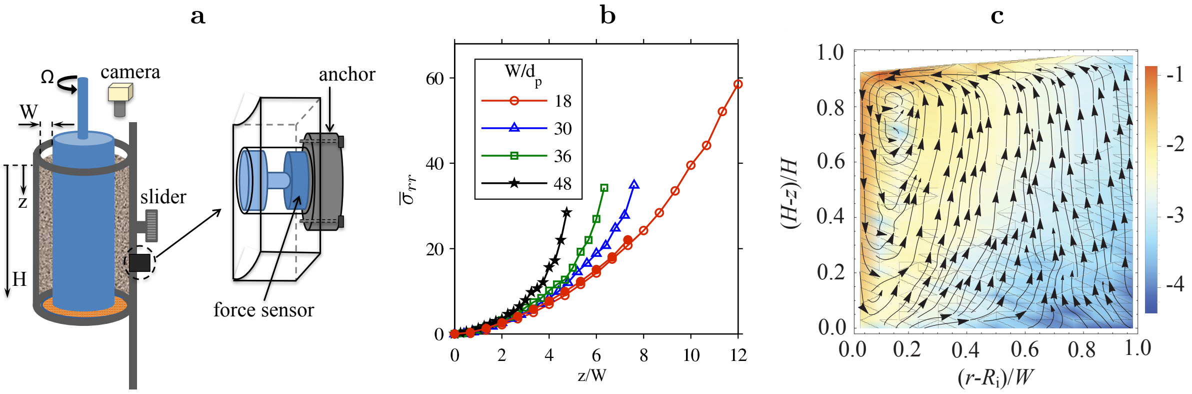

Figure 1: (a) Schematic figure of our instrumented cylindrical Couette apparatus. (b) The radial normal stress on the outer cylinder (scaled by $\rho g W$) for glass beads of mean diameter $d_p \approx 0.83$ mm as a function of the depth for different Couette gaps (from Ref. [2]). (c) The secondary flow in a vertical cross section of the Couette device – the streamlines represent the velocity vector in the cross section, and the colors indicate the magnitude of $\log(v_r^2 + v_z^2)^{1/2}$ (from Ref. [5]).

by shear-induced dilation. Using a simple plasticity model, we showed that the secondary flow explains the puzzling of the stress anomaly. This study underlines the importance of the coupling between density and flow, as it shows that dilatancy, which was thought to be relevant only in thin shear layers and ignored in continuum models, drives a macroscopic secondary flow that has a large rheological signature. This led us to propose a non-local constitutive model that incorporates dilatancy – the features of the model are described in §1.2.

1.2 Theoretical model

Continuum theories for granular flows enforce the balances of mass and momentum,

$$\mathrm{D}\rho/\mathrm{D}t = -\phi \boldsymbol{\nabla}\boldsymbol{\cdot}\boldsymbol{v}, \quad \mathrm{D}\boldsymbol{v}/\mathrm{D}t = \boldsymbol{\nabla}\boldsymbol{\cdot}\boldsymbol{\sigma} + \rho\,\boldsymbol{g} \tag{1a, b}$$

where $\mathrm{D}/\mathrm{D}t$ represents the material derivative, ρ is the density, $\boldsymbol{v}$ the velocity vector, $\boldsymbol{\sigma}$ the stress tensor and $\boldsymbol{g}$ is the gravitational body force. For closure, a constitutive model for $\boldsymbol{\sigma}$ is needed; the commonly used model for the regime of slow flow is that of classical plasticity [6, 7], comprising a yield condition that specifies the states of stress for which plastic flow can occur, and a flow rule that relates the components of the strain rate and stress tensors. The choice of a simple yield condition and flow rule leads to the constitutive relation [7]

$$\boldsymbol{\sigma} = -p\,\boldsymbol{I} + \frac{2\mu\, p_{\mathrm{c}}(\phi)}{\dot\gamma}\,\boldsymbol{D}, \quad p = p_{\mathrm{c}}(\phi)(1 - \frac{\mu_{\mathrm{b}}}{\dot\gamma}\,\boldsymbol{\nabla}\boldsymbol{\cdot}\boldsymbol{v}). \tag{2a, b}$$

Here p is the pressure, ϕ is the powder volume fraction, $\boldsymbol{D}$ is the strain rate tensor whose scalar magnitude is $\dot\gamma \equiv (2D_{ij}D_{ji})^{1/2}$, and $p_{\mathrm{c}}(\phi)$ is the pressure at the *critical state* of isochoric deformation [6]. The model parameters are the Coulomb friction coefficient μ and the bulk plastic modulus μ_{b}. This model has been used in several studies [8–10], but it suffers from three crucial deficiencies: (a) the velocity profile in simple shear flows is indeterminate; (b) it does not predict dilation (or compaction) at constant pressure, which was shown to be important in §1.1; (c) for time-dependent flows, the model results in a mathematically ill-posed problem [11].

We have recently proposed a non-local model [12] that overcomes all the deficiencies of classical plasticity, and is superior in significant ways to other non-local models proposed in recent years [1, 13]. Our model is based on the simple idea that the strain rate and density at one spatial location are caused not only by yielding at that point, but in a small region around it. This idea reflects inhomogeneities observed in experiments, such as force chains, and correlated motion of groups of grains. The resulting constitutive relation is

$$\boldsymbol{\sigma} = -p\,\boldsymbol{\delta} + \frac{2\mu\, p_{\mathrm{c}}(\phi)}{\dot{\gamma}}\,(\boldsymbol{D} - \ell^2\,\nabla^2\boldsymbol{D}), \tag{3a}$$

$$p = p_{\mathrm{c}}(\phi)[1 - \frac{\mu_{\mathrm{b}}}{\dot{\gamma}}(\boldsymbol{\nabla\cdot v} - \ell^2\,\nabla^2\boldsymbol{\nabla\cdot v})] - \ell^2\,\frac{\mathrm{d}p_{\mathrm{c}}}{\mathrm{d}\phi}\,\nabla^2\phi. \tag{3b}$$

Here, the terms multiplied by ℓ^2 (highlighted in red) are the non-local terms, with ℓ being the mesoscopic length scale that characterizes non-locality. It is clear from (3b) that the volume fraction ϕ can vary even when the pressure is constant, which is indeed commonly observed in the form of dilation in shear layers. Equation (3) is the constitutive model we will be using in the initial part of our investigation on non-cohesive powders; we will subsequently incorporate the effects of cohesion.

2 Proposed programme

The early application of continuum models for screw feeders [14] considered the idealized condition of perfect slip at the screw and casing surfaces, and the slope of the free surface determined from the static balance of forces between friction at the screw surface and gravity. Recent studies using DEM simulations [15] have found that the actual flow rate differs significantly from the idealized estimate, largely due to the complexity of the flow arising from the shear forces on the powder imparted by the screw(s) and casing. Therefore, to derive more realistic estimates of feed rates, and relate them to the feeder geometry and powder properties, detailed modelling of the flow, guided by DEM simulations and validated by experiments, are essential. The description of our recent work in §1.1 and §1.2 would hopefully have made the case that we are well placed to carry out this study. An outline of the proposed work under each of the elements is given below, followed by brief descriptions of the specific elements of our study in §2.2.

2.1 Outline of proposed work

Theoretical modelling
I propose to begin the modelling effort by first considering non-cohesive powders. Firstly, the exercise of posing the problem mathematically will give us useful heuristics for the feed rate as a function of the various dimensionless parameters that arise, whose influence can be tested systematically in the experiments. For the detailed numerical solution of the governing equations, the complexity of the geometry suggests that it is prudent to approach the problem in steps, going from a simple geometry that mimics some important features of a screw feeder (Fig. 2c) and finally reaching the time dependent flow in the full domain (Fig. 2a,b). There are also other challenges to be overcome in our modelling effort, such as choosing physically reasonable boundary conditions. The second phase of our modelling efforts will concentrate on incorporating cohesion in the constitutive model. The extension will require more than simply modifying the yield condition, as is often done – we must consider how cohesion alters the flow rule, and thereby the kinematics in the

shearing regions. Details on each of these aspects are given in §2.2 below.

Experiments
We will attempt to make measurements of the gross feed rate as a function of material properties and geometric parameters. Moreover, we will make detailed measurements of the stress and density at the casing as a function of axial position, and the velocity on the free surface of the powder bed. These studies will useful not just for validating our model, but also suggest ways in which the model may be refined, particularly for cohesive and aeratable powders.

DEM simulations
Apart from validation of the stepwise approach of our theoretical modelling, we expect DEM to provide information on the flow in the bulk that is difficult to obtain from experiments. Unlike the solution of the theoretical model, the complexity of the geometry poses no serious difficulty for DEM. The simulations will be particularly useful in model formulation and refinement for cohesive powders, for which constitutive models remain poorly developed.

2.2 Specific elements of the proposed investigation

A. Identification of dimensionless groups and heuristic analysis for feeder performance: The first outcome of posing the problem mathematically is that the relevant dimensionless groups that control feeder performance will become apparent. The idealized analysis of Ref. [14], discussed earlier, gave the volumetric feed rate in a single screw feeder as $\alpha A \Omega p$, where A is the cross section area of the feeder, Ω the frequency of screw rotation, and p their pitch (Fig. 2b). The 'efficiency factor' α depends on the angle of inclination of the screw surface to the radial line and the coefficient of wall friction μ_w of the screw feeder. For a twin screw feeder in a more realistic scenario, we expect shear of the powder, the slip coefficient K at boundaries (see item B below), the degree of intermeshing of the screws, powder friction coefficient μ and cohesion stress σ_{coh} (see item D below) to determine feeder performance, thereby giving rise to additional dimensionless parameters, such as μ/μ_w, $\sigma_{\text{coh}}/(\rho g D)$, K, etc. that α will depend on. This will now allow us to conduct a sensitivity analysis by experiment and DEM, and thereby determine the controlling parameters that determine the feed rate.

B. Detailed modelling of the flow of non-cohesive powders: Substituting the relation for the stress tensor $\boldsymbol{\sigma}$ from (3) into the momentum balance (1)b, we get a system of partial differential equations of fourth order in $\boldsymbol{v}$ and third order in ϕ. Solution of the equations requires sufficient boundary conditions for the velocity and volume fraction in each direction than for classical plasticity. The lack of physically realistic boundary conditions has been a lacuna in modelling of powder flow: for example, the majority of studies assume no-slip, while there is clear experimental evidence of slip. In our earlier studies [1, 12], we have used the boundary conditions

$$\boldsymbol{u} - \boldsymbol{u}_w = -K d_{\text{p}}\, \boldsymbol{n} \times \boldsymbol{\omega}, \quad \boldsymbol{n}\cdot\boldsymbol{\sigma}\cdot\boldsymbol{t} = \mu_w\, \boldsymbol{n}\cdot\boldsymbol{\sigma}\cdot\boldsymbol{n}, \quad \boldsymbol{n}\cdot\nabla\phi/\phi = \boldsymbol{n}\cdot\nabla\boldsymbol{v}\cdot\boldsymbol{t}/\boldsymbol{v}\cdot\boldsymbol{t} \quad (4\text{a, b, c})$$

where $\boldsymbol{n}$ and $\boldsymbol{t}$ are the unit normal and tangent vectors to the boundary. Above, (4a) determines the slip velocity, with K being the slip coefficient and $\boldsymbol{\omega}$ the powder vorticity, (4b) specifies that the ratio of the shear and normal stresses for plastic yield, and (4c) specifies the volume fraction at the boundary. These boundary

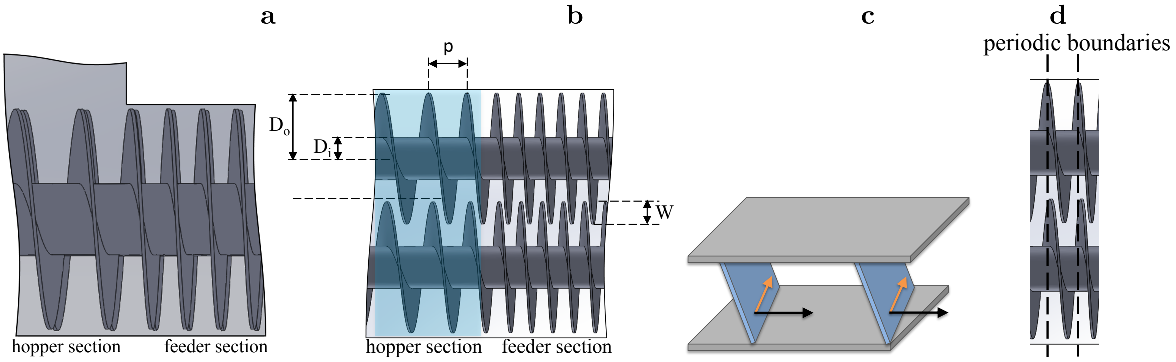

Figure 2: (a, b) The side and top views of the full domain, including the hopper and feeder sections. (c) Simplified rectangular mimic of the screw feeder. The two planar 'scrapers' (blue), which simulate the screw have constant velocity components in the axial and lateral directions. (d) The domain of width equal to one pitch of the screw with periodic boundaries on the left and right boundaries (dashed lines).

conditions make good qualitative predictions for flow in a split-bottom Couette device [12], but their validation by DEM simulations and experiment in other flows is necessary.

The governing equations will be solved numerically by discretizing the spatial domain using the finite volume method. Before solving the full time-dependent problem that includes the hopper and feeder sections (Fig. 2a,b), it is prudent to proceed in steps, and test the computations against DEM simulations at each step. The first step, shown schematically in Fig. 2c, is to simulate a simplified rectangular mimic of the helical screw – the screw is replaced by planar 'scrapers' that are inclined to the top and bottom walls, and have velocity components in the axial and lateral directions. Despite the simplification, the flow in the cross section will be non-trivial, and we expect this exercise to not only provide confidence in our theoretical model, but also provide insight into the swirling flow generated by the screws.

The next step will be to solve for the flow in the 'fully developed' feeder region by considering a domain of width equal to one screw pitch (Fig. 2d), with periodic boundary conditions applied at the left and right boundaries. Particular attention will be paid to understanding the flow in the intermeshing region between the two screws, as it will provide useful information on the enhanced effectiveness of twin screw over single screw feeders. We will finally consider the time-dependent problem over the full domain, including the hopper and feeder regions, wherein the time variation in the feed rate do to imposed variations in the hooper flow (such as refill events) can be explored. The time-dependent analysis will also be useful in designing a realtime feed-back control protocol for the feed rate.

C. DEM simulations We propose to use the open source LAMMPS and LIGGHTS packages for our simulations; the latter allows the user to insert a complex moving surface into the flow domain. This significantly eases the handling of the complex screw geometry, allowing us to concentrate on the physics of particle-particle and particle-wall interactions that determine feeder performance. The DEM simulations will be used for validating of the predictions of our theoretical model in each of the steps mentioned in item B above, and along with the experiments, suggest refinements and course corrections in the modelling.

Perhaps the most important utility of DEM will be in providing insight into

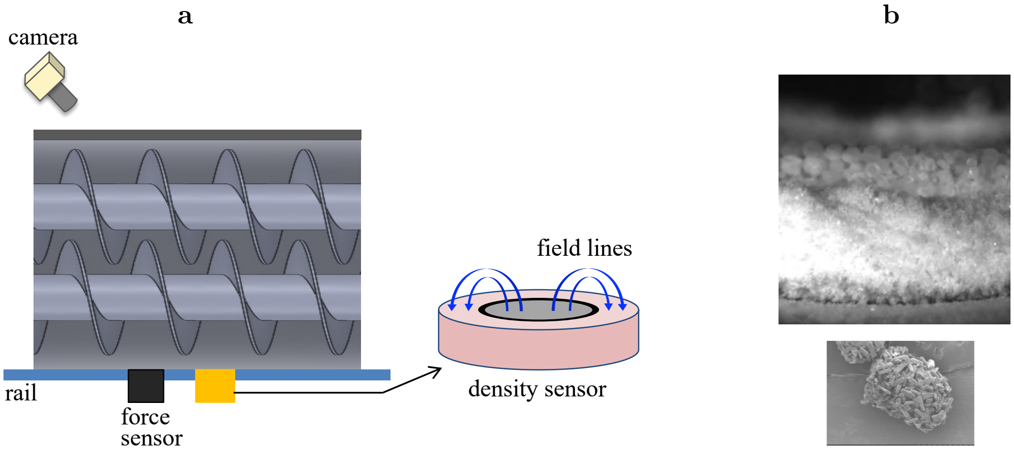

Figure 3: (a) Schematic of the proposed experimental apparatus, with stress and density measurements at the casing of the screw feeder. The sensors will be mounted on a sliding rail, and the force sensor and mounting will be similar to Fig. 1a. The density sensor will be a coaxial electrode capacitance/inductance sensor. The velocity field on the free surface of the powder will be measured by vide imaging. (b) Observation that the formation of particle agglomerates enhances shear of cohesive powders. The top panel shows the free surface of a powder sheared in our Couette device, where the formation of agglomerates near the rotating inner cylinder is apparent. The bottom panel is an SEM image of an agglomerate.

modelling cohesive and aeratable powders, discussed in item E below. We propose to use simple models for particle cohesion in DEM (e.g. van der Waal attraction, liquid bridge cohesion) and understand how cohesion alters the wall stress, flow and density fields. This information will help us build models for cohesive powders, and also inform how the experiments should be tailored to answer questions on how cohesion affects feeder performance.

D. Experiments We will measure as a function of time the feed rate by monitoring the weight of material at the exit vessel, the stress and density on the casing as a function of axial position using flush-mounted force and capacitance/inductance sensors, and the velocity at the free surface of the powder by video imaging, as shown in Fig. 3a. From these measurements, we will extract the mean quantities and their fluctuations. The latter will be important in assessing the variability of feeder performance for different materials and feeder geometries, and also in assessing how variations in the inlet conditions alter the flow rate at the exit of the feeder. We hope to determine the optimal design of the feeder that will buffer the exit flow rate against variations in the inlet conditions. Most importantly, all our measurements will be used to validate the theoretical predictions, described in item A and B above. As already mentioned, we expect that the DEM simulations to help us refine our experimental protocol and measurements, and help ask the right questions.

E. Extending the theoretical model to cohesive and aeratable powders Though listed last, this is an aspect we will start thinking about from the very beginning, as it is the most challenging aspect of the proposal. The conventional method for incorporating cohesion is to add a tensile component σ_{coh} to the pressure, i.e. by replacing the pressure p in (2a) and (3a) by $p - \sigma_{\mathrm{coh}}$. While this does increase the threshold shear stress for plastic yield, it does not alter the kinematics. The kinematics is determined by the flow rule, the simplest (and commonly used) form of which is $D'_{ij} = \dot{\lambda}\,\sigma'_{ij}$, where $\dot{\lambda}$ is termed the 'fluidity', and the primes on the stress and strain rate components indicate that they are the deviatoric parts. For non-cohesive powders, it can be shown that $\dot{\lambda} = -\dot{\gamma}/p_{\mathrm{c}}(\phi)$ [7], which was used to derive the constitutive relations (2) and (3). For cohesive powders, $\dot{\lambda}$ must be a function of σ_{coh} – while we have some preliminary ideas on how this could be incorporated, we await careful DEM simulations and imaging experiments to provide a clearer picture.

One aspect of cohesive powders that we have observed in some recent experiments is the native powder does not shear initially (but just slips at the moving wall), but with time the formation of agglomerates enhances the fluidity, after which the material shears almost like a non-cohesive powder – this is illustrated in Fig. 3b. This suggests that an evolution equation for agglomerate formation must also be included in the theoretical model, and that the fluidity must depend on the volume fraction of agglomerates. This will be an aspect that we will look into, and here again we will rely on careful imaging experiments and DEM simulations to guide model development.

In aeratable powders, the particles are fine enough that air drag make a significant contribution to the force balance on the particles. In the theoretical model, the equations of motion must be supplemented by the those for the gas, with a drag force linking the two. Such models have been widely used to study fluidization of powders, and reasonably accurate correlations for the drag are available in the literature. Hence, we do not see this as a significant challenge.

2.3 Critical unknowns that may affect programme outcome or direction

Most of the critical unknowns relate to cohesive powders: for theoretical modelling, the question is how the constitutive model for the stress (3) should be modified to model the effects of cohesion in a physically realistic manner. For DEM simulations, the question is what form of the cohesive force is representative of the interaction of powders that are important to industry. We are hopeful that the synergistic combination of theory, DEM simulations and experiments will answer these questions, but we will very much benefit from the experience and knowledge of domain experts in IFPRI.

There are some relatively minor unknowns that may affect the course of the programme, such as the numerical method used to solve the governing equations in §2.2B. There are instances when the finite volume method is numerically unstable, and if we encounter this we will have to use another numerical method. However, I am confident that our step-wise approach will identify and solve these problems early in the programme.

2.4 Expected year-wise accomplishments (with reference to itemized list in §2.2)

Year 1: Item A would be completed; the first step of item B, namely the rectangular mimic would be underway; item C for the rectangular mimic and the fully developed feeder section would be completed. Building the apparatus for item D would be underway. Some efforts in item E would have been initiated.

Year 2: The second step of item B, namely the fully developed feeder section is expected to be completed, and the third step (time dependent solution of the full domain) initiated. Work under item C for cohesive powders would be ongoing.

Under item D, experiments of model non-cohesive and cohesive powders would be ongoing. The first attempt at modelling of cohesive powders in item E would be initiated.

Year 3: Items B, C and D are expected to be completed. Under E, it is expected that some candidate constitutive models for cohesive powders would have been formulated, and numerical computations of the theoretical model would be completed. Comparison of the results of theory, DEM simulations, and experiments (under items B, C, D and E) would be concluded.

2.5 Leveraging current programmes in my research group for the project

As explained in §1.1, I have an active ongoing programme on the rheology of dense powders – I expect this project to be a nice extension of our current work. My group has also initiated a programme on characterization of the rheology and 'flowability' of cohesive powders. Application of our experience in theoretical modelling to the twin screw feeder will be challenging, but also satisfying due to its practical relevance to industry.

2.6 Support from IFPRI members

Support from IFPRI members would come in useful in the following ways:

1) Provide model powders of industrial relevance for which precision feeding is important.

2) Provide samples of "brittle, ductile, and elastoplastic" materials mentioned in the project brief, which we could characterize rheologically.

3) Access to feeders of different scales and design would be very welcome.

4) We would appreciate receiving data logged during screw feeding of "difficult" powders, if available, for comparison with our experimental data on model powders.

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Precision powder feeding: Theoretical understanding and predictive modeling to link material properties to the performance of twin screw feeders

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Scope

This effort addresses the International Fine Particle Research Institute (IFPRI) Research Grant Opportunity: Modeling Precision Feeders. The proposed research project aims at: (i) developing and implementing a predictive continuum model for predicting twin screw feeder performance and (ii) validating the model with results from an experimental characterization campaign conducted using a powder and a screw geometry relevant to IFPRI members.

Background

Powder feeding is critical in a wide array of manufacturing processes since the feeding step sets the mass flow rate and ratio of a formulation's components. If critical formulation components cannot be fed in a controlled manner, then the resulting product may have unacceptable quality. Unfortunately, many powders have poor flow properties, including being highly compressible and cohesive. Models that can provide guidance on how to better design and operate a screw feeder for poorly flowing, or "difficult", powders is highly desirable.

A number of screw feeder and screw conveyor models have been previously published, with many of these previous works focused on "well-behaved" materials. These previous works have included empirical (Rehkugler and Boyd, 1962; Das and Grace, 2011; Sander and Schonert 1999), analytical (Darnell and Mol, 1956; Tadmor and Broyer, 1972, Lovegrove and Williams, 1973; Hyun et al., 1997; Yu and Arnold, 1997; Das and Grace, 2008; Patterson, 2014), and computational (Hong et al., 2007; Moysey and Thompson, 2008; Owen and Clearly, 2009; Kretz et al., 2016; Mazor et al., 2017) studies to predict flow patterns, stresses, mass flow rate, and screw torque/power, with a focus on non-cohesive materials and single-flighted screws.

Empirical models rely extensively on experimentation. Such models are essentially curve fits to considerable experimental data. As such, their generalizability to feeder designs and materials not used to generate the data is questionable. In addition, empirical models provide little fundamental understanding concerning a process. The analytical models on screw feeding provide excellent fundamental insight, but must rely on modeling simplifications and assumptions in order to be manageable for analysis. These simplifications significantly limit their use for practical implementation, e.g., the current published analytical models are for incompressible, cohesionless materials in simple screw geometries. The state-of-the art computational models utilize the discrete element method (DEM), which tracks the movement of individual powder particles. These models have good generalizability, but the DEM method is limited by the number of particles that can be tracked computationally. As a result, the models assume particles are much larger than in reality, e.g., particle diameters on the order of millimeters as opposed to microns, with simplified properties, e.g., particles are assumed to be spherical. Furthermore, the particle properties used in DEM models are challenging to measure, making their quantitative predictions questionable.

This proposal describes a continuum computational model for predicting screw feeder flow dynamics. This approach is generalizable, provides fundamental insight, and avoids the limitations and difficulties found with the DEM approach. In addition, the PIs have previous experience applying similar continuum models to tableting (Sinha et al., 2010a, 2010b; Swaminathan et al., 2016), roll compaction (Muliadi et al., 2012a, 2012b; Liu and Wassgren, 2016), and blending and segregation (Liu et al., 2018a, 2018b, 2018c) powder systems with excellent quantitative success.

Proposed Objectives

This three year project has the following objectives that work toward the goal of developing, implementing, and validating a predictive continuum model for predicting the feeding dynamics of powders in a screw feeder and, thus, understanding equipment performance.

1. Produce a literature survey document summarizing published theoretical and empirical models for predicting screw feeder performance.
2. In collaboration with IFPRI, obtain a computer aided drawing (CAD) model of the screw, barrel, and hopper geometry of a “target” twin screw feeder.
3. In collaboration with IFPRI, identify a powder to be used in model and experimental testing. The powder should be safe for handling in a university laboratory environment.
4. Obtain modified Drucker Prager Cap (mDPC) elasto-plastic constitutive model properties of the powder identified in Objective 3. These properties will be measured at the Particle, Powder, and Compact Characterization Laboratory located at Purdue University, or obtained from the literature. The mDPC properties include the powder’s elastic modulus, Poisson’s ratio, cohesion, internal friction angle, cap eccentricity, and hydrostatic yield stress. These properties will be made for the range of solid fractions anticipated in the screw feeder. The model will not account for interstitial fluid effects or strain-rate dependence.
5. Develop a continuum model using the finite element method (FEM) with an mDPC material model to predict material flow dynamics, screw torque, powder bulk density at the exit, and mass flow rate, and variability thereof, for the screw feeder identified in Objective 2 and the material properties measured in Objective 4. This model will be developed using the commercially available Abaqus software.
6. Experimentally measure the flow behavior of the powder identified in Objective 3 in the screw feeder identified in Objective 2. These measurements should take place at the IFPRI member’s facilities where the target screw feeder is available. Ideally, the graduate student working on this project would travel to aid in the testing, if additional funding support is available, e.g., through one summer internship provided by an IFPRI member. Alternately, IFPRI can provide the measurements via internal testing. The parameters to measure will include the mass flow rate, powder bulk density at the exit and, if available, screw torque or power. The screw should operate in volumetric mode during these tests in order to maintain a constant screw speed. In addition, if possible, the screw should be pulled out of the barrel during testing so that material build-up on the screw can be documented and compared to model predictions.
7. Using the continuum model developed in Objective 5, conduct parametric studies on the dependence of feeder performance on powder properties, e.g., internal friction angle, wall

friction angle, cohesion, hardening behavior, and system parameters, e.g., screw/barrel size and screw speed. The baseline properties will correspond to the screw feeder identified in Objective 2 and the material properties measured in Objective 4, and each parameter will be varied while holding the others constant.

Benefits to IFPRI members

The successful completion of this project offers several benefits to IFPRI members, in particular, and to the academic and industrial communities in general. These include:

1. Identification of promising feed screw designs, operating conditions, and material parameters relevant to controllable screw feeding.
2. More focused experimentation and a reduction in Design of Experiments testing for proper operation of screw feeders.
3. Improved process understanding.
4. Better control of screw feeder operation, its optimization and its scaling-up.

Schedule and Deliverables

Milestone (Deliverable)	**Time from Project Start**
Identification of screw feeder system and associated CAD drawings	Y1 – Q1
Identification of test powder	Y1 – Q1
Literature survey (written report)	Y1 – Q3
Powder mDPC properties (table of values)	Y2 – Q1
FEM-mDPC model development complete	Y2 – Q3
FEM-mDPC model predictions complete	Y2 – Q4
Experiment data measured	Y3 – Q2
Parametric studies complete	Y3 – Q3
Capstone final report (written report, Abaqus input and user files)	Y3 – Q4

Existing Activities at Purdue's Center for Particulate Products and Processes (CP3)

The proposed research project could leverage on the following existing programs and research projects at Purdue's CP3:

a. Purdue's "Pharmaceutical Engineering", a Graduate Assistance in Areas of National Need (GAANN) grant from the U.S. Department of Education (supplement with 1/4 RA Ph.D. student)
b. Purdue's Particle, Powder, and Compact Characterization Laboratory (mDPC and other powder characterization equipment available)
c. Purdue's Rosen Center for Advanced Computing large scale computing clusters (both PIs have nodes on different clusters that will be used for the computations)
d. Two U.S. Food and Drug Administration (FDA) grants titled "Advance regulatory science to support the implementation of continuous solid dose manufacturing systems, equipped with control systems that are capable of handling raw material variability and assuring product quality in real time" and "Industry 4.0 Implementation in Continuous Pharmaceutical Manufacturing" (opportunity to pursue the development of a mechanistic reduced order model, based on the predictive continuum model developed under IFPRI support, and use it for model-predictive control of Purdue's Continuous Solids Processing Pilot Plant).

Budget

The total project budget is US$38,000 per year for three years. This budget will be used to support a 1/4 RA Ph.D. student to perform the work, faculty time for guiding the student's work and managing the project, and laboratory expenses. Note that, as stated in the Proposed Objectives, the budget does not include the cost of making feed screw measurements at the IFPRI's member facility. If Purdue personnel are involved in this task, additional sources of funding will be needed in the form of at least one summer internship for the Ph.D. student involved in the project.

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IFPRI Research Project Brief

Bridging the Gap Between Model and Industrial Colloidal Formulations

The International Fine Particle Research Institute (IFPRI) wishes to fund a project to develop and characterize models of complex industrial colloidal formulations. We are calling these "simplified industrial formulations" (SIFs). Real industrial formulations have complex compositions that make detailed mechanistic analysis of rheology difficult. Academic systems are designed specifically to make detailed characterization possible, but their simplicity may hide or eliminate rheological behavior exhibited by the industrial formulations. Thus, the long-term goal of this project is to ascertain what properties need to be included in model formulations (e.g. particle shape, roughness, porosity, surface chemistry) to reproduce behavior of real formulations. This will involve:

- working with IFPRI member companies to understand the composition of their formulations and the function of ingredients and to remove ingredients believed to have minimal impact on rheological behavior. The resulting SIFs will be synthesized by the member companies, including Syngenta (simplified agricultural concentrate) and Chemours (simplified paint).
- characterize the key behavior of the SIFs, i.e. rheology and structure evolution
- incrementally evolve exiting model systems to include greater complexity that can reproduce the behavior of the SIFs

IFPRI research proposal: Converging the suspension rheology of academic and industrial particulates

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1. Summary: Although particulate suspensions have been ubiquitous in many applications for decades, there is still an unmet need to connect the rheology of academic systems with their industrial counterparts. Most IFPRI projects tend to focus on the science of model colloids before translation to industrial systems. Unsurprisingly, the knowledge gap persists because the field of suspension rheology was built on a foundation of well-characterized colloids, while industrial formulations typically include mixtures of additives and particle shapes that are challenging to quantify. **The overarching goal of this research is to create a paradigm shift in bridging academic and industrial suspensions, while developing contact interactions as a new scientific concept to unify attractive and repulsive systems (FIG. 1).**

To accomplish this goal, we will work closely with IFPRI member companies from the start to obtain simplified industrial formulations (SIFs). Examples include organic crystals, milled active pharmaceutical ingredients, and calcite powders. These non-spherical and rough particulates are readily found in the coatings, chemicals, and consumer sectors. It is also known that surfactants, stabilizers, and thickeners are important additives in these SIFs. **An outstanding question in colloidal suspension rheology – one that has never been fully addressed – is whether there are any common structural frameworks applicable to suspensions with different interparticle interactions**. Based on our earlier insight gained from colloidal gels [1] (under the IFPRI project for Solomon/Furst) and from dense suspensions of rough colloids [2], in which we drew heavily from the disparate fields of granular systems and tribology, I hypothesize that the *contact interactions* between particles can be used to predict the rheology of a broad class of particulate suspensions. **Industrial collaboration goes hand-in-hand with new scientific understanding here**, because the hypothesis is best tested with model colloids and SIFs where differences in the particle morphology, microstructure, rheology, and handling techniques can be immediately quantified and refined.

For the 3-year period of this proposal, we focus on the creep and recovery of dense colloidal suspensions (diameters 500 nm ≤ $2a$ ≤ 10 µm) in which the particle asphericity, sizes, and interactions are adjustable. Creep has important applications for dense suspensions driven by stresses below the macroscopic yield stress ($\sigma \leq \sigma_y$), for example in times when paints or coatings dry on a vertical surface. Particle aspherity and roughness may impart surprising advantages, as demonstrated by preliminary studies in which dense suspensions of bumpy colloids exhibit longer relaxation times and remnant elasticity that were not seen with smooth spheres. Creep flow is also compatible with particle-level imaging due to the slow velocity profiles. Our research objectives and work program are as follows:

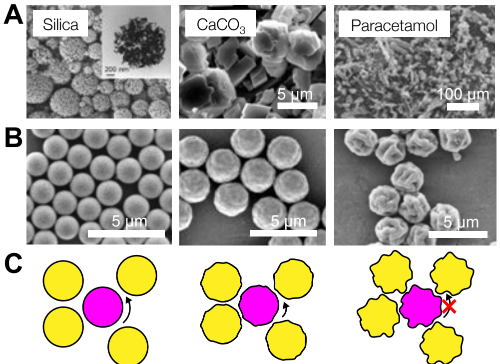

FIG. 1. How do we bridge ideal model particles to industrial systems? Particle geometry, pairwise interactions, and rheology of IFPRI SIFs will be used to tune the properties of our model colloidal suspensions. A unified structural framework based on particle contacts could generate a fresh perspective on suspension rheology.

<u>Objective 1: Match particle-level morphology, pairwise interactions, and suspension microstructure for SIFs and model colloids.</u> Together with IFPRI members such as Syngenta and Chemours, we will use a combination of atomic force microscopy (AFM), scanning electron microscopy (SEM), and confocal laser scanning microscopy (CLSM) to characterize SIFs and

model colloids in parallel. Our model colloids are poly(methyl methacrylate) (PMMA) stabilized by a grafted layer of poly(12-hydroxystearic acid) (PHSA), where we have control over their surface morphologies and shapes [2, 3]. Tunabe particle-level morphologies include asphericity and roughness parameters [2, 4]. Pairwise interactions for SIFs containing a limited number of additives will be matched to the pairwise interactions of model colloidal suspensions. These interactions will be tuned using depletion agents, salts, and surfactants [1, 5]. Microstructural details include particle positions and contact distributions in quiescent suspensions at volume fractions below jamming ($\phi \leq \phi_J$).

<u>Objective 2: Characterize particle contacts in creeping suspensions.</u> Our group has a fully operational confocal rheometer that is capable of simultaneous imaging and stress measurements at high resolutions. We plan on imaging and analyzing creeping flows containing fluorescent PMMA colloids that have been matched to the conditions of SIFs, as described in Objective 1. Local clusters with correlated mobilities are expected to result in avalanche-like deformations, which we have observed in our bulk rheometry experiments. Other microstructural parameters such as the radial distribution function and number density fluctuations will also be obtained for colloids with different surface geometries. The microstructural parameters will be directly connected to rheological measurements of creep and flow cessation (**FIG. 2**).

<u>Objective 3: Simulate suspension rheology using microtribology models.</u> The whole point of characterizing contact microstructure is to estimate the tribological variation at the particle level for densely packed suspensions. Our preliminary studies on lubricated microtextured elastomers show that the friction coefficient is a strongly nonlinear function of sliding speed, normal forces, and solvent viscosity. The strategy here is to measure and model the tribological behavior of textured surfaces, then use computational fluid dynamics (CFD) simulations of particulate systems in which the friction coefficient depends on the local velocity and contact microenvironment of each particle. Data from SIFs and model colloids will be used as inputs.

2. IFPRI member involvement: The creeping flow and recovery of dense particulate suspensions are important across a broad range of industries. However, the presence of surfactants and additives often dramatically alters processing conditions in a difficult-to-predict way. **We invite IFPRI members to provide us with a few sets of SIFs with known additive interactions and particle size/shape distributions, even if the exact values are not known.** The SIFs will enable us to perform benchmarking and validation of our model system. Regularly planned meetings with SIF providers to discuss differences in observations between the SIFs and model systems will be helpful in fine-tuning our experimental measurements.

3. PI's other projects of interest to this proposal

- Synthesis of monodisperse non-Brownian smooth and rough PMMA colloids ($2a \geq 8$ μm) that are stable in aqueous media;
- Calibration and build of a customized confocal tribometer;
- Modeling the micro-elastohydrodynamic lubrication behavior of a broad class of microtextured substrates, ranging from steel to poly(dimethyl siloxane) (PDMS).

4. Background

Colloids are micron-sized particles that exhibit thermal fluctuations when suspended in a fluid. These materials are exploited to maintain consistency and stability across a range of pharmaceuticals, foods, and consumer products. The flow properties of colloidal suspension are classically known to depend on ϕ and interparticle forces [6], but there is **increasing evidence that the dissipative forces should scale universally as the number and area of**

microscopic contacts that form between particles [7, 8]. The exact nature of the contact is certainly important, but these contacts would form whether the suspensions are attractive or repulsive. This is because *the dynamical arrest brought on by bond formation in attractive systems is also brought on by cage formation in dense repulsive systems [9].* This begs the question: is there a single microstructural parameter that links attractive and repulsive systems? **Addressing this question is important industrially, because the predictions could potentially work for many SIFs regardless of their additives, flow conditions, and particles shapes.**

New answers to this old problem must build upon parallel advances in the colloidal and granular literature. It is now accepted that the overall stress of a flowing suspension is a combination of the ensemble-averaged hydrodynamic and contact stresses (if present) from each particle [10, 11]. Multiple studies collectively suggest that the *number and distribution of particle-level contacts are key parameters that control the elastic response of particulate suspensions*. This statement has been supported for both dilute attractive systems and shear thickening suspensions. Our group, along with others, have discovered that localized dense clusters serve as load-bearing structures that contribute to elasticity in sheared depletion gels [1]. For discontinuously shear thickening dense suspensions, particles tend to overlap with one another because of an added push from flow; the contacts give rise to a frictional interaction that drastically increases suspension stresses and manifests as force chains in simulations [8]. Separately, the granular literature has focused on the connection between the shear modulus and the friction coefficient of particles in contact [12]. Although this is typically discussed within the context of packings above ϕ_J, such concepts could be equally valid for flowing particulate suspensions below ϕ_J in the dense regime. The instabilities generated by flow, along with random Brownian motion of individual colloids, are likely contributing to the presence of transient clusters that support stress-bearing networks.

An insight that we gain from these disparate fields is that **the solid-like stresses borne by densely packed particles depend on their microscopic contact distributions, which in turn depend on material and processing conditions**. The contact distribution is important because it is a measure of the friction coefficient experienced by particles in the suspension. Yet, there are *no known experimental studies that have directly probed the connection between contact distributions and mechanical properties for colloidal suspensions*. In addition, experiments are prone to uncertainties from instrumental and material fluctuations; the effect of these uncertainties on the precise definition of contact have not been studied *in situ*. What exactly is the role of interparticle separation in defining whether two particles are in contact? How does the nature of this contact vary if particles are aspherical and surfaces are uneven? Can we predict suspension rheology based on a statistical analysis of different contact parameters?

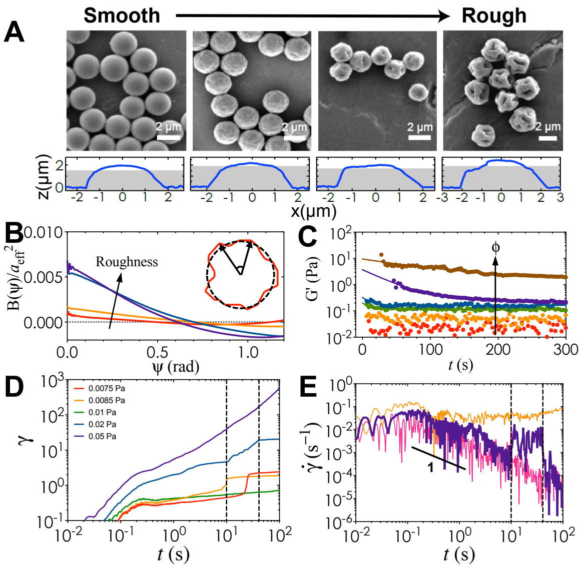

FIG. 2. Influence of particle surface morphology on suspension rheology. Details of the surface morphology and asphericity directly impact contact distributions and friction. This manifests as an unexpected remnant elasticity after cessation of flow, random strain jumps in creeping flow, and avalanche-like behavior which could impact the conformation of industrial coatings.

The interparticle separation distance (*h*) during flow is particularly important, because it dictates the particle friction coefficient, *μ* [13]. The value of *μ* is the ratio of the shear (F_s) and normal forces (F_n) on a particle, both of which diverge as h decreases in lubrication flow ($F_s \sim 1/h$ and $F_n \sim 1/h^2$) [14]. Even for a perfectly smooth and flat surface, **the value of μ is a non-trivial function of the sliding speed and solvent viscosity**, as captured in the so-called Stribeck curve in tribology. Our group has shown that **this dependence of μ is even more complex when surfaces are roughened**, due to geometry-dependent transitions in the elastohydrodynamic lubrication (EHL) regime. This understanding motivates us to apply microtribological frameworks to understand the suspension rheology of smooth and rough particles. Because the sliding speed, viscosity, and contact distances are measurable for each particle, we will be able to extract the local value of μ and use it as an input to CFD simulations in which the particle geometry, interparticle interactions, and flow conditions are experimentally defined. The end goal for this proposal is to use microtribology principles to obtain rheological predictions for both SIFs and model colloids.

5. Research plan

The deliverables of this project include **generalized parameters that are translatable between model colloids and SIFs in terms of morphology, microstructure, and rheology**. It will also introduce a **new microscopic structure-property framework based on contact interactions between particles**. Our group has significant expertise in confocal microscopy and rheometry techniques for colloidal suspensions. We will combine experiments and simulations to connect particle-level contact information to the microtribology and rheology of particles in creep flows.

5.1 Methodology

Materials. We will synthesize fluorescent PHSA-PMMA colloids with diameters ranging from 500 nm ≤ $2a$ ≤ 5 μm. The surface morphology is tunable from smooth to bumpy to mimic industrial particulates (**FIG. 2A**). The colloids are stable in a variety of organic media, ranging from cyclohexyl decalin blends to squalene, depending on whether density/refractive index matching is needed. Hard sphere behavior to charged interactions are possible through the addition of salts such as tetrabutylammonium chloride. Attractive interactions can be generated by deliberating changing the refractive index of the solvent, by addition of depletion agents such as polystyrene, or by switching to an aqueous solvent which introduces van der Waals interactions. The switching to aqueous systems is possible because we have synthesized poly(vinylpyrrolidone) (PVP)-stabilized PMMA particles with diameters up to 10 μm.

Roughness and asphericity characterization. AFM measurements in tapping mode will be used to obtain the 3D surface morphology of our model colloids and SIFs (**FIG. 2B**). The topography measurements will be fitted to an effective sphere and deviations from the spherical geometry will be characterized. Measures like the autocovariance, root-mean-squared roughness, and slopes of asperities will be obtained.

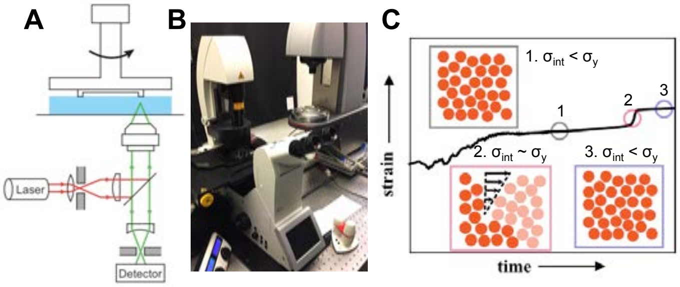

FIG. 3. Simultaneous imaging and stress measurements on a confocal rheometer allow us to probe local changes in contact distribution, velocity correlations, and other microstructural changes for dense creeping flows.

Bulk rheometry. Preliminary studies on a stress-controlled rheometer have shown that rough colloids exhibit reduced values of ϕ_J, likely because frictional interactions increase excluded volumes in flow [2]. We also found that the suspension elasticity relaxes much more slowly in dense suspensions rough colloids after shear ceases (**FIG. 2C**). Furthermore, the suspensions undergo stochastic strain jumps when creep flows are applied at $\sigma < \sigma_y$ (**FIG. 2D**). Between intermittent strain jump events, suspensions exhibit strain rates that scale inversely with time (**FIG. 2E**). This so-called Andrade-like creep behavior has been observed in protein gels and granular solids [15]. Our results provide early evidence that it is also found in dense colloidal suspensions. Collectively, these data suggest that particle geometry strongly affects the structural relaxation of aspherical particles.

Confocal rheometry and microstructural analysis. Our group has completed the build of a confocal rheometer that is capable of imaging particulate suspensions and measuring bulk stresses during shear flow (**FIG. 3A, B**). This technique allows us to pinpoint the microstructural origin of strain jumps in creeping flow, perhaps due to collective rearrangements and avalanche-like behavior (**FIG. 3C**). The CLSM images rapidly in 3D and standard image processing algorithms are used to identify particle centroids during flow, as we have shown earlier for colloidal gels [1]. Imaging can be done at very high speeds (f = 24kHz, meaning 1-μm particles diffuse no more than 1% of their radius per frame even with water as a solvent) and high resolution (down to 120 nm in the xy-plane). We expect to identify cluster correlation lengths such as that shown in **FIG. 4A**. These clusters could be quite important in connecting microstructure to rheology, such as the type described by nonlocal models for sheared granular systems [12]. Within each correlated cluster, the number of contacts for smooth and rough colloids is expected to be different due to frictional interactions (**FIG. 4B**). The microstructure and pairwise interaction potential will be quantified using the radial distribution function (**FIG. 4C**), the contact number distribution and mean contact number $<z>$ (**FIG. 4D**), as well as the measured maximum packing of smooth ahd rough colloids under sedimentation (**FIG. 4E**).

Tribology measurements and modeling. The contact information and local velocity of particles obtained from confocal rheometry allows us to estimate the friction coefficient at the particle surfaces based on the Derjaguin approximation (**FIG. 5A**). This approximation states that at small enough length scales, circular bodies can be conceptualized as flat surfaces. We have conducted preliminary measurements of microtextured soft surfaces using a ball-on-three-plate tribology accessory on our stress-controlled rheometer (**FIG. 5B, C**). These textured surfaces are made out of PDMS, which is an elastomer with well-characterized mechanical and surface properties. Our data demonstrates that friction is highly complex with textured surfaces, even in the completely lubricated regime. The Stribeck curves for various surface geometries show an intermediate friction peak as a function of the non-dimensional Sommerfeld number, which embodies the sliding velocity and solvent viscosity (**FIG. 5D**). We have made significant strides in developing a scaling theory to predict these Stribeck curves (**FIG. 5E**), which has never been successfully done in the tribology literature. We plan to develop these frameworks for more complex surface geometries and to use them as input to simulations of particulate suspensions.

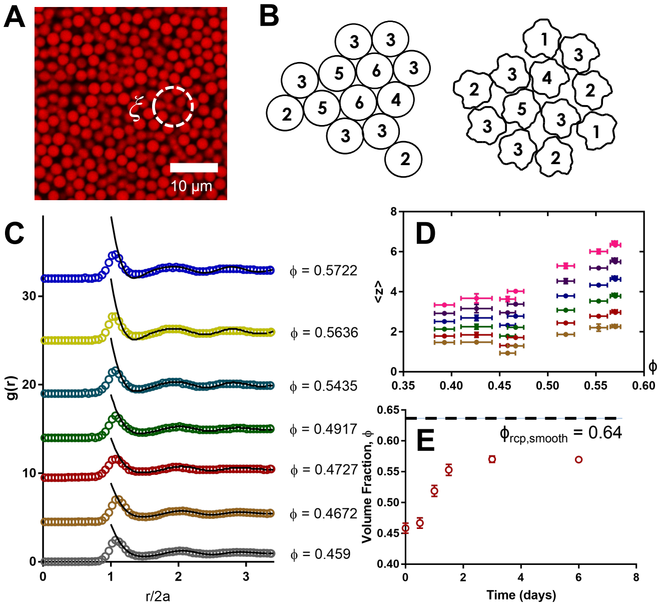

FIG. 4. The nature of particle contacts dictates local friction, which dramatically alters bulk rheology. Contact distributions and microstructure will be quantified with high speed imaging during creep flow on our confocal rheometer platform, using model systems and SIFs.

CFD simulations of particulate suspensions. We will use COMSOL Multiphysics as a first step to simulate the behavior of particulate suspensions in unconfined creep flow. The geometry of the particles will be defined with the AFM experimental data. If particles come into contact, we will impose additional frictional forces depending on the local velocity and geometry of the particles. The form of the friction will be estimated from the Stribeck behavior for microtextured surfaces. Simulation results will be validated against macroscopic rheology and microscopic structural signatures obtained from experiments.

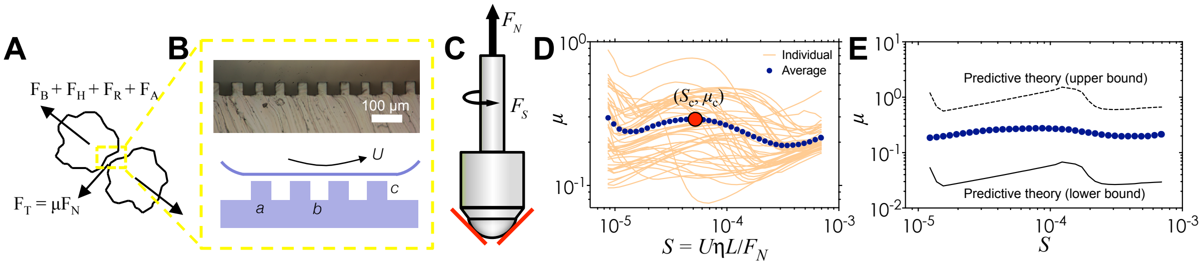

FIG. 5. The friction between rough particles may be estimated from the tribology of microtextured surfaces in lubricated flows. We have developed a scaling model that predicts the elastohydrodynamic lubrication transitions for a very broad class of textured materials, including soft elastomers, metals, and high molecular weight polymers. This model will be used as input to CFD simulations of particulate flows in which the friction force at contact can be defined as a function of particle geometry and local flow velocities.

5.2. Project timeline

Year 1

- Characterize the 3D surface profiles for SIFs and model colloids with AFM;
- Extract estimates of pairwise interactions for SIFs with different additives and particle shapes, either by light scattering or microstructural characterization;
- Match experimental conditions of model colloidal suspensions to SIFs.

Year 2

- Image and quantify the particle-level contact microstructure of model systems with various particle geometries and additives;
- Quantify cluster correlation lengths in model suspensions during creep and recovery;
- Measure macroscopic rheology of SIFs as a third benchmarking tool.

Year 3

- Set up CFD simulations with particle geometry, local velocities, and Stribeck curves for various contact configurations as obtained from experiments;
- Establish general frameworks for how particle asphericity, pairwise interactions, and surface morphology impact contact microstructure in SIFs and model systems.

5.3 Budget: We request $38,000 per year for 3 years to partially fund a Ph.D. student to work on this project. The remainder of the student's stipend and tuition will come from a federally funded project with complementary objectives. The tentative allocation of this annual budget is as follows: $29,000 will be assigned to student support, $3,000 for faculty salary support, $3,000 for travel, and $3,000 for materials and consumables.

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Tuning Complex Colloidal Systems to meet Industrial challenges:

Exploiting thixotropy and handling ageing

Principal Investigator (PI): George Petekidis
Host Organization: IESL-FORTH, Crete
Duration of proposed research work: 36 months

Outline:

We propose to develop and characterize model colloidal systems, with varying tunable interactions that can mimic the basic ingredients of complex industrial colloidal formulations. The latter have complex compositions, with interparticle interactions and surface effects often not well understood as well as significant shape and/or size polydispersity. Such effects render a detailed mechanistic analysis and prediction of their rheological response difficult. Therefore tailored design of new materials and formulations with improved properties is not possible since as in-depth understanding of the underlying science is not available. On the other hand colloidal particles used as model systems in academic research are well characterized, but their simplicity hides the rheological behavior exhibited by their industrial counterparts.

An example is systems that exhibit ***"thixotropy"***, a rheological response detected in many complex industrial formulations where rheological properties are affected by the mechanical history [1]. Such response has been studied in model colloidal gels where external fields (such as steady or oscillatory pre-shear shear) were demonstrated to affect or even tune their mechanical properties. Another related phenomenon is ***"ageing"*,** i.e. the time evolution of the underlying structure and/or particle interactions affecting the mechanical properties of a system. Understanding the origins of such time evolution at rest and under external stimuli (shear/flow/shaking etc.) requires probing them structure and dynamics at microscopic or even single particle level.

The knowledge of the underlying mechanisms responsible for thixotropy and ageing may be applied to a variety of similar industrial formulations (such as paints, slurries, foodstuff, cosmetics, agrochemicals etc.) enabling design of improved products, and fine tuning of industrial processes (for example in oil recovery, pipe flows, concrete setting etc.).

Towards this aim the first goal of this project is to ascertain what properties need to be included in model formulations (e.g. particle shape, roughness, porosity, surface chemistry) to reproduce behavior of real formulations. These systems will then allow efficient and detailed experimental studies providing answers to important problems of industrial systems. To this end **our specific aim is to develop structure-property relationships as a basis for designing materials with tunable mechanical properties via the application of external shear/flow and to be able to predict and alter ageing effects.**

To achieve these goals **we plan to work in close collaboration with IFPRI industrial partners** in order to i) determine open problems to be targeted and ii) develop model Simplified Industrial Formulations (SIFs). These will be real industrial formulations properly modified synthetically to strip down their complexity but keep their basics rheological response. As an example two systems that may be studied are simplified agrochemical formulations (in collaboration with Syngenta) and simplified paints (in collaboration with Chemours). In parallel a series of model systems commonly used in academia (where FORTH has large experience) will be tuned and incrementally evolve to reproduce the response of SIFs. Such Complex Academic Formulations (CAFs) together with the SIFs will allow bridging the two worlds (applied industrial with fundamental academic research)

Using SIFs we will perform state-of-the-art experiments to investigate their mechanical properties and link to underlying structure and dynamics at different length scales. Similar measurements in CAFs in addition to prior knowledge on model systems will allow further tuning of SIFs to attack the specific industrial problems under consideration.

State of the art

Understanding the **flow and microscopic dynamics** of complex colloidal systems is of profound scientific and technological importance since these systems cover a broad range of applications such as traditional consumer products (foodstuff, paints, agrochemicals etc.), cutting-edge emerging technologies (photonics, phononics, optoelectronics, 3D printing), oil recovery, mining flows, biological applications and complex intracellular functions [1, 2]. When mesoscopic units (typically 10 nm to 10 μm), such as colloidal particles or polymer chains are dispersed in a medium (usually liquid solvent) Brownian motion is of central importance and the interplay between equilibrium thermodynamic phases (fluids and crystals) and metastable states (glasses and gels) is dictated by the volume fraction and details of interparticle interactions (e.g. strength and range of attractions)[3, 4]. Tuning of the final macroscopic material properties (mechanical, thermal, electrical) may be achieved by either changing constituents and interactions or imposing external fields. The latter can lead to temporary structural (and mechanical) changes (e.g. equilibrium phases in electric/magnetic fields) or even permanent effects in the case of metastable frustrated states [1, 5].

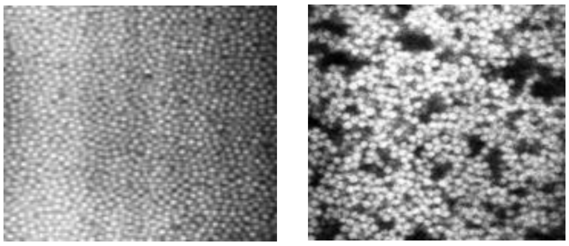

Figure 1: Confocal Microscopy Images from (left) a sterically stabilized PMMA particles in a glass state (ϕ=0.6) and (right) a depletion gel at intermediate volume fraction (ϕ=0.44, interaction energy, U=-16kT, and attraction range ξ=0.05). From Koumakis et al. Soft Matter, 2015 [6]

Out-of-equilibrium, metastable states: Colloidal glasses and gels as model systems for industrial products and processes

Concentrated colloidal suspensions, emulsions and polymers undergo a transition from a fluid phase to disordered, **out-of-equilibrium solid states such as glasses or gels** which exhibit **complex internal dynamics, viscoelastic properties, yield stress and ageing** [1]. This often involves strong thixotropic response, i.e., time-evolving properties that depend on the preparation history [1, 7].

The glass transition arises when many constituents interact cooperatively and prevent the system from reaching equilibrium, with a classic colloidal paradigm the one of hard spheres that are trapped in the glass state at volume fractions ϕ≥0.58 (figure 1, left), whereas the thermodynamic equilibrium state would be that of an FCC crystal [4]. Moreover when attractive interactions are present, colloidal systems (similarly to polymers) also form gels (figure 1, right) where particles agglomerate in clusters and form a space spanning network with a solid like response. In general, kinetic arrest describes the different ways (density, temperature, flow) by which the ability of a system to flow is lost [1, 8].

The interplay between thermodynamic equilibrium and metastable (out-of-equilibrium) states is also affected from (or other times leads into) ageing, i.e. a time evolution of macroscopic (and microscopic) properties with waiting time. In colloidal gels for example microstructure coarsening through bond reorganisation usually leads to an increase of the gel strength and an evolution of its rheological properties [9, 10], while often times gravitational effects intervene causing a delayed gel collapse [11, 12], a phenomenon that originates from an interplay of structural coarsening of the gel (more pronounced at low and intermediate volume fractions gels with weak attractions), and gravity induced stresses on the gel network.

Tunability of material's properties by shear and flow

While thixotropy is a common phenomenon in industrial colloidal systems such as carbon black or clay suspensions, bentonite slurries etc., several investigations in model systems such as colloid-polymer depletion gels have showed how external fields can been used to tailor colloidal gel structure formation, mechanical and flow properties [1].

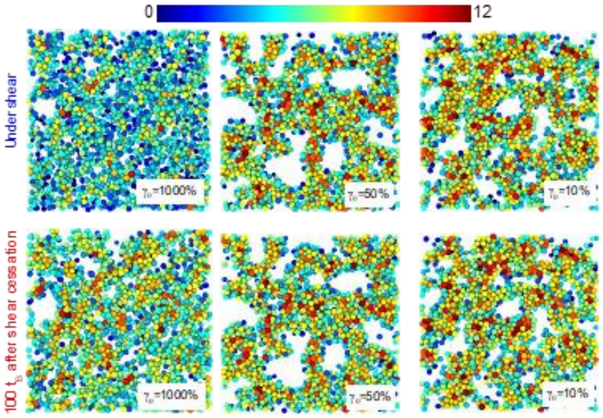

Figure 2: Shear-induced tuning of colloidal gels: Varying strain amplitude under oscillatory shear or shear rate under steady shear leads to metastable gel states with different structural heterogeneities and tunable linear and nonlinear mechanical properties. From Moghimi et al. Soft Matter, 2016 [5].

One way to tune metastable states is by external fields such as steady or oscillatory preshear which allows the system to access microstructures (figure 2) that cannot be easily reached by changing thermodynamic variables [5, 6]. Shearing these systems produces a wide variety of structures with different mechanical properties [5, 6, 13]. Depending on the shear rate, enhanced cluster formation or strong bond breaking may take place. Eventually shearing at high rates (or strain amplitude) leads to stronger and more homogeneous gels, as opposed to lower shear rates which create inhomogeneities and weaker gels. Such effects have strong impact also on the yield stress, delayed yielding and collapse of a gel network [5, 6] and are important in various technological applications. Examples include processing conditions that affect structure and mechanical properties, vitrification during solvent evaporation and film formation that may localize internal stresses and create inhomogeneities, ageing and sedimentation of attractive colloidal formulates that alters their mechanical and flow properties or re-dispersion effects during mixing.

Main Goal & Objectives

Our goal is to **unravel the main mechanisms related with thixotropy and ageing in specific industrial formulations** and **exploit them in order to tune and control their microstructure and mechanical properties**. Emphasis will be given on effects of shear and ageing on the mechanical properties of industrial formulations in simplified forms that consist of colloidal gels, concentrated colloidal suspensions and mixtures.

We propose to study simplified systems (SIFs) of two main system categories: a) based on colloids stabilized by steric or electrostatic repulsions and b) colloidal systems with dominant and/or time evolving attractive interactions. Along these lines SIFs' properties and their evolution with time will be studied under different conditions, i.e. both at rest (as during storage) as well as under shear and flow (such as in processing, spreading, mixing, spraying, printing, etc.). Our research program will cover an extensive range of the parameter space relevant to industrial applications, by carefully varying single particle properties (size, shape, polydispersity), changing interparticle and surface interactions (range and strength of attractions or repulsions, surface roughness), particle concentrations, composition and mixing rations, as well as environment (temperature, pH, pressure) and external fields (shear and flow rates, confinement in constricted flows at and near surface etc).

Research Methodology/Implementation plan: Below we present a detailed research plan of the proposed program (for the initial 3 year period) and the experimental resources that will be used:

Model industrial prototypes (SIFs)

The characterisation of interactions, aggregation phenomena and rheological properties as a function of ageing time after slow sedimentation (mimicking long time storage), and subsequent re-dispersion via shear/shaking/mixing under different conditions (shear rate/time etc) will be explored within **three main case studies.** The effect of ageing and shear induced redispersion (or rejuvenation) or shear/shaking induced agglomeration will be studied via linear and nonlinear rheometry. More specifically the shear thinning response (with limiting zero and high shear viscosities as well as intermediate rate behavior) and the existence and variation of the yield stress and thixotropic response will be examined under various conditions (over time, after and under shear, with changing temperature, pressure and/or pH).

We expect to work mainly on the following three case studies:

1) ***Simplified paint formulations:***

Extensive rheological testing in a variety of conditions and ageing times will be performed in SIFs prepared by IFPRI partner industries (for example Chemours) based on real industrial products such as PVC latex paints. These may contain water based mixtures of polymer particles with calcium carbonate particles ($CaCO_3$) or silica particles and or TiO_2 particles. Typical volume fractions will range from 30 to 50%, similarly to what is used in commercial paints. Within this framework different SIFs with varying composition of TiO_2 or $CaCO_3$ and resin will used to investigate ageing and shear induced effects on the rheology. The latter will be linked with the microscopic structure and interparticle and surface interactions via combined experimental techniques including scattering, microscopy and rheometry. Note that the lab has extensive experience on rheological studies of similar type model systems as well as with their industrial counterparts.

2) ***Simplified colloidal agrochemical formulations:***

These systems typically comprise of polydisperse micron size particles (of organic crystals) dispersed in water with suitable dispersants, initially at volume fractions of 30-40%, while they may be further diluted with the addition of components, including high molecular surfactants. Different SIFs will be designed together with IFPRI partners (such as Syngenta) incorporating particles (possible prepared with a variety of procedures), ionic dispersants, macromolecular anti-settling agents (such as xanthan gum and/or bentonite clay particles), and salts. The effort here will be to understand the key mechanisms affecting colloidal stability, aggregation and sediment formation over time, as well as possible procedures (shaking/shearing etc) that may allow full and efficient re-dispersion of the system under different conditions (temperature for example). The target is the design of systems with minimal ageing (evolution of interactions and size) and sediment formation that are also fully rejuvenatable via shearing/shaking etc. Different competing mechanisms will be probed and will be contrasted with current knowledge in model colloidal and polymeric systems. For example introduction of depletion attractions by the addition of polymeric species versus stabilization and increase of medium viscosity against sedimentation of dispersed particles.

3) ***Other applications*** *potentially relevant to industrially systems*

In addition we wish to explore the use of existing state-of-the-art experimental infrastructure and our know-how in colloid and polymer rheology and dynamics for other potential industrial problems related with the ***effects of high pressure*** (as an alternative thermodynamic) on bulk systems, and thrixotropic/ageing phenomena in ***surfaces and interfaces***. Related with the former we can monitor the stability and aggregation process in certain formulations under high pressure (up to 1000 bar) via dedicated high pressure scattering and microscopy set-ups. Regarding the latter, near wall DLS and interfacial rheometry provide powerful tools to study such effects in 2D. During the first 6 months we will explore any relevant interest among IFPRI partners for such studies that are relevant to applications such as flow of drilling muds and oil products underground and/or in confined environments and in surface/interfaces.

<u>Synergies with ongoing studies and expertise:</u> Ongoing studies in our lab on colloidal glasses and gels of spherical and rod-like particles, as well as in soft polymer grafted colloids, ultrasoft polymer microgels and multiarm stars demonstrate our strong know-how and foster extensive collaborations with several world-class experts in synthetic chemistry, computer simulations and theory. The large in-house expertise in powerful combinations of experimental techniques (in-situ rheometry /scattering /microscopy) will provide additional warranty for a smooth progress of the project.

<u>Local research team - Expertise and state-of-the-art infrastructure:</u> The work will be performed at the **Polymer & Colloid Lab (Univ. Crete, Dept. Materials Science & Technology and IESL/FORTH).**

The lab consists has a longstanding experience in the fundamental study of structure, dynamics and rheology of polymer and colloid-based materials. Its strength is the combination of a broad range of dynamic techniques in order to address the molecular origin of the materials response. The group collaborates closely with leading groups around the globe, including world class chemists. The group currently includes 2 post-doctoral fellows, 7 graduate students and 2 technicians and is part of large European Soft Matter Infrastructure (EUSMI, Horizon-2020, 2017-2021). External collaborations are foreseen with existing collaborators such as Univ. Edinburgh (W.C.K. Poon), Caltech (J. F. Brady), ETH/Zurich (J. Vermant), Univ. Dusseldorf (S.U. Egelhaaf) and others.

The local team members (with expertise and allocated time) that involved in the project are:
Prof. George Petekidis (PI) (Light scattering, rheology colloidal glasses and gels, 15% of his time),
Prof. Dimitris Vlassopoulos (co-PI). (Rheology of soft matter systems, 10% of his time),
Dr Benoit Loppinet (Light, X-ray and neutron scattering, interfacial phenomena, 5% of his time),
Mr. Antonis Mavromanolakis (technician, Polymer and Colloid lab, 10% of his time).
Within the project we plan to additionally hire **1 new PhD student (36 months)** and **1 new Post-doc researcher (24 months)** with background in soft matter physics (experiments and/or simulations). They will work full time on the project.

Experimental Techniques (Provide broad spatio-temporal range via a combination of techniques):
a) Light Scattering (Static/Dynamic) for particle characterization (size, polydispersity, interactions), study of aggregation and particle dynamics in concentrated suspensions, 3D-DLS for studies of turbid media and multispeckle DLS for slow dynamics and ageing in non-ergodic systems,
b) Shear rheometry with several strain and stress controlled rheometers (9 in total) covering applications on solutions, melts, low and high temperatures, as well as interfacial rheometry (via a Langmuir-Blodget trough and bicone geometry) are available,
c) Light Scattering (SALS or LS-echo) under shear (with rheometer and shear cells) allowing structural probe under shear and detection of particle dynamics and irreversible rearranges under LAOS,
d) Fluorescent rheo-confocal, rheo-imaging and Rheo-DDM (Dynamic Differential Microscopy) for monitoring particle structure and dynamics at different length scales,
e) Static and dynamic light scattering (DLS, SALS, DWS), enabling also microrheology, under high pressure (up to 1000 bar). Complementary, real space imaging with a confocal microscope under high pressure is also available.

Outline of Work Plan: Our work plan will be organized in work-packages (WPs) as follows:
WP1: Identify relevant industrial systems and problems (duration: month 1-4)
Collaborate with IFPRI member companies to define the open problems and the composition of the relevant industrial formulations and the function of their ingredients,
WP2: Preparation of Systems (month 2-12; Fine tuning throughout the project)
Task 1: Prepare a detailed plan to produce SIFs from industrial formulation by removing ingredients believed to have minimal impact on rheological behavior. Synthesis will be provided by IFPRI member companies,
Task 2: Utilize model colloidal systems, appropriately modified (CAFs) to resemble industrial formulations. Example are sterically or charged stabilized particles (polymeric or silica), soft colloids (polymer-grafted or microgel particles, rubbery and rough particles) and attractive colloids (thermosensitive sticky particles or depletion systems).
WP3: Characterization of SIFs (month 3-18; Fine tuning throughout the project)
Task 1: Perform a comprehensive characterization of chosen SIFs: a) single particle characterization (sizes, shapes, interactions etc.) and b) concentrated phase behavior and structure
Task 2: Map to model system response of the basic rheological behavior of SIFs and CAFs
WP4: Understand simplified paints (month 12-36)
Explore via combination of experimental techniques the identified problems discussed above.

WP5: Understand simplified agrochemical formulations (month 12-36)
Explore via combination of experimental techniques the identified problems discussed above.
WP6: Exploration of other relevant industrial problems (month 18 -36)
Identify additional industrial problems and explored related with applications under high pressure, in confinement and near surfaces/interfaces.

Contingency planning:
Regular assessment of the specific project tasks and consulting with IFPRI partner (every 3months) will reveal unforeseen problems and critical unknowns. We will then proceed with the appropriate redesign of systems and experiments to ensure successful completion of the project.

Deliverables: A yearly report and presentation of results in meetings planned with IFPRI partners

Indicative proposal budget: (36000 $ or ~32000 euro per year)

The total budget for 3 years (about 96000 euro) will cover the following:

- **Personnel cost (80000 euro)**: We foresee the following personnel costs throughout the project:
a) 36 PhD months (27000 euro), b) 24 post-doc months (38000 euro) and c) other (15000 euro).
- **Travel (10000 euro)**: Will cover 4-5 trips of FORTH members to IFPRI partners and 3-4 visits of members of IFPRI partners in FORTH/Crete.
- **Consumables (10000 euro):** Will cover various running lab costs

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IFPRI BRIEF PROPOSAL: SIMPLIFIED INDUSTRIAL FORMULATIONS DESIGN CHALLENGES

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1. Introduction

The International Fine Particle Research Institute (IFPRI) wishes to better understand the rheological properties of complex industrial colloidal formulations. To this end, a key question is if simplified industrial formulations (SIFs) can be designed which mimic the more complex industrial formulations. Even the simplest colloidal suspensions, consisting of spherical particles in a Newtonian matrix, display very rich and nonlinear rheological properties. For example the viscosity may vary over orders of magnitudes and in the same suspension shear thinning and shear thickening can occur. These phenomena arise because of a complex interplay between colloidal and hydrodynamic interactions. Much has been learned by looking at the simplest case of Brownian hard-sphere suspensions and by mapping the behaviour of other colloidal particles onto effective hard spheres as excellently reviewed in the book by Mewis and Wagner[1]. The number of parameters which govern such Brownian hard spheres are limited and include the *effective hard sphere* volume fraction (ϕ), the maximum packing (ϕ_m), the medium viscosity ((η_m and the particle size (a). This has been successfully applied to for example industrial latex dispersions [2]. But also for complex cementitious materials the expected shear stress-dependent effects of shear thickening and size scaling were used to distinguish between surface interactions, such as lubrication and volumetric contributions and also including the packing effects and admixtures could be defined by Lafarge guided by these principles [3]. However not everything could be predicted so far, and effects of colloidal interactions and surface topology of particles have been shown recently to play an important role as well, for example friction leading to discontinuous shear thickening in the same cementitious materials, to an extent not predicted for smooth Brownian hard spheres [4]. For stable suspensions there is a need to go beyond Brownian hard spheres, bringing the key aspects elated to how particles pack (shape, softness) and interact in real systems (heterogeneity, roughness) to the forefront.

Attractive colloidal suspensions display far more complicated properties, often a solid-like behaviour at rest is observed due to their flocculated structure, and they liquefy (with non-Newtonian properties) when subjected to mechanical stress. In terms of material functions, the rheological properties of aggregated suspensions are described by an elasticity that depends on shear history, a yield stress, and a viscosity that not only changes reversibly with shear rate but also with time [5]. In addition to physicochemical details (the volume fraction, the pair potential, the particle size and size poldispersity), the flow history plays an important part in the details of the microstructure, such as the local coordination number and the fractal dimensions, and the resulting mechanical properties [6, 7], which may reflect a strongly anisotropic microstructure in the mechanics [8]. Aggregated systems will need to be represented separately with some key effects (shape and percolation and noncentral forces) being investigated here.

As a final step, it could be investigated what the effects are of making a medium viscoelastic, due to polymeric additives. This would be a final step in complexity. Much progress has been made in understanding the changed hydrodynamics in viscoelastic suspensions (see e.g. [9] for a review) but translation of these results towards industrial systems seem to be lacking. This is however not incorporated into the scope of this proposal, but should be kept in mind as matrix formulations will be of importance as well in real formulations. However, we propose to focus on the inherent control of suspension rheology.

In this brief we propose to develop a number of simplified industrial formulations" building upon our understanding of model systems, characterising these suspensions by both integrative measurements (such as flow curves, LV properties) as well as potentially using some techniques which interrogate the physics more directly (High frequency rheology and orthogonal superposition rheometry).

2. Creating a particle toolbox

2.1. **Stable dispersions.** On way to produce simplified industrial formulations is to render the current model systems more complex. But in inducing complexity we can try to render model systems more realistic in such a way that they enable us to interrogate different effects of changes in either geometry, surface topography or interactions. A possible sequence of enhancing particle complexity is given in figure 1.

The "fruitflies" of colloid science have been suspensions o systems such as poly-methyl methacrylate (PMMA) stabilized by grafted layers of poly-hydroxystearic acid (PHSA) (typically a few oligomers of the latter) and dispersed in an organic solvent, or similar systems based on silica particles. These sterically **stabilised suspensions** are models for Brownian hard sphere suspensions, when the particle size is in the order of microns and the stabiliser layer thin. Much has been learned by looking at this simplest case of Brownian hard-sphere suspensions and by mapping the behaviour of other colloidal particles onto effective hard spheres [1]. Some silica systems sterically stabilized by silane coupling agents (or using electrosterical stabilization) have also been discussed quite extensively as reference systems [10]. The data of these systems can be taken as benchmark or a relevant industrial mimic system should be identified.

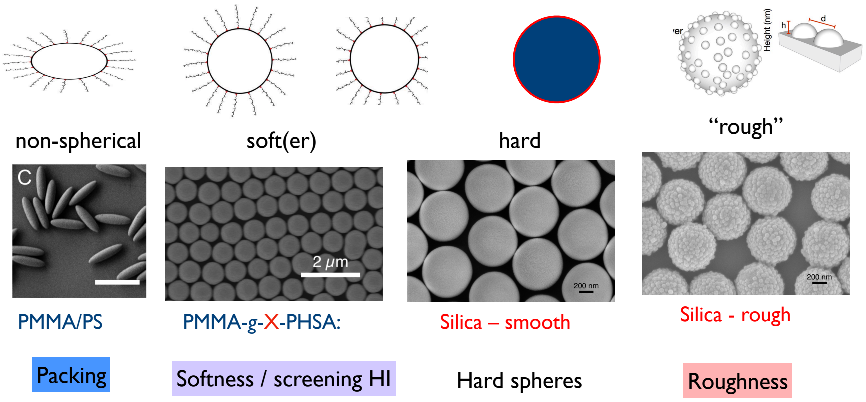

Figure 1. Recent trends in **bottom up** increase of complexity of colloidal building blocks: modulating the interactions (softness), the packing (shape) and the topography (roughness).

Softness is another aspect which has been imparted to particles and use as a form of ”inherent” rheology control [11]. For example, recently our group has been able to increased the length of the brush in PM-PHSA systems so that by combining particle size control with brush control over the **softness** of the particles in the same model systems has been achieved. Similarly a lot of know-how has been obtained on microgel particles which have revealed how softness can be used as a design parameter in engineering the rheology of suspensions, typically by screening the hydrodynamic interactions[12] or improving the film forming properties of colloidal suspensions [13]. Finally, particle **shape** is an exciting aspect to tailor particle rheology, as both the maximum packing in the random jammed state and the orient-ability of the constituent particles , impart ways in which to separate control of shear and extensional properties. Methods for producing both oblate and prolate ellipsoids in sufficient quantities are now available (in part developed in our group) [14] and also model rod like particles can be readily produced [15]. Recently, the Isa group at ETH has developed particles with **controlled roughness**, which is obtained by employing charge-stabilised raspberry-like silica colloids with tuneable asperities [16]. The roughness (RB) can be characterised via the ratio of the height of over the distance between asperities, going from smooth to RB.4→RB.5. These model systems can be produced in sufficient quantities to measure the bulk rheology, while being well characterized and monodisperse, or controlled polydisperse. The different systems represented in figure 1 represent the archetypes of ”inherent” rheology modification as they interrogate how the particle characteristics influence the a complex interplay between colloidal and hydrodynamic interactions. Softness of the interaction (or the particle) and effects of shape on packing and the effects of flow induced orientation are at least qualitatively understood. The influence of surface roughness and friction on discontinuous shear thickening has been the subject of several recent studies [17, 18]. Such non-central interactions were observed to be important for other phenomena as well, such as for the rigidity of colloidal aggregates and gels [19, 20, 21] (see further).

Concluding, a toolbox of particles as shown in figure 1 could be viewed as to represent the essential methods in which to control (inherently) the rheology of colloidal systems consisting of a simple building block. The use of these particles has lead to relative good model predictions or at least scaling laws to predict the rheological properties, where both levels of viscosity, degree of shear thinning and shear thickening can be controlled[1]. It should be noted that it is my personal opinion that further progress is only going to be achieved if there is also strong coupling with numerical simulations required, as some groups now can achieve both the scale relevant for predicting bulk properties in stable suspensions and gels and the feedback between simulations and experiments has proven extremely useful [22].

Building blocks for simplified industrial formulations: We propose to challenge the industrial partners to come up with less ideal particles which nevertheless capture the essential features of figure 1: changes in softness, shape and roughness or chemical heterogeneity.

Charcaterizing these or similar systems will require an important body of work, and prioritisation of the selected effects in light of the industrial realm will be required. Here Feedback of IFPRI members will be essential, as to highlight the most important characteristics, i.e. shape effects, roughness or chemical heterogeneity or deformability.

2.2. **Flocculated dispersions.** The rheological properties of aggregated suspensions are more complicated as their rheology depends on shear history, and typical rheological material functions are now a yield stress, and a viscosity that not only changes reversibly with shear rate but also with time. The difficulty with this kind of network structures is that they are inherently metastable. Hence, in addition to physicochemical details (the volume fraction, the pair potential), the flow history plays an important part in the details of the microstructure, such as the local coordination number and the fractal dimensions, and the resulting mechanical properties [5]. To investigate to what extent shape (orientability and change in percolation) and the occurrence of non-central forces on-central interactions are playing a role, the proposal is to investigate these properties in year 2 and 3 of the project for selected systems, for a limited range of volume fraction close to percolation. To this end it would be best if flocculation could be induced by screening the repulsive interactions (e.g; by influencing the solvent quality of a stabiliser layer or screening electrostatics).

Selected effects in thixotropic systems: We propose to focus on the role of shape effects and inducing non central interaction (roughness or heterogeneity) in flocculated suspensions .

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[1] Note that this represents probably more than 30 years of research in the whole field of rheology, including many IFPRI projects

3. Benchmark systems and properties

I believe this project only will be meaningful if there is a closer than usual connection between the industrial and the academic partners with predefined feedback moments. The proposed research here would start by defining an **simplified particle toolbox** as in figure 1. Three to four particle types should be identified and it is important that they can be produced in sufficient quantities. Most likely the effects of softness are least relevant. As a fallback situations the model systems as in figure 1 could be scaled up to larger quantities, but then particles based on silica surface and having aqueous dispersion media seem warranted, as this will simplify the study of relevant flocculated dispersions. The first month of the project, an inventory should be obtained of possible particles, with some initial screening measurements.

It is also essential that an inventory is given of the benchmark properties desired, i.e. what flow profiles, thixotropic responses and possibly extensional properties are desired. The analysis of the desired properties should be carried out also at the start of the project.

It would be worthwhile to set, towards the end of the project, a design challenge where a certain rheological profile is set as a challenge. this could for example be a material with a specified yield stress, a predefined ratio between high and low shear viscosity, and a predefined recovery time (for example for applications in 3D printing).

4. Analysis methodology

The particles will be characterised by dynamic light scattering, SEM and TEM and their surface properties will be investigated using zeta potential measurements. For the rough Particles single particle AFM measurements can be performed if these are sufficiently large (several micron). Rheological measurements will be characterized by standard rotational rheometers (Anton Paar MCR 502, ARES-G2 and DHR-3), using different geometries to evaluate slip. Unless this would be desirable and come out of discussion with the IFPRI partners the elongational properties would be left aside.

To get insight in the local interactions high frequency rheology will be used. It as been established in earlier IFPRI projects that total deviatoric stress tensor in a suspension $\boldsymbol{\Sigma}$ can be written as [23]:

$$\boldsymbol{\Sigma} = 2\eta\dot{\boldsymbol{\epsilon}} + \boldsymbol{\Sigma}_p = 2\eta\dot{\boldsymbol{\epsilon}} + \big(\boldsymbol{\Sigma}^H + \boldsymbol{\Sigma}^B + \boldsymbol{\Sigma}^P\big). \tag{1}$$

Here, $\dot{\boldsymbol{\epsilon}}$ is the bulk strain-rate tensor so that $2\eta\dot{\boldsymbol{\epsilon}}$ represents the stress in the suspending fluid. The particle contribution to the stress $\boldsymbol{\Sigma}_p$ can be further decomposed into direct hydrodynamic ($\boldsymbol{\Sigma}^H$), Brownian ($\boldsymbol{\Sigma}^B$) and interparticle ($\boldsymbol{\Sigma}^P$) contributions. The hydrodynamic terms are responsible for a HF limiting viscosity η'_∞. The linear viscoelastic response of the suspensions in the high-frequency regime can hence be used to interrogate on the stresses at the particle level. This requires a limited number of measurements at relatively high volume fractions.

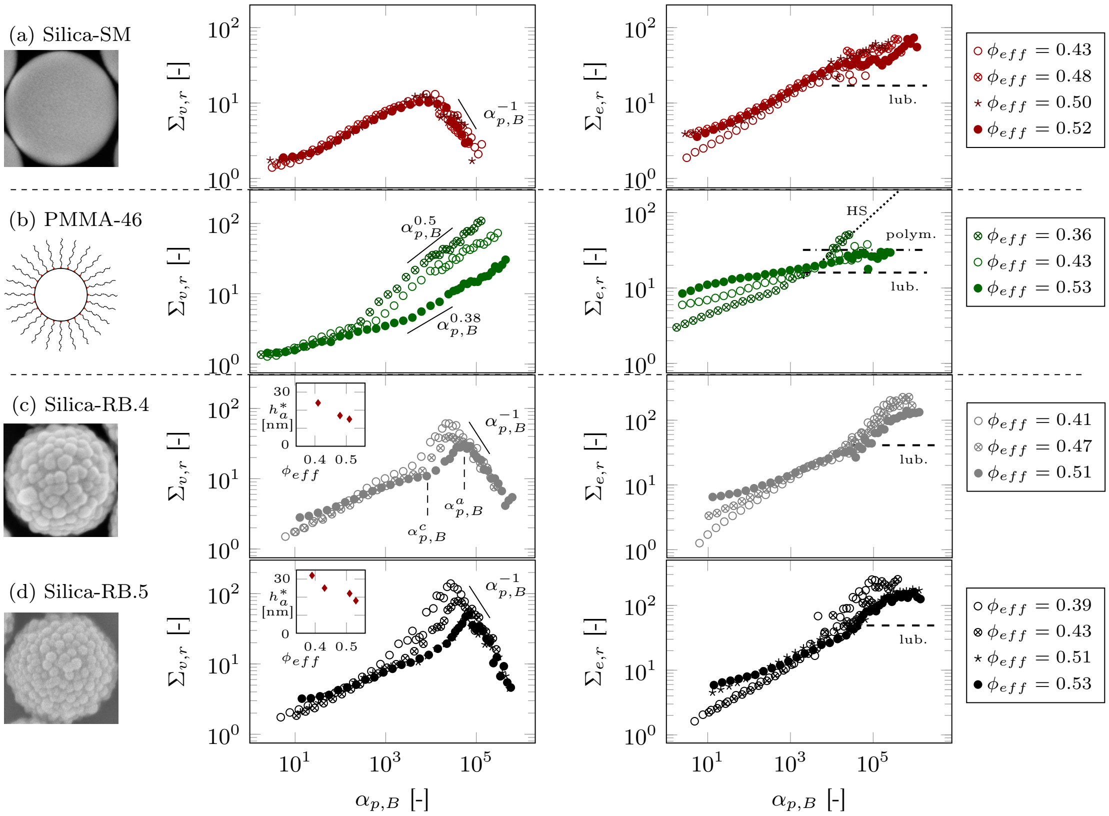

FIGURE 2. Reduced viscous (left) and elastic (right) stresses as a function of rescaled frequency for different volume fractions of (a) smooth, hard particles (Silica-SM), (b) particles with long polymeric brushes (soft) (PMMA-46) and (c,d) rough particles (Silica-RB.4, Silica-RB.5). (left) The solid lines indicate the experimentally observed scaling exponents in the HF regime. $\alpha_{p,B}^{c}$ and $\alpha_{p,B}^{a}$ (c) indicate the boundaries of the intermediate regime for RB suspensions at $\phi_{eff} = 0.51$. (right) Dashed, dotted and dashed-dotted lines present model predictions for $\Sigma_{e,r}$ based on lubrication [24], hard-sphere [25] and polymer-polymer interactions [26]. The inserts show estimates of the thickness of the rough layer thickness based on the interparticle distance at ϕ_{eff} and diffusive boundary layer thickness. Data from Schroyen et al. (submitted)

Scaling out the direct hydrodynamic ($\mathbf{\Sigma}^H$) and Brownian ($\mathbf{\Sigma}^B$) stresses and rescaling frequency by the characteristic Brownian frequency $\alpha_{p,B} = \frac{f}{f_{p,B}}$, data for hard silica-SM suspension in fig. 2 (a) $\Sigma_{v,r}$ decreases $\propto \alpha_{p,B}^{-1}$ and $\Sigma_{e,r}$ is constant within measurement accuracy,as a consequence of lubrication [27]. Soft PMMA suspensions (fig. fig:hf(b)) show a remarkably different asymptotic behaviour, depending on the thickness of the stabilising layer. For longer grafted chain lengths, the exponent increases and varies as a function of frequency, reflecting a different degree of permeability of the layers [22]. Finally, in case of a suspension of rough silica particles (fig. 2 (a)) the behaviour is drastically different. At intermediate frequencies ($\alpha_{p,B} \sim 10^4$) both $\Sigma_{v,r}$ and $\Sigma_{e,r}$ strongly increase. A lubrication regime is found only at higher frequencies compared to the smooth particles. It is proposed to apply these high frequency rheology techniques to understand how the industry particle interact on a local scale. These local scale differences account for differences in shear thinning and shear thickening responses under steady state shearing flows. Having these local interactions quantified with a fairly simple screening tool will be an important step in understanding to control the rheology of colloidal systems consisting of a simple building block. Clearly this is only a stepping stone to more complex formulations.

In order to understand how the nonlinear rheological properties are linked to changes in the shear induced microstructure, studying the frequency dependent moduli, during flow seems worthwhile. Orthogonal Superposition Rheometry (OSR) can be used to study the flow behavior of colloidal gels and suspensions, allowing to probe how the different relaxation times of the material are affected by shear[8]. This will be done only or selected systems only, but having a technique which interrogates how the elastic and viscous properties of these systems evolve seems important for rational design of these systems (stress jumps would be an alternate, LAOS may also provide some insights).

5. WORK PLAN - EXPECTED OUTCOMES

We would propose a staged approach.

1. Inventory of potential particulate samples should be identified with IFPRI members (D.1, month 1).
2. Inventory of desired benchmark rheological properties and profiles, with request for feedback (D.2, month 1).
3. Report on the characterisation of the particle systems (D.3, month 6)
4. Basic rheological characterization of the linear viscoelastic behaviour and the flow curves of the stable suspensions (D.4, year 1)
5. Full rheological chracterization including high Frequency rheological chracterization to rationalize (D.5, month 18)
6. Rheological characterisation of selected thixotropic suspensions (D.6. month 30)
7. DESIGN challenge by IFPRI members (MO30-36)

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IFPRI Research Project Brief

A Systems Engineering Approach to Dry-Milling with Grinding Aid Additives

The International Fine Particle Research Institute (IFPRI) wishes to fund a project in a systems approach to particle size reduction via dry-milling with grinding aids. Typical IFPRI projects run for 3 years, with an opportunity to renew for an additional three years, totaling 6 years.

The systems approach should consider scale-up and productivity of dry-milling processes where product flow and process energy are critical to the product quality and process efficiency. Please address differences between small batch testing versus continuous processing circuits, the latter with systems integration of unit operations (e.g., mill, classifier, recycle, conveying and handling). The approach should be supported using functional breakage models (i.e., in high-stress zone), unit operation models including flow into breakage zones and residence time distributions for process optimization and scale-up, and systems-level modelling (e.g., flow sheets) for process integration.

The industrial process objective is throughput rate and energy efficiency; and the product objective is to achieve target size and sharpness (i.e., narrow distribution) of the product. The research objective is to develop a fundamental understanding of various process and material parameters using a combination of modeling and lab-scale testing, toward the systematic manipulation of same to meet process objectives in an integrated system.

The use of grinding aids should be considered toward the productive manipulation of material and process parameters. The preferred scope, at least during the first three-year grant, may be selected from:

- Dry milled materials such as inorganic minerals, cements, ceramics, pigments, etc.
- Dry milling processes, including media mills, jet mills, hammer mills, high-speed pin mills, etc.
- Grinding aids, preferably in class of liquid additives that may affect surface energy and flowability relative to other particles, milling media or other in-process surfaces, e.g., glycols, organic acids, alcohol amines, surfactants…

As an extension of this scope, please consider how to re-apply the above systematic approach using grinding aids to other classes of materials, e.g., dried organic materials, that are commonly processed in dry-milling. This extended scope may be addressed in parallel or sequentially (e.g., years 4-6) to the main proposal.

A Systems Engineering Approach to Dry-Milling with Grinding Aid Additives

IFPRI Research Project Proposal

1. Introduction

Many different aspects need to be considered for optimizing continuously operated dry grinding processes in terms of product quality, product throughput and energy efficiency. Thereby, the most important parameters can be found in a) the stressing conditions provided by the mill for a certain set of process parameters, b) the breakage behavior of the particles under the present stressing conditions, c) the particle and powder behavior during the stressing event, d) the material transport through the mill which influences aspects like the retention time distribution and the energy efficiency, as well as e) further process units within the grinding plant such as air classifiers and conveyors. Generally, the stressing behavior of a mill can be described by the kind of applied stresses (e.g. slow compression of single particles or particle beds, impacts …), the frequency of stresses inside the mill as well as the stress energies. In detail, each mill can be characterized by a frequency distribution of the stress energies. In order to describe the effect of stresses per product particles, further aspects need to be considered, such as the number of stresses per product mass as well as the stress intensity (e.g. the area specific force or the mass specific energy acting in a single stressing event). Here, the mass of particles that is stressed in a single stressing event becomes very important. Moreover, the energy transfer inside the grinding machine has be considered for any kind of dry-milling process: Only that proportion of the energy, which is transferred to the product particles and not dissipated into heat by friction or other aspects, can finally be used for stressing and breaking the particles.

Efficient stressing of particles is often complicated by attractive particle-particle forces which become more decisive with decreasing particle size. In general, these forces lead to a variety of challenges, in particular caused by a high state of agglomeration, a decrease of the powder flowability as well as material adhesions on the machine and plant equipment. It is well known that these aspects may complicate the comminution within industrial grinding plants on various levels simultaneously (e.g. regarding the grinding efficiency between the grinding tools, the performance of air classifiers as well as the material transport and retention time inside the single devices). In order to control these forces, so-called (mostly liquid) grinding aids, which reduce the particle-particle forces by adsorbing on the surface of the product particles, are often used as stabilizing additives. However, even though grinding aids are established in various industrial processes, their selection and application is still mostly based on empirical knowledge. A review article on the state-of-the-art of grinding aids, which is currently prepared by our institute on behalf of IFPRI, reveals that grinding aids may have strong impacts on several of the above-mentioned aspects. Especially the aspects listed under c) to e) may be strongly affected by the presence of those additives. As shown in the report, their mode of action is mainly caused by influencing various product properties, such as the powder flowability, the agglomeration tendency of the particles, the adhesion tendency of the particles on surfaces as well as their fluidization behavior. Thereby, various sub-processes inside the grinding plant may be strongly affected by these additives. Thus, an efficient selection of appropriate grinding aids is very complex and still not fully understood. This is further complicated by the fact, that significantly different grinding aid effects have been reported depending on the used milling type or operation mode.

The aim of this project is to develop a system engineering approach for optimizing and scaling industrial dry fine grinding processes, with a special focus on the manipulation of the material by grinding aids. Thus, the approach will not only cover common parameters such as the mill type, process parameters, plant design or material as well as energy flows. In particular, the most important influences of applied grinding aids on the sub-processes inside the grinding plant are also taken into account. The developed approach can then be used as the basis for later flow-sheet-simulations of different complex industrial grinding processes. The investigations of a first 3-year-funding-period focus on the grinding aid impacts on the grinding behavior inside the mill. Within this funding period, the focus is put on two exemplary grinding principles, namely dry grinding in tumbling ball mills as well as impact milling in high-speed pin mills. The stressing conditions provided by these different mill types are investigated by means of DEM simulation. The breakage behavior of single particles will be determined experimentally for two different inorganic model materials, which are selected according to the demand of the IFRPI members. In addition to the breakage behavior, the particle and powder behavior between (or near) the grinding tools will be characterized by model experiments in order to describe the impact of the product formulation on the particle stressing. Together with functional grinding models and population balance models, these information will be used to predict particle size distributions and energy consumptions. For validation, grinding experiments will be performed in mills of different types and scales. In a last step, the energy utilization will be characterized as a function of both the milling conditions (mill type/geometry/size as well as grinding parameters) and the product formulation. The aim is to identify possible criteria to transfer grinding aid application to other mill types or optimize grinding aid application while scaling up processes. In a second 3-year-funding-period, the system engineering approach will be extended to continuously operated grinding processes.

2. First 3-year-period

The studies within the first funding period focus on defining a general system engineering approach as well as the investigation of grinding aid impacts on the particle stressing and the grinding performance inside the mill. Following work packages are planned:

2.1. Development of a System Engineering Environment for dry fine grinding processes

In a first instance, a system engineering environment is developed for characterizing simple lab-scale dry grinding processes. The approach is based on a model representation regarding the stresses acting on a particle as well as the energy flow inside a grinding machine. Similar to the approach of Kwade for wet grinding processes [1], the energy transfer from the mill drive to the particles as well as the associated energy dissipations inside the milling chamber (described by the energy transfer factor ν_E) will be evaluated according to the scheme in Figure 1. The utilization of the energy transferred to the particles is determined by the applied stress intensity, which should have a value that the particles just break. Also, the systems engineering approach will be used for modeling grinding processes with a special regard on the two different mill types. Therefore, data and findings from the different scales need to be coupled and included into a population balance model. Appropriate grinding models for the two selected grinding principles are selected based on own studies and studies from the literature. For each grinding principle, one mill related model (describing stressing energies and frequencies provided by the mill) and one breakage model will be selected in order to describe grinding conditions inside the mill as well as breakage behavior of the material, respectively.

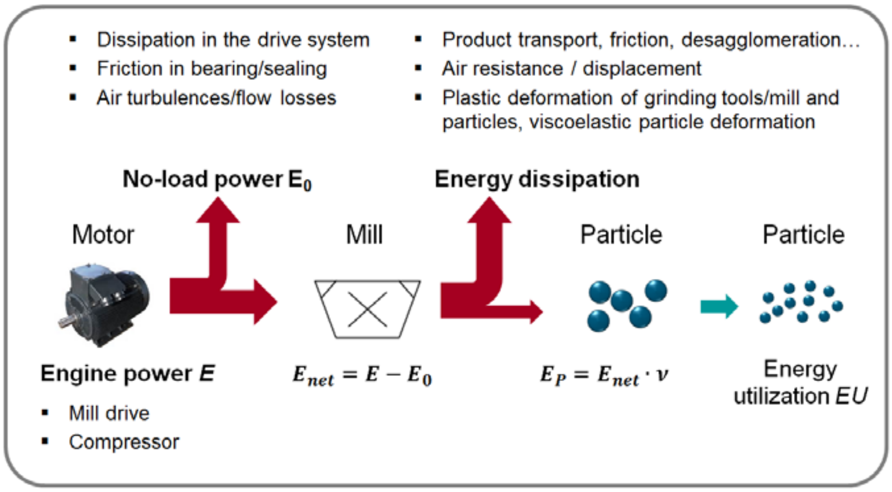
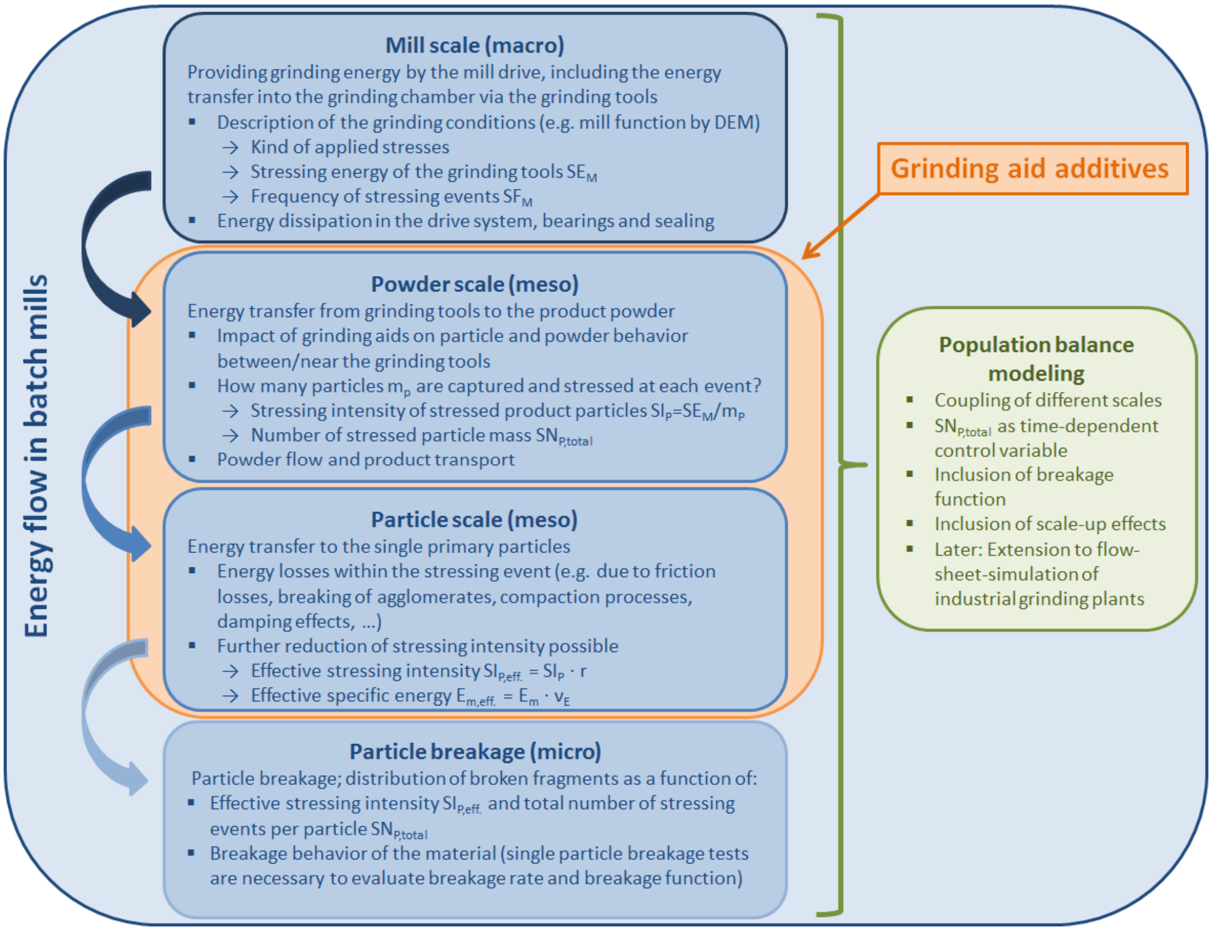


Figure 1: Scheme of energy flow in mills.

For meeting the special requirements of this project, it is especially considered how far the product formulation may influence the individual sub-processes in those grinding machines and how these effects can be embedded in the system approach and the later population balance modeling (see scheme in Figure 2). Moreover, grinding-aid-specific scale-up effects will be identified and – if necessary – included in the approach.



Mill scale (macro)

Providing grinding energy by the mill drive, including the energy transfer into the grinding chamber via the grinding tools

- Description of the grinding conditions (e.g. mill function by DEM)
  - → Kind of applied stresses
  - → Stressing energy of the grinding tools SE_M
  - → Frequency of stressing events SF_M
- Energy dissipation in the drive system, bearings and sealing

Powder scale (meso)

Energy transfer from grinding tools to the product powder

- Impact of grinding aids on particle and powder behavior between/near the grinding tools
- How many particles m_p are captured and stressed at each event?
  - → Stressing intensity of stressed product particles $SI_P = SE_M / m_P$
  - → Number of stressed particle mass $SN_{P,total}$
- Powder flow and product transport

Particle scale (meso)

Energy transfer to the single primary particles

- Energy losses within the stressing event (e.g. due to friction losses, breaking of agglomerates, compaction processes, damping effects, …)
- Further reduction of stressing intensity possible
  - → Effective stressing intensity $SI_{P,eff.} = SI_P \cdot r$
  - → Effective specific energy $E_{m,eff.} = E_m \cdot v_E$

Particle breakage (micro)

Particle breakage; distribution of broken fragments as a function of:

- Effective stressing intensity $SI_{P,eff.}$ and total number of stressing events per particle $SN_{P,total}$
- Breakage behavior of the material (single particle breakage tests are necessary to evaluate breakage rate and breakage function)

Population balance modeling

- Coupling of different scales
- $SN_{P,total}$ as time-dependent control variable
- Inclusion of breakage function
- Inclusion of scale-up effects
- Later: Extension to flow-sheet-simulation of industrial grinding plants

Figure 2: Considerations of grinding aid effects for the system engineering approach.

2.2. Macro scale: Determination of the stressing conditions in different mill types

Within this working package, the stressing conditions provided by the two different mill types are evaluated based on Discrete Element Method (DEM) simulations. Parameters like stressing energy distribution and stressing frequency are essential to feed the mill related model of the system engineering approach. Within this project, two different concepts are chosen to describe the stressing conditions for the two different grinding machines:

DEM-Simulations of the grinding ball motion are carried out for the two tumbling ball mills of different scale. The milling process will be simulated for selected parameters (e.g. mill speed, grinding ball size/material/filling ratio) that are chosen based on appropriate settings from grinding experiments from working package 2.5. The parameters will further be held constant for both mills. The outcome of the DEM study is mainly the frequency distribution of stressing energies for different kinds of stresses (normal stress, shear stress …). Since only the grinding balls are simulated due to computing capacities, appropriate DEM input parameters need to be chosen to describe possible influences of the product particles on the restitution and friction behavior of the mill load. In a first instance, the DEM input parameters for the simulation (e.g. coefficient of restitution or friction coefficients) are chosen based on results obtained from previous studies. However, the results of the material motion which was also determined in working package 2.5 will also be considered. Thereby, it will be identified whether grinding aids may change the motion behavior of the mill load to such an extent, that the stressing behavior provided by the grinding balls is influenced by the product formulation significantly.

The stressing conditions inside the high-speed pin mills UPZ40 and UPZ100 are also estimated based on DEM simulations. However, instead of own DEM simulations, data from previous IFPRI projects as well as studies from the literature shall be applied within this project. For instance, impact velocity distributions as well as collision frequencies for grinding with the pin mill UPZ100 at different rotation speeds are estimated based on current IFPRI project “Milling and Material Grindability” [2]. For instance Ooi et al. determined the number of stressing events as a function of the impact velocity within the UPZ100 by means of DEM for different feed rates and rotary speeds. A down-scaling of these parameters to approximate the stressing conditions inside the smaller UPZ40 is carried out using the scaling-approach of Juhnke [3]. Since the motion of the rotor and the stator inside pin mills is independent of the product formulation, the impact of grinding aids on the mill function is negligible at this point.

2.3. Meso scale: Systematic investigation of grinding aid impacts on the particle stressing

According to the above mentioned findings from own investigations and studies from the literature, the interactions between grinding aids (including their influences on the product properties) and the stressing conditions provided by the mill have to be well-known for an effective selection of appropriate grinding aids (e.g. [4-9]). Therefore, different basic laboratory tests will be performed to investigate the particle stressing for different mill types. The experimental setup comprises the grinding aid influences on the powder properties as well as the particle and powder behavior inside the mill, but especially between or near the grinding tools.

Even though the actual breakage behavior of single particles is not affected by grinding aids (e.g. [10-13]), the stressing behavior of the material is strongly influenced by the presence of these additives. The reason for that is the change of the particle and powder behavior as a consequence of adsorbed grinding aid molecules. It particularly changes the behavior of the material between or near the grinding tools, leading to a change of the stressing intensities and stressing numbers. Consequently, two important aspects have to be well known to estimate the impacts of grinding aids on the stressing behavior: First, the impacts of the additive on the powder properties need to be characterized. Secondly, rules, in how far these properties determine the material behavior between or near the grinding tool under realistic and dynamic conditions, should be derived. Thereby, also the energy transfer coefficient v_E which describes the proportion of the energy being finally transferred to the product particles needs to be estimated and considered. To investigate these phenomena, following tests are included:

On the one hand, the impacts of three different typical grinding aids (alcohol amine, glycol, carboxylic acid) on selected particle and powder properties of the model materials are determined. Therefore, both model materials will be evaluated in three different, comparable size fractions. Prior to the characterization, the grinding aid molecules will be dry-mixed to the different size fraction using a plug-shear-mixer. For each of the three grinding aids, one identical and appropriate grinding aid concentration in the range of typical industrial applications is chosen. After dry mixing, the grinding aid effects are analyzed by measuring the powder flowability with a Schulze ring shear tester, the tendency of agglomeration by dry particle size analysis as well as the fluidization behavior by powder rheometer measurements. On the other hand, the same powder samples will be used for evaluating the particle stressing between the grinding tools.

The experimental characterization of the particle stressing under real stressing conditions is highly time-consuming and exceeds the scope of this project. Since similar investigations are the subject of a parallel iPAT-project, only exemplary tests using the selected model materials will be carried out within the IFPRI-project. For evaluating the stressing behavior in media mills, two different tests will be used: First, a recently designed experimental set-up based on a drop-weight-tester is chosen to investigate the particle behavior between rapidly approaching grinding balls. Thereby, especially the particle capturing between the balls will be investigated as a function of the feed size and the applied grinding aid. Secondly, a modified Hardgrove test will be used to characterize the particle behavior below rolling grinding balls, which is also an important mechanism that contributes to the particle stressing in tumbling ball mills. Both tests will be evaluated by mass balances and high speed videos. The results are used to estimate the mass of material that is stressed at each stressing event. This parameter is highly important to derive a relation for describing the actual stressing intensities SI_P (how much energy is transferred per mass of particles at each stressing event) and product related stressing numbers SN_P (how often is each particle stressed within the process) as a function of both, the stressing conditions provided by the mill as well as the product formulation. Also, the formation of strong agglomerates as well as of material coatings on the balls are evaluated in order to identify critical processing conditions, where the particle stressing between grinding balls could become less efficient due to both, energy losses while breaking agglomerate structures as well as damping effects caused by adhesion layers on the balls. Aspects like this will be considered for describing further energy losses, and thus, calculating the effective stressing intensity $SI_{P,eff.}$. In contrast to media mills, the stressing conditions inside pin mills are assumed to be less dependent on the powder behavior. Here, the stressing intensities SI_P and product related stressing numbers SN_P are rather determined by the process parameters such as pin geometry and rotary speed. However, grinding aid effects are still possible in pin mills, since the formation of strong agglomerates and product adhesion on the pins may reduce the effective stressing intensity $SI_{P,eff.}$. Therefore, the surface energies of the model material will be measured by means of inverse gas chromatography as it was done in a previous study [14]. The surface energy values will then be used to calculated the strength of agglomerate structures towards impact stresses (compare e.g. [15]) and correlated with the size reduction efficiency of the actual primary particles, which is determined from the grinding experiments within working package 2.5. Moreover, air-jet-supported dry dispersion experiments (similar to the Scirocco procedure introduced by Bonakdar et al. [16]) will be performed to investigate how far the extent of agglomeration is not only determined by the product formulation but also by the dry dispersing intensity. Thereby, the extent of agglomeration is analyzed by measuring the dry particle sizes in air flows of different velocities by laser diffraction. The aim is to identify whether the grinding aids help to disperse the particles in a dry and turbulent environment, which may lead to an increased impact stressing of single particles instead stressing of agglomerates. Using this method as a real breakage tester – as it was originally used by Bonakdar et al. for soft organic products – is hardly possible in the present case: Most likely, the stressing intensities inside the dispersion unit are not high enough to enable breakage of the primary particles of these fine and comparatively hard inorganic materials.

2.4. Micro scale: Investigation of the breakage behavior

The breakage behavior of single particles is measured by a two-roller-tester. Since the breakage behavior of single particles is independent of grinding aids for realistic grinding conditions (e.g. [10-13]), these tests are only performed for the raw particles without any additive. For both model materials, particles of different sizes between 30 – 300 µm are analyzed in order to determine breakage rates and breakage function under defined stress loads. These breakage data will then be used as input parameters for the breakage model, which is embedded in the system engineering approach. Furthermore, experimental tests using a modified "picozirk" impact unit (Hosokawa Alpine) will be used to validate the influences of the grinding aids on the impact stressing of the model materials.

2.5. Grinding experiments

Within this working package, a number of dry fine grinding experiments will be carried out for the two selected model materials. Thereby, both milling principals (tumbling ball milling as well as impact milling) will be investigated using two mills of different scale each. Within these tests, the specific energy consumption as well as the product particle size distribution will be evaluated.

For ball milling, two different batch-wise operated tumbling ball mills with volumes of 4.4 L batch mill and 60 L batch mill will be used. Different grinding times will be applied to realize grinding in a wide range of specific energies as well as product finenesses. The milling will be carried out under selected process parameters for both mills. The focus of this investigation is also put on the impacts of the different grinding aids on the macro processes inside the mill. Besides the grinding result and the energy consumption of the mill, the motion behavior of the mill load will be evaluated while milling with different grinding aids. Thereby, the side plates of the drum will be equipped with transparent lids to enable the investigation of the material motion by high speed cameras.

Impact milling will be performed in a high-speed pin mills, either UPZ40 or UPZ100 (Hosokawa Alpine). Thereby, the stressing intensity will be varied by different circumferential speeds of the wheel. For the experiments, the energy consumption of the motor unit as well as the product particle size distribution will be measured. In order to obtain also very fine material in the lower micron range (thus the size range, where particle-particle interactions become more decisive), the product material will be processed in several grinding cycles. Since impact mills have comparably low mixing capabilities, the grinding aids are dry-mixed to the feed material prior to the grinding, instead of being added directly into the grinding chamber.

For all grinding experiments, the amount of product adhesions on the mill equipment will be determined for different specific energies. While for the ball milling mainly the adhesion on the grinding balls will be taken into account, the material coatings on the pins (rotor and stator) are evaluated for the pin mill. Thereby, adhesion-induced poor stressing conditions caused by damping effects at the coated grinding tools can be identified and correlated to parameters like product fineness and product formulation. If necessary, a these effects will be considered within the effective stressing energy (see above).

2.6. Population balance modeling

Since the size distribution of the final ground product is of major interest for this project, Population Balance Models (PBM) instead of simplified grinding models need to be incorporated in the present system engineering approach. Therefore, already existing PBM approaches will be used and coupled with the characteristic stressing parameter, especially the frequency distribution of stress energy, obtained from the DEM simulations. In the present case, these so-called PBM-DEM approaches are further extended with the findings from the model experiments on the particle stressing, in order to depict the impacts of the particle and powder behavior, and thus, a more realistic grinding environment. Furthermore, the energy transfer factor will be embedded to include further aspects of energy dissipations within the single stressing events.

For instance, a procedure similar to the mechanistic ball mill model of Tavares and co-workers [17] will be used as the basis for the ball mill modelling. As mentioned above, breakage rates and function for single particles can be taken from the two-roller-test. Stress loads can be estimated by the stressing intensities SI, which is the critical variable within this model. This parameter will be calculated by the stressing energies inside the mill obtained by the DEM simulation as well as the active stressed particle mass m_A per stressing event, which is approximated by a model developed from the model experiments. The product related stress number SN will be embedded as the time-dependent control variable with the population balance model. The populations balance modeling will allow a relation of product particle size distribution and energy consumption as a function of both, milling conditions as well as product formulation.

2.7. Development of transfer and scale-up criteria

Within this working package, the grinding aid effects will be evaluated with a special regard on differences between mill type and mill size. All considerations are based on the systemic investigations from the shown studies. The aim is to identify, how far grinding aid applications depend on the applied grinding principal and whether it is possible to transfer them to other grinding processes. Also, aspects of adjusting grinding aid application while scaling up grinding processes are taken into account.

For enabling such a procedure, the actual energy utilization is considered as a function of both, machine related parameters and product formulation. Therefore, the total amount of specific energy, which is introduced into the grinding chamber over the processing time, is related to the actual amount of energy, which is finally transferred to the product particles and can be thus used for breakage. It is then estimated which aspects of energy dissipation depend on both, grinding aid application as well as (geometrical) scale effects. Finally, the above-mentioned energy transfer factor, which considers all grinding aid as well as scale dependent energy dissipations, will be calculated for each of the two grinding processes that were investigated. This parameter will then be examined for its suitability to be used as critical values for scaling and transferring grinding aid applications. Thereby, it is also evaluated how far the configuration of the particles during stressing (single particle vs. multi-particle stressing vs. particle beds) determines the energy transfer.

3. Second 3-year-period

As already mentioned above, the system engineering approach for the ball mill will be extended to continuously operated grinding processes in a second 3-year-funding-period. Based on this approach, a flow-sheet environment for modeling industrial grinding processes will be created. The aim of the flow sheet simulation is to model whole continuously operated grinding plants (in open- as well as closed-circuit mode) for different material/grinding aid combinations. The investigations within this funding period will first of all focus on continuous grinding processes of inorganic materials in ball mills, and will be based on the materials, processes and results of the first funding period. Also, a transfer of this approach to grinding of organic materials will be evaluated experimentally. Therefore, we recommend the use of a pilot scale impact mill, with or without an additional air classifier. Upon request of IFPRI, the developed approach can also be validated for other mill types such as dry operated stirred media mills. This of course would reduce the scope of the other investigations.

In a first instance, the impact of different grinding aids on the material transport through a ball mill in open circuit mode is investigated. Thereby, the residence time distribution will be determined experimentally in order to enable the calculation of the total number of stressing events per product particle within one grinding passage. These essential information will then be included in the system approach by transport models, which are extended with parameter describing the powder flow attributes to enable an inclusion of the grinding aid effects. Then, the system approach is extended with further models for describing the air classifier performance. As a basis, the impacts of grinding aids on dynamic air classification are also identified experimentally. The corresponding effects are included in the approach by classification models, which also consider appropriate powder characteristics (such as the agglomerate strength or the fluidizability) to include grinding aid effects.

This extension of the approach is then validated by experimental grinding aid studies in an exemplary closed-circuit grinding process. A detailed outline of the proposal for the second funding period will be submitted later.

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IFPRI Review Brief
Fine Particle Coating

The International Fine Particle Research Institute wishes to commission a comprehensive critical literature review on coating of fine particles, i.e. smaller than 100-200 microns. The review should survey traditional and novel coating technologies for fine particles and discuss the interplay between type of coating process, process conditions, and characteristics of the coating such as morphology and transport properties. The review should include a gap analysis of both coating applications and the engineering science of coating.

The scope of the review is limited to particles smaller than ca. 200 microns and to technologies that are or have the potential to be used industrially. We have particular interest in coatings for moisture barriers and adhesion control, although the review should not be limited to this.

IFPRI Report

Fine particle coating

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Abstract

This report provides a critical overview of process technologies for the coating of particles up to a size of 200 µm. Traditional as well as novel technologies are reviewed, assessing their potential in design of coating layers with specified characteristics, for example moisture and adhesion control. The interplay between coating mechanism, process conditions and resulting structure of coating layers is presented. Equipment for coating of fine particles is presented and the limits of (industrial) operation are discussed.

Introduction

In this introductory section, a working definition and general overview of coating and its purposes is given. Several important layer characteristics, like morphology/porosity and surface roughness, are introduced and links to product properties, like flowability (interparticle adhesion), and moisture diffusivity, are established. This section will also introduce *main theoretical concepts*, for example from heat and mass transfer, and electrostatic interaction (e.g. adhesion/van der Waals interaction), that are required for the presentation of the main coating mechanisms. Furthermore, *main measurement techniques* to access layer properties are introduced.

Definition
Purposes and requirements
Theoretical concepts
Measurement techniques

Coating mechanisms

The presentation of the coating mechanisms will be divided into the following groups:

- Coating by mechanical means, e.g. dry coating
- Coating by physical and chemical interaction, e.g. physical and chemical vapour deposition
- Coating by thermal means/drying, e.g. spraying of solid containing liquids (suspensions, solutions)
- Coating by electrostatic interaction, e.g. electro-spray
- …

Presentation of different coating mechanisms
Interplay of process conditions and layer properties
Approaches to process modelling

For each group, the mechanisms are introduced, the interplay of process conditions on layer and coated particle properties is discussed, and process limits are presented, for example the transition from coating to agglomeration in thermal spray processes.

Additionally, a brief overview of the current *state of modelling* of the different mechanisms will be provided. Here, the focus will not only be on single particle modelling but also on multi-particle interaction. Some key ideas and results from literature are presented, for example from the field of *discrete element simulation* (DEM), *computational fluid dynamics* (CFD) and *population balance modelling* (PBE).

Coating equipment

For each of the groups of coating mechanisms, equipment for its (industrial) realisation will be presented, highlighting challenges in operation and pointing to expectable deviations (with respect to modelling approaches) in product properties. Traditional equipment, for example mixers, and novel approaches, like atmospheric plasma-assisted fluidised beds, will be discussed. For the novel approaches, an assessment of potential of industrial application will be performed. Where available, a critical review of the *state of control of process* and equipment will be given.

Presentation of main equipment for coating of fine particles

Overview of process control in application

Selected applications

From each group of mechanisms, a few practical examples of successful coating of fine particles at industrial scale will be presented in detail. Examples range from functionalised powders for use in *additive manufacturing* to design and production of multi-layer coatings in *pharmaceuticals, and food and feed*. Information on achievable product properties will be provided as well as required improvement in design and operation of coating processes and equipment for fine particles.

Applications:
Additive Manufacturing
Pharmaceuticals
Food and feed

References

The given list will be *annotated*, i.e. a few comments on the content and outcomes of each reference are given. In addition to cited works, (commented) *links to other sources* will be provided for further reference.

Abbreviations and nomenclature

IFPRI Review Brief
Measurement and Quantification of Fines in the Presence of Large Particles

The International Fine Particle Research Institute wishes to commission a comprehensive critical literature review on the detection and quantification of nanoparticles (0.010-0.5 microns) in a particle mass population comprised mainly of large particles. (greater than 1 micron). Examples of where this is important are reconstituted liposomal emulsions with a small number population of 20-micron particles and large number population of 100 nm particles and alumina dispersions with a volume-mean particle size of 10 microns but significant number concentration of sub-200 nm particles. Single particle sizing methods are not able to characterize materials like these completely.

This review should discuss existing, new, and emerging experimental methods including sample preparation and data analysis for bridging multiple size characterization techniques.

IFPRI Review Brief

Confronting the Powder Flow Grand Challenge: Relating Particle Properties, Microstructure, and Bulk Powder Flow

The International Fine Particle Research Institute wishes to commission a comprehensive critical literature review of the relationships between particle properties, flow microstructure, and bulk flow dynamics in granular and cohesive powder flow. We are interested in the current state of understanding of the length and time scales of fluctuations in flow velocities, stress fields, and packing fraction and how system geometry and boundary conditions affect these. The review should cover both characterization and modeling, including:

- Direct measurement of tensile and compressive stresses between particles, in clusters, and in bulk isostatic systems
- Predictive models for small, high-intensity zones and "average" models for bulk behavior, including progress in multi-scale homogenization approaches for modeling.

THE RELATION BETWEEN PARTICLE PROPERTIES, FLOW MICROSTRUCTURE, AND BULK POWDER FLOW

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MultiScale Mechanics, TFE, ET, MESA+

University of Twente

Contents

Abstract

Bulk handling, transport and processing of particulate materials such as powders and granules are integral to a wide range of industrial processes in many fields or natural, geophysical phenomena. Particulate systems are difficult to handle and display unpredictable behaviour, which represents a great challenge for both design and operation of unit operations and plants, but also for the research community of Powders and Grains. Granular materials and powders consist of discrete particles such as individual sand-grains, agglomerates (comprising of many primary particles), or bonded solid materials like sandstone, ceramics, or some metals or polymers sintered during additive manufacturing. The primary particles can be as small as nano-metres, micro-metres, or millimetres covering multiple scales in size and a variety of mechanical interaction mechanisms. Those interactions include friction and a variety of cohesive forces, which becomes more and more important the smaller the particles are. All these particle systems have a particulate, usually disordered, inhomogeneous and often anisotropic micro-structure. which is at the core of many of the challenges one faces when trying to understand powder technology and granular matter. The flow behaviour of granular materials is inherently related to the kinematic and collective behaviour of the microscopic components. On the macroscale, it is noted that the particulate nature and the salient details of the contact mechanics are not adequately captured in the constitutive relations that are needed to solve the continuum equations. The influence of the particles on the bulk behaviour has to be better understood to ultimately provide effective predictive tools for particulate flows. One promising development in bridging from micro-mechanical insights at particle- and contact-level to the next generation of superior continuum models will come from the coarse-graining methodologies. Bridging the gap between the particulate, microscopic state and the macroscopic, continuum description is one of the challenges of modern research. This work gives an overview of recent progress about the flow behaviour of collection of deformable particles and the relation with the smaller scales involved.

The key point for a better understanding of the flow behaviour is the multiscale characterisation of powders, starting from the ***microscopic*** scale of individual primary particles, to the ***macroscopic*** scale of the bulk flow, including the ***mesoscale*** that lays in between, relevant for the granular fabric and aggregates. After an introduction section, where the main differences between dry granular materials and cohesive powders are highlighted, the first part of the paper reviews both classical and state of the art experimental techniques

used in the laboratory at different scales. Section 2.1 is devoted to the characterisation of individual particle properties, as relevant for granular flows. Specifically, the focus is on mechanical properties (e.g. density using pyconometry, stiffness using atomic force microscopy or nano-indentation nano-indentation equipment, restitution coefficient - using collision test) and particle morphology (surface roughness using Atomic Force Microscopy, specific surface area using nitrogen sorption technique, roundness/sphericity using Scanning Electron Microscopy, etc.). In Section 2.2, experimental techniques developed for the analysis of the mesoscale are reviewed, typically at the size of clusters/agglomerates. First, methods used to determine compressive/tensile mechanical responses are introduced, followed by an overview of advanced techniques for the analysis of the structure at the mesoscale, namely via photoelastic force measurements and 3D μ-CT study during compression and shear of granular materials and powders. The largest macroscopic scale of the flow is discussed in Section 2.3. A distinction is made between non-cohesive granular materials (analysed e.g. by particle image velocimetry - PIV or Positron Emission Particle Tracking - PEPT) and cohesive powders where the tracking of individual particles is extremely difficult due to small size. In this case, the flow properties properties are usually obtained via shear cells (bulk density and friction), FT4 device (powder flow energy), Freeman Lenterra Flow Sensor System for force measurements, rotating drum and the classical angle of repose test.

Besides experiments, the methods used to explore the micromechanical behaviour of particle systems involve numerical particle simulations and micro-macro transition methods, where the latter in general attempt to connect the particle scale with the process macroscale. In recent decades, the Discrete Element Method (DEM) that models the motion and interaction of individual particles has become very popular as a computational tool to model granular systems in both academia and industry. To date, not only due to increasing computer power available, considerable scientific advances have been made in the development of particle simulation methods, resulting in an increasing use of DEM. However, careful verification of the various numerical codes and validation of the simulation results with closely matching experimental data is essential to produce satisfactory quantitative predictions with added value for design and operation of industrial processes. One fundamental step towards this goal is the determination of the simulation parameters for the DEM particle model. This topic and the strategies to approach it are reviewed in Section 3.2.2, where the link with the microscale experiments is highlighted. Experiments need to be deployed (see Section 2.1), in order to measure particle-contact parameters and use them *directly* in particle simulations. However detailed contact information is only available for some materials such as glass spheres or rather large particles, whereas realistic, industrially relevant fine powders

can hardly be measured and contact level. In those cases, the microscale parameters must be inferred *indirectly* via comparison with simple lab scale element tests.
Once the numerical model has been calibrated and further validated, it can be used to study the mesoscale, and inform continuum models at the macroscale. In order to transfer information across the scales, some averaging or coarse graining techniques are required, that translate discrete particle data in continuum fields, as described in Section 3.4. Local macroscopic quantities such as density, velocity, stress and fabric can be extracted from the discrete simulation data (particle positions and velocities, interaction forces and torques). Note that both time- and space- averaging are required to obtain reasonable statistics, the latter being appropriate in the case of steady states. The methods and tools for this so called micro-macro transition are often applied to small representative volume elements (RVEs), where all particles can be assumed to behave similarly. Following the pioneer work by Goldhirsch, advanced numerical techniques have been developed in recent years, where the resulting coarse-grained fields exactly satisfy the momentum equations locally.
The final part of this section (Section 3.5) is dedicated to the representation of engineering setups directly via DEM simulations. These so-called mesoparticle simulations represent many particles as an entity, and as such catch the essential phenomenological features but are not directly related to the interaction parameters of the primary particles. A mesoparticle model is a valuable upscaling approach that allows for the simulation of large systems, including boundary values problems.

In spite of their versatile applicability and benefits, numerical methods have limitations such as excessive computational requirements, round off or truncation errors, and an intrinsic dynamic that sometimes does not reflect the experimental reality. Continuum models are still the most widely used to describe the process macroscale. Continuum mechanics theories solve the conservation equations for the whole medium i.e., the balance of mass, momentum and when necessary, energy. Although the balance laws are easily deducible, defining the constitutive relations poses the bigger challenge. Section 4 introduces the general rheological framework to describe the flow behaviour of granular materials and powders. The same section reviews existing granular rheological models derived using characterisation experiments as well as discrete simulations and micro-macro transition.
Classical approaches describe the flow rheology in terms of particle properties and system characteristics, like pressure or density, i.e., information attainable by conventional experiments in Sections 2.1 and 2.3. The kinetic theory in its standard form (SKT) is applicable in the very dilute regime, where the grains interact mainly through binary, instantaneous, uncorrelated collisions. Following the statistical mechanics approach, the generalization

of the kinetic theory of granular gases provides a meaningful hydrodynamic description, in accordance with the empirical Bagnold scaling between stresses and the square of strain rate. On the other hand, when the system is very dense, its response is governed by enduring contacts among grains, which are involved in force chains, that continuously rearrange during deformation. In these conditions, the granular material behaves like a solid, showing an elastic response in which stresses are rate independent. The corresponding flow regime is usually referred to as quasi-static. In the transition phase, where flows are dense, the grains interact via both force chains and collisions, and granular materials experience a phase-transition of - from a solid-like to a fluid-like Intensive studies on this topic have been conducted in the last decades. Recently, the French research group GDR-MiDi has suggested that dense granular materials obey a local, phenomenological rheology, known as $\mu(I)$-rheology, that can be expressed in terms of relations between three non-dimensional quantities: volume fraction, friction μ, and inertial parameter I. This theory has been developed for ideal systems, made of rigid, perfectly elastic, monodisperse particles. Attempts for an extension of the $\mu(I)$-rheology to deal with soft, deformable particles, are also described. The rigorous STK and the phenomelogical $\mu(I)$-rheology are finally compared to empirical laws derived by laboratory and plant observations.

Section 4.3 is dedicated to the most recent theories, aimed to enrich the existing formulations with relevant features at the intermediate mesoscales, including permanent/transient fabric, structures and force chains.

In Section 4.3 local and non-local approaches to model granular heterogeneity are compared. The cooperative motion of grains causes the bulk properties at some location to be influenced by the flow taking place at all other locations. Works that belong to the first class assume that the flow can be described locally, when the appropriate set of state variables is identified, and their values in every material point are known. In the case of non-local approaches, a characteristic length scale is build directly into the model, as related the size of the grains themselves and the system properties, e.g. density. A number of other manifestations of finite-size effects in granular flows, with special focus on boundary effects, are finally highlighted.

IFPRI Review Brief
A Gap Analysis of Particulate Systems Modeling, Sensor Capability, and their Integration

The International Fine Particle Research Institute (IFPRI) wish to commission a critical review of the current capability in modeling and sensors for systems integration of particulate processes. IFPRI will use this review as a foundation for a future workshop on systems engineering and automation of particulate processes.

Rather than a conventional review, IFPRI would like a gap assessment and analysis. This should evaluate the state of the art and identify critical gaps in particulate systems modeling and sensors, including:

- Flowsheets used to integrate unit operations into systems, having mass and energy balances with distributed streams (particulate attributes) that are necessary to control desired product quality attributes.
- Mechanistic models of sensors (e.g. to account for systematic errors in PSD measurements of non-spherical particles by laser diffraction) that will allow better validation of models that are subsequently used for optimal design and operation.
- Additional models such as advanced process control (APC) models suitable to link many-to-many relations among process sensors, actuators, and desired product attributes.
- Sensor and measurement technologies for in-line, on-line, at-line, and inferential sensing of process streams, including distributed attributes.
- Opportunities to adapt sensor models for more efficient process control purposes.

Outline/Draft for IFPRI Systems Engineering Framework

P. Mort, IFPRI/Elsevier Liaison, PrM3 Consulting LLC

This draft summarizes content for the IFPRI Systems Engineering Framework. It builds on the previous Forward Framework document that was included in the 2018 AGM materials[1] and proposes additional review scope relevant to the initial brief from 2016, providing perspective on Systems Engineering (SE) as it applies to particulate processing. It includes open-ended questions (*blue italics*) intended to seed further discussion within IFPRI and the broader community. Feedback on these and other questions is welcome and can be addressed in the full review, teleconferences, and/or AGM programming discussions.

An intent of the original 2016 brief was to identify topics for an IFPRI workshop having a Systems Engineering focus. At the 2018 AGM, we planned to move forward opportunistically with a Granulation Systems Engineering Workshop, to be held at PARTEC in Nuremberg, 12-April-2019, organized jointly by the International Fine Particle Research Institute (IFPRI) and the Working Party on Agglomeration of European Federation of Chemical Engineering (EFCE).[*] My original plan for this review was to focus on granulation as an example for the Systems Engineering Framework, including the workshop and its proceedings as content for the review. The exercise of writing the review would also meet the need of documenting the workshop. However, joint workshop planning efforts have not progressed, forcing us to cancel the workshop. An alternate review plan is not proposed (Table 1) with detail following.

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[*] The proposal for the Granulation Systems Engineering Workshop, joint with IFPRI and EFCE, was based on ad-hoc discussions including Stefan Heinrich, Satoru Watano, Willie Hendrickson and Paul Mort at the April 2018 WCPT. At that meeting, we agreed on content including:

- Workshop Announcement: Systems Engineering Framework for Granulation.
- Workshop Objective: The objective of the workshop is to advance a Systems Engineering framework for a Granulation Processes and associated Products. The focus includes process and product models, process sensors, and methods needed to support better integration of Performance-Structure-Process relations. We will further consider advances in unit operations and supporting physical technologies needed to achieve said objective. Organization of the Workshop is a joint effort by the International Fine Particle Research Institute (IFPRI) and the Working Party on Agglomeration of European Federation of Chemical Engineering (EFCE).
- The Workshop will be held on Friday 12-April-2019, as a 1-day supplement to the PARTEC meeting in Nuremberg. We will start with a Welcome Event on the evening of the 11th after the close of PARTEC.

IFPRI proposed to develop a more detailed agenda, as follows; however, we have not been able to align this with Stefan Heinrich in time for PARTEC. It is included here as a reference point.

- Workshop Agenda: The Workshop is designed as an interactive event aimed at describing the pre-competitive scope of Systems Engineering that is relevant and required to advance both academic research and industrial practice of granulation. A sequence of three sessions with address:
  - Systems framework for product design using granules as a product form or as an intermediate to a product, with a focus on product efficacy;
  - Systems approach to process design having integrated unit operations, focus on process efficiency and control;
  - Critical needs for modeling and measurement technologies, hard and soft-system approaches.

  Each session will start with a concise problem statement featuring an industrial and academic viewpoint, followed by discussion in smaller breakout groups (~6-10 people / group), then reconvening as a full group with topline sharing from the breakouts. A final session will attempt the synthesize the input of the above, and to develop an outline for publication of the outcomes.
- Workshop Pre-Work: Participants will be provided background reading in advance of the event covering:
  - Perspective on Granulation research supported IFPRI and EFCE Working Party on Agglomeration;
  - A curated list of talks scheduled for the main PARTEC meeting that are of relevance to the Workshop and their abstracts.

Proposed Review: IFPRI Systems Engineering Framework for Particulate Products and Processes

Table 1. Summary of proposed review

The original brief requested:	The proposed review covers:
• Flowsheets used to integrate unit operations into systems, having mass and energy balances with distributed streams (particulate attributes) that are necessary to control desired product quality attributes. • Mechanistic models of sensors (e.g. to account for systematic errors in PSD measurements of non-spherical particles by laser diffraction) that will allow better validation of models that are subsequently used for optimal design and operation. • Additional models such as advanced process control (APC) models suitable to link many-to-many relations among process sensors, actuators, and desired product attributes. • Sensor and measurement technologies for in-line, on-line, at-line, and inferential sensing of process streams, including distributed attributes. • Opportunities to adapt sensor models for more efficient process control purposes.	• Brief survey of flowsheet tools either in development (including academia) or commercially available. Comparative testing and/or assessment of built-in process models is not in scope. See “Process Flowsheets” • Sensor model focusing on 2D image analysis, where 3D particles are reduced to a 2D orthographic projection based on their orientation in the field of view. See “Sensor Models.” In scope: o Sampling: dynamic and static sampling with both front and/or back illumination. o Various distribution bases (number, length, area, calculated volume). o Length measurements (minor, major, average chord, minimum chord through centroid, maximum chord, equivalent circular diameter). o Shape analysis (aspect ratio, circularity, perimeter measurements). o Multi-modal analyses of distributed data. • While the physics of sensors for fine powder and/or colloidal dispersions are not in scope, the use of their data for multi-modal size analysis can be included. • Product-process relations will be given a brief overview. If a deeper dive is desired, it is necessary to narrow the scope; see discussion under “Product/Process Framework”. • For the purpose of process control, the review will consider how to combine multi-modal analyses of image data with mechanistic process models.

Product/Process Framework

System Engineering approaches have been applied across a range of petrochemical and other commodity chemical industries, balancing optimization of product quality and process efficiency in both R&D and manufacturing. In the solids processing industries, process-structure-performance relations are more complex. Some success has been achieved in application of PAT tools in the pharmaceutical industry, for example in control of liquid-solid reactors such as crystallization.[2] Zoltan Nagy’s IFPRI project has furthered this capability by integrated milling of seeds in a closed loop.[3] A similar concept is explored in a seeded granulation loop, using a mill to control seed size.[4]

A broader view considers a range of product performance criteria, where products may comprise particulates and/or where particulates are a critical part of an intermediate process. In either case, the product quality depends on the combination of material input streams, particulate processes involving those streams, and subsequent assembly processes required to convert particulates into a product form.

This chain of dependency, from constituent materials, particulate processing, product design and in-use performance is illustrated by reading Figure 1 from right to left.

A Systems Engineering approach can consider the inverse problem, starting with product performance criteria, then identifying product form options, process routes, and material requirements. The systems approach enables model-based optimization of said options, providing a left-to-right perspective of the relationships in Figure 1. While IFPRI does not consider proprietary scope or claims related to product design, we can consider the SE relations in terms of derivative properties that are relevant to in-use performance.

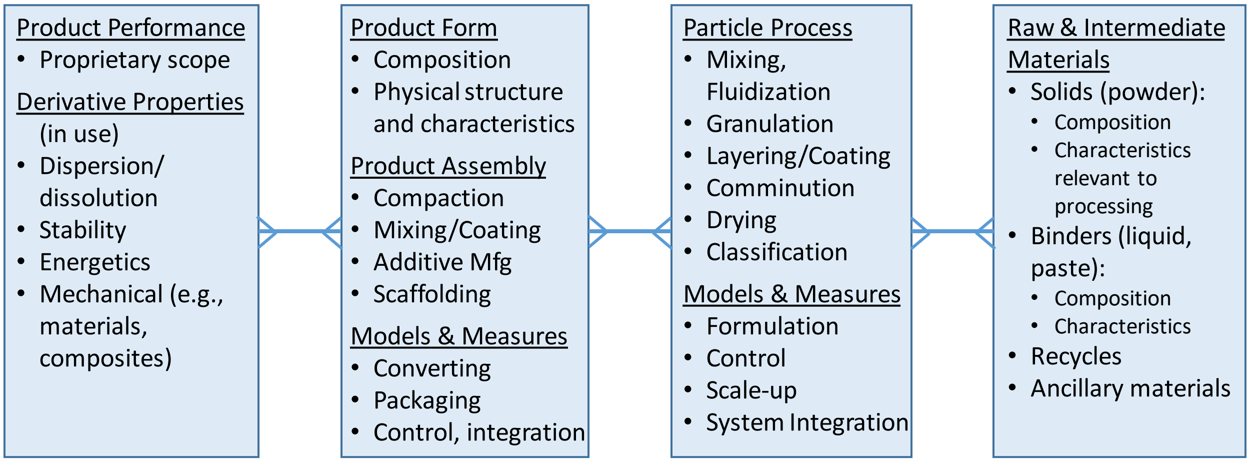

Figure 1. Relationship diagram for Process / Structure / Performance relations. Connection symbols denote many-to-many relations among blocks in the diagram:

- Input raw materials, their specification and inherent variability;
- Processing, understanding of process capability, control and adaptability to variations in raw materials, environmental conditions, etc.;
- Structure and product characteristics as an output of processing, note specifications may have distributed attributes (e.g., particle size, shape, composition in mixtures…); and
- Derivative properties and in-use performance of products as a function of composition and structure.

In my opinion, the systematic consideration of process-structure-performance relations is a key opportunity for IFPRI to exploit in the Systems Engineering area. The following three questions were a part of the Forward Framework[1] and are relevant to the discussion around Figure 1.

A potential goal for the IFPRI SE effort could be to develop and/or improve tools for process/structure/performance integration, especially in ways that facilitate inverse solutions (i.e., specifying structure and process models based on performance requirements).

Do we have sufficient models to solve the inverse problems, i.e., for a desired product performance, what must be true of product structure, processing thereof, and materials used in that process? If so, are such solutions amenable to optimization, even multi-objective optimization?

Another goal can be to describe, e.g., via expert systems, details of the many-to-many relations between blocks in Figure 2. For example, detailed mapping of the relations between processes, materials and achievable structures or specifications.

While these are important questions, and I encourage IFPRI members to push forward on their discussion and resolution, my current plan is <u>not</u> to pursue these topics in detail as a part of the full review. The overall scope is very broad; my intent is to do only a broad survey of available tools and modeling approaches, where they have been applied, and the prognosis for further application in solids processing. If there is strong interest among IFPRI companies, with specific feedback, I can add some additional perspective on specific focus areas such as:

- Granulated products requiring storage stability and in-use dispersion (e.g., detergents, fertilizers, processed foods/dietary supplements),
- Compacted particulates (e.g., pharmaceutical tablets, powder metallurgy and/or ceramics),
- Particulate composites (e.g., particles as filler in a matrix phase, or perhaps particles in a scaffolded structure).

Process Flowsheets

The following discussion is updated from the Forward Framework;[1] it asks whether current flowsheets that work by linking unit-op models are sufficient to capture the degradation of product quality and loss in operating efficiency associated with intermediate solids handling. Conversely, there are implied opportunities to improve quality and efficiency via systems approaches aimed at minimizing intermediate handling.

Industrial systems typically include primary unit operations having control objectives (e.g., crystallization, granulation, milling) along with ancillary processes (separation, classification, recycling) that can be used to further refine output quality. System models use flowsheets to integrate unit operations with flow streams having distributed characteristics. Flowsheet platforms having solids processing capability include gPROMS Formulated Products, Process Systems Enterprise (https://www.psenterprise.com/products/gproms/formulatedproducts/solids) and Dyssol under development at TUHH with funding from the DFG Priority Program SPP 1679 "Dynamic Simulation of Interconnected Solids Processes," (https://www.tuhh.de/spe/research/research-areas/flowsheet-simulation-of-solids-processes.html). Both are dynamic simulations capable of tracking distributed particle and other critical attributes, assuming suitable models are available to inform the simulations. This requires a practical combination of (1) unit-op models having distributed input and output streams with sufficient detail to predict product quality objectives; and (2) sufficient measurement data to compare against the models' predicted stream distributions. On one hand, detailed models (e.g., multi-dimensional PBM's) may be challenging to implement because they require more detailed data for comparison purposes; on the other hand, grossly simplified models may not be able to adequately predict distributed characteristics relevant to product quality specifications.

Flowsheets can be used to track process efficacy, i.e., capability to meet specifications on distributed characteristics, for example particle size, shape, composition, porosity or other structural attributes of particles. A process systems approach can be used to achieve quality objectives for distributed characteristics based on integrated monitoring and control.

Issues with process systems startup, operating efficiency, reliability and throughput capability are often traced to problems with solids handling. This is a common experience among many IFPRI members and among the broader solids-processing community. Merrow's reports from 30 years ago cited insufficient physical understanding of solids handling, raw material feeds, and solid waste-stream handing as primary contributors to poor start-up and performance of solids-processing plants.[5] Specifically, Merrow cited common problems resulting from the physical tendency of solids to "plug, stick, flow unevenly, and go where they should not (often, in the form of dust)."[6] Pinch points were cited in feed systems, classification screens, conveyors, and bucket elevators. While IFPRI has funded considerable research in dry powder flow over the interim, these physical problems persist. In fact, challenges with solids handling, transport, and ability to control flow continue to be bottlenecks to improved process systems efficiency and efficacy (product quality).

Related to the above, many particulate process systems rely on recycle streams to achieve required product specifications while minimizing material losses. Physical handling of recycles (typically particles that are either too fine and dusty or too coarse and sticky) can be challenging. A recycle strategy that minimizes handling may seem like a good idea; however, some processes such as granulation have an undesired feedback response to direct feedback of recycles (e.g., absent other control action, increasing feedback of fines in a granulation circuit will typically drive the process to produce even more fines). In such cases, surge capacity and controlled metering of recycle streams may be needed for process control. The addition of recycle surge bins and feeders pushes against challenges with solids handling.

From a product quality and quality specification perspective, solids handling and transport can be consequential, especially in cases where quality specifications rely on distributed attributes in a mixture of particles. A product that may conform to product specifications at one sampling point may degrade simply as a consequence of de-mixing and segregation during subsequent handling, e.g., by emptying storage bins, processing through packing lines, etc. More generally, particulate products are susceptible to attrition, caking and other forms of degradation that may occur in handling and storage.

On one level, systems thinking tends to separate transformations into distinct sub-systems as a means to simplify control and optimization – i.e., a simple one-to-one relation between transformations and sub-systems may be desirable in theory. In practice, such simplified approaches often ignore the consequences of handling solid materials between sub-systems.

A "solids-handling-woke" version of systems thinking seeks to minimize consequences associated with intermediate transport and handling. Combining this awareness with flowsheet modeling, one can analyze overall system efficiency and efficacy (product quality) as a function of sub-systems choices (e.g., unit operation capability) and integration thereof.

Are consequential transport and handling models sufficiently developed, i.e., relative to process efficiency, reliability, etc.? Are such models sufficient for use in flowsheets?

Recognizing the cost, operational and quality implications of solids handling, how can advances in unit operations and close-coupled integration thereof be especially advantageous to solids-processing industries?

In an effort to minimize negative consequences associated with handling and transport of intermediates and recycles, what are the priorities for advancing unit operations with control capability for multiple transformations? How can measurement and modeling of internal (unit-op) solids flow and stress fields promote and enable such developments?

Sensor Models

The review will focus on the multi-modal analysis of particle data, preferably acquired by 2D Imaging, including size, shape and other illumination effects (e.g., color, edge clarity, etc.). In principle, the multi-modal methodologies are applicable to any sensing technology that can provide cumulative distribution data. The distribution models rely on cumulative functions that can be linearized by transforming measured cumulative distributions to corresponding probability distributions. Multiple modes can be seeded according to residuals the linear regression of particle data against the probability distribution. Because of the transformation to and from cumulative distribution and probability scales, weighted regressions must be used. The review will focus on Gaussian and Stretched-Exponential distribution functions, applied on a geometric basis (i.e., Log-Normal and Weibull distributions).[7] Details of the methodology will be shared in a separate paper that is currently under preparation by the author.

The first example (Figures 2-8) uses image data from granules in a previous granular-flow study including flow field tracers.[8] The image analysis data were collected using dynamic sampling and front lighting to measure the tracers by color, where tracer granules were coated with a thin red layer (Solid Sizer, JM Canty, Buffalo, NY). This imaging method has been used for in-line process measurements. Figure 9 uses the same imaging method to explore distributions with fine and coarse tails. Figures 10-12 explore a finer powder sample using back-lit static imaging at higher magnification (Morphologi, Malvern Panalytical, Egham, UK); this is an off-line method.

Calculation of best-fit estimates of the geometric mean size, d_g, and geometric standard deviation, σ_g, can be done by weighted linear regression of x (log(d)) on y (linear model based on cumulative data) (Figure 2a). The weight functions are derived from the cumulative data (2b). In this case, the linear model is a Gaussian cumulative probability function and the cumulative distribution is based on particle 2D area data. For a single mode, log(d_g) is the x-intercept of the regression and log(σ_g) is the slope dx/dy. The multi-mode fit is derived based on the residual analysis of the single-mode linear regression (Figure 3), providing a significant reduction in the weighted mean square error, *wmse*. For display, the multi-mode results are replotted with cumulative and frequency ordinates in Figure 4.

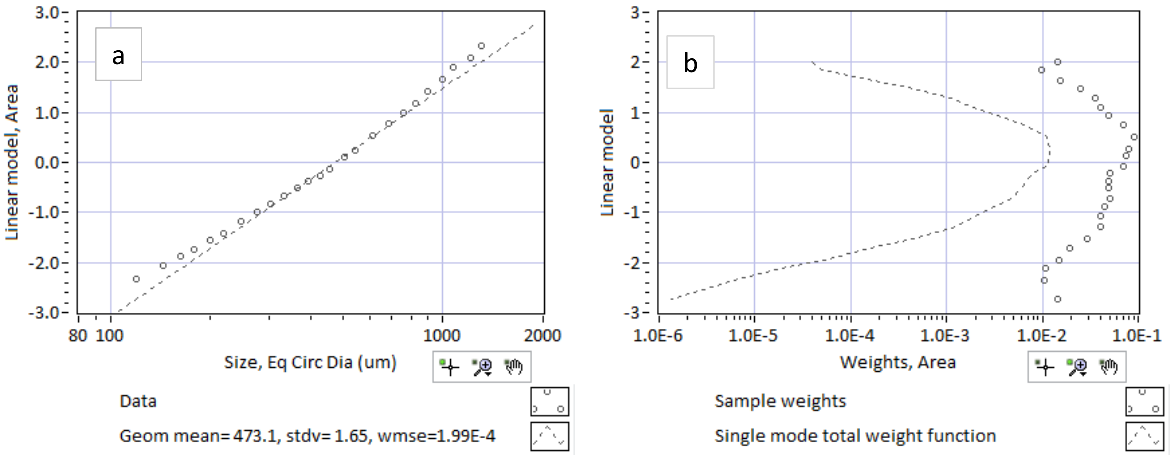

Figure 2. a) Single-mode fitting via weighted regression of log(d) on the cumulative probability function (i.e., linear model); b) weight function based on cumulative data and transformation functions.

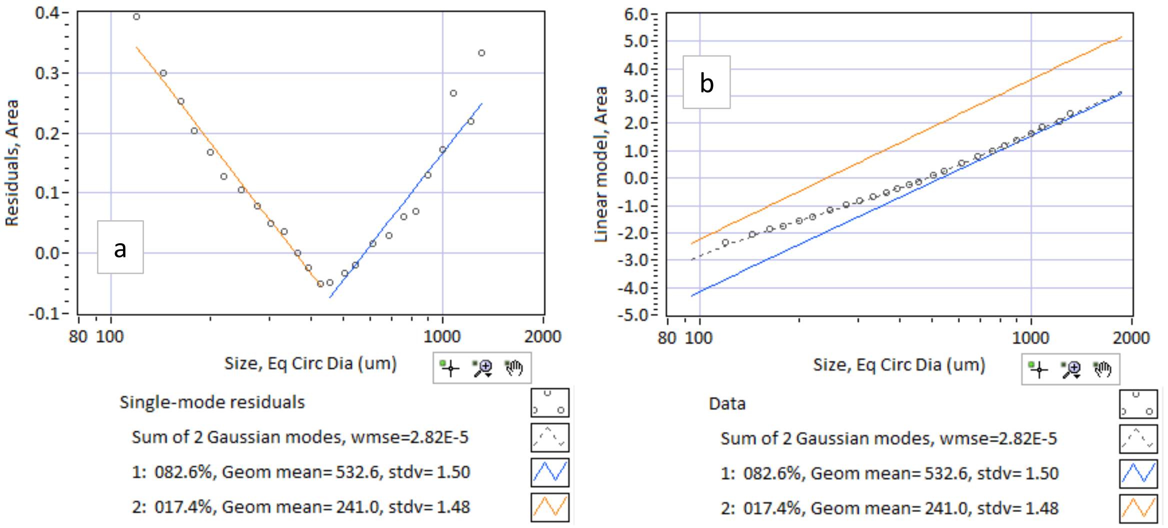

Figure 3. a) Multi-mode peak identification using residual analysis and b) resultant linear model fit.

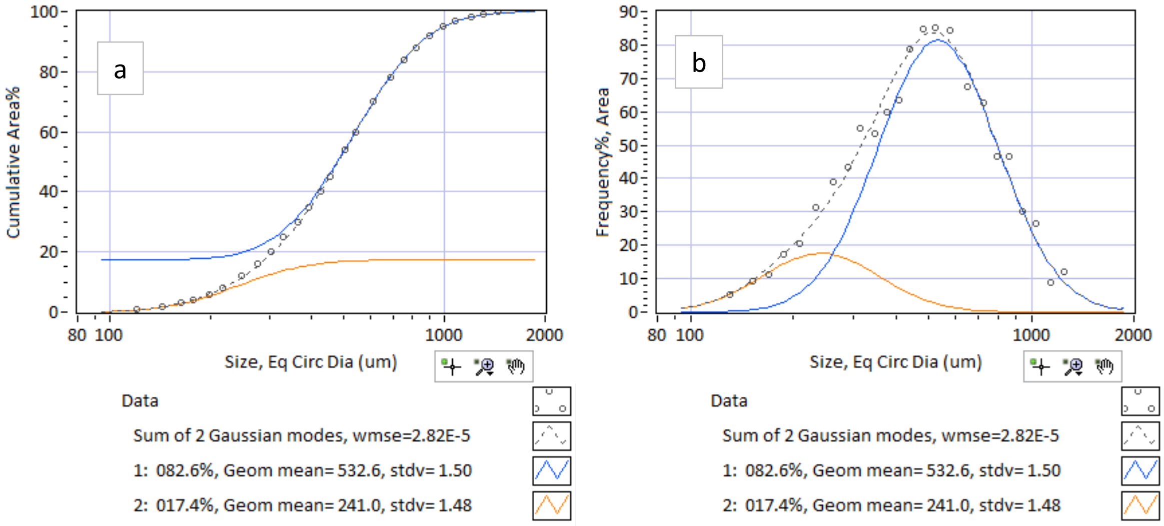

Figure 4. Replotting the multimodal fit derived above in terms of a) cumulative and b) frequency destributions. Note the frequency plot is the deriviative of the cumulative function with respect to x, where x = log(*d*).

Various bases may be used for the cumulative distribution including number, length (or perimeter), area, and calculated volume (Figure 5).

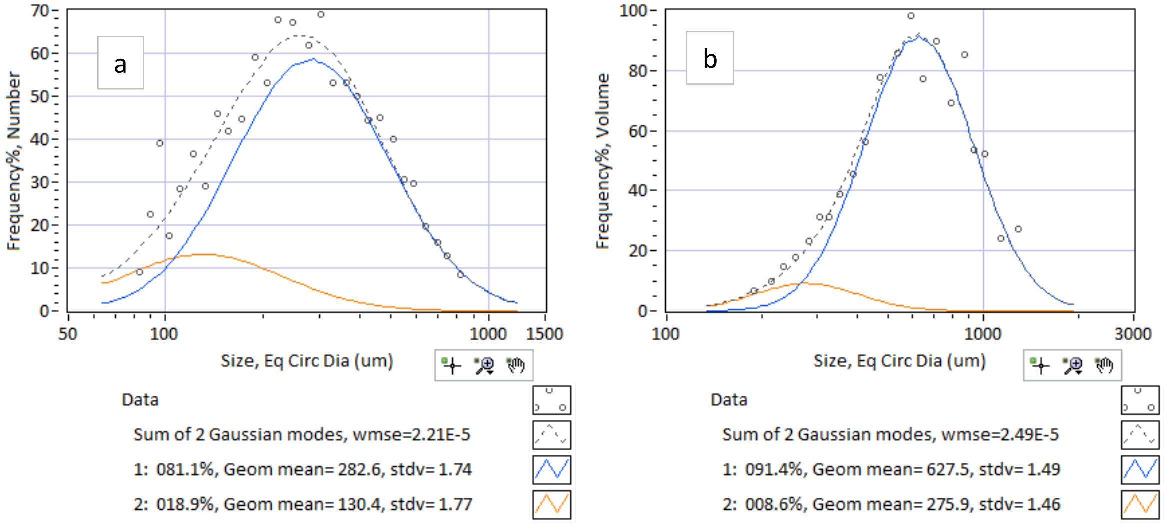

Figure 5. Comparison of bimodal fitting with a) number and b) volume-basis cumulative data; compare to 4b for area basis. In this example, bimodal character is preserved across bases; note the increase in the breadth of the number-basis distribution occurs for both modes; this behavior may vary from sample to sample.

Various length measurements may be used to describe the particles. The equivalent circular diameter shown in previous figures is calculated based on measured area of the particle. Figure 6 shows the minor and major axis length distributions; compare to Figure 4a.

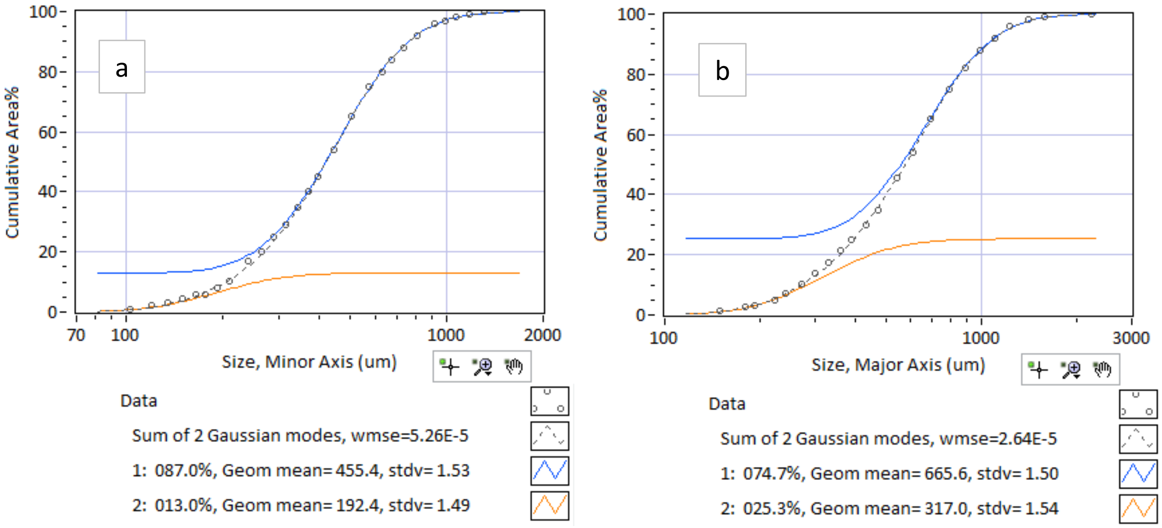

Figure 6. Comparison of bimodal fitting with a) minor axis and b) major-axis particle features; compare to 4a for equivalent circular diameter. Note the relative shift in modes as d increases.

Particle shape is often important to processing and product quality, yet it is often underspecified and/or under-controlled because of challenges in its measurement and analysis of its distribution. Figure 7 explores possible approaches to shape factor analysis and the distribution thereof. The objective is to define a reasonable descriptor of shape that is apparent from 2D imaging and is further consistent with available distribution functions.

- The Aspect Ratio (AR) is a commonly used shape factor (major/minor axis). It is observed that the log of its inverse fits reasonably well to a stretched-exponential cumulative function, where log(d*) is the intercept and n is the slope of the weighted regression. The Perimeter Ratio (PR) is defined as (measured 2D perimeter) / (equivalent elliptical perimeter of a particle having the measured area and aspect ratio). While PR has the desired feature of being a shape descriptor that is orthogonal to AR, it is not scaled to the same magnitude; i.e., the comparative use of AR and PR for shape analysis and control may require some re-scaling of PR. Both AR and PR have logical minimum values of 1. The Shape Vector (SV) is defined as the vector sum of the excess AR and PR measures: $SV = 1 + \sqrt{(AR-1)^2 + (PR-1)^2}$; its inverse is also plotted in Figure 7a.
- The circularity ratio (measured 2D perimeter) / (equivalent circular perimeter of a particle having the measured area) is another commonly used shape factor, also having a logical minimum of 1. While it is somewhat similar to PR, but is not orthogonal to AR. It is shown in 7b with a bimodal arithmetic analysis, i.e., sum of Normal distributions.

The tracer study is illustrated in Figure 8, showing multi-modal versus thresholding analyses to discern tracer particles (coated red) from the bulk of the granular distribution. In this example, the color of the base particles was white. A white particle has equal RGB color components, i.e., R = 33.3%. The bimodal analysis (8a) suggests the main mode is 33.6% Red, with a second mode having a mean of 36% red; the tracers are affecting the second mode. In comparison, 8b uses color thresholding to split the particles into two discrete populations. Using Red%=36 as a threshold, we see that the tracer population has a mean color of 40% Red and represents about 5.0% of the overall distribution.

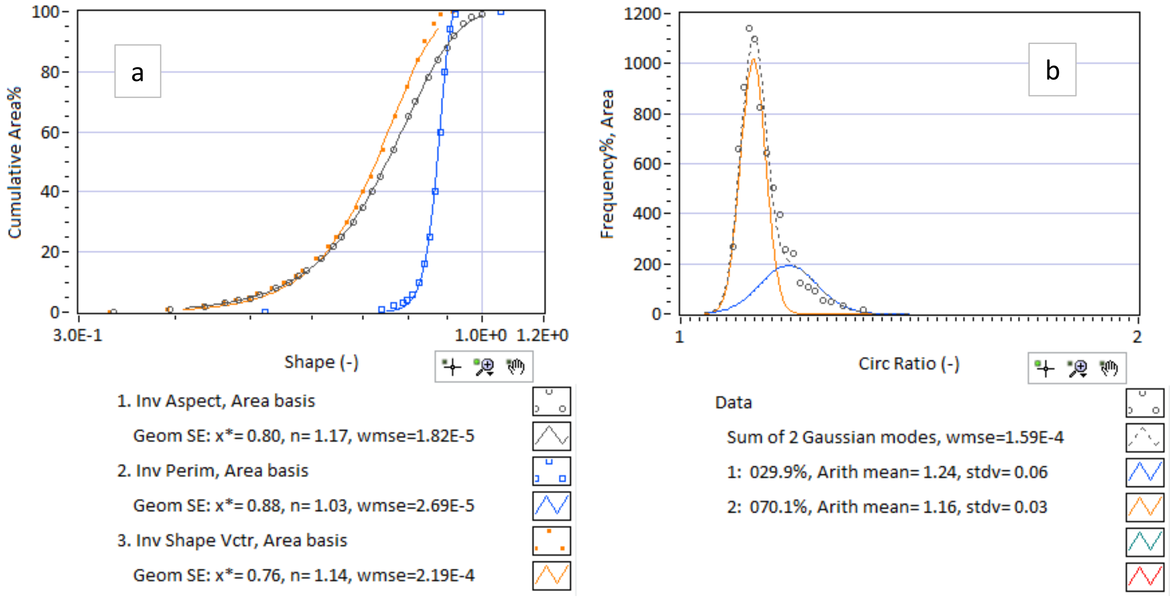

Figure 7. Shape factor distributions: a) single-mode fitting of inverse aspect ratio, inverse perimeter ratio and inverse shape vector obtained by weighted regression of the log(shape) on the stretched-exponential cumulative function. Note the aspect ratio is the dominant factor contrbuting to the shape vector; re-scaling of the perimeter ratio may be appropriate. Also note that difficutlies in accurate estimates of the perimeter can result in values of $PR < 1$; this is due to difficulty in converting from pixelated image analysis data, a sensor issue.

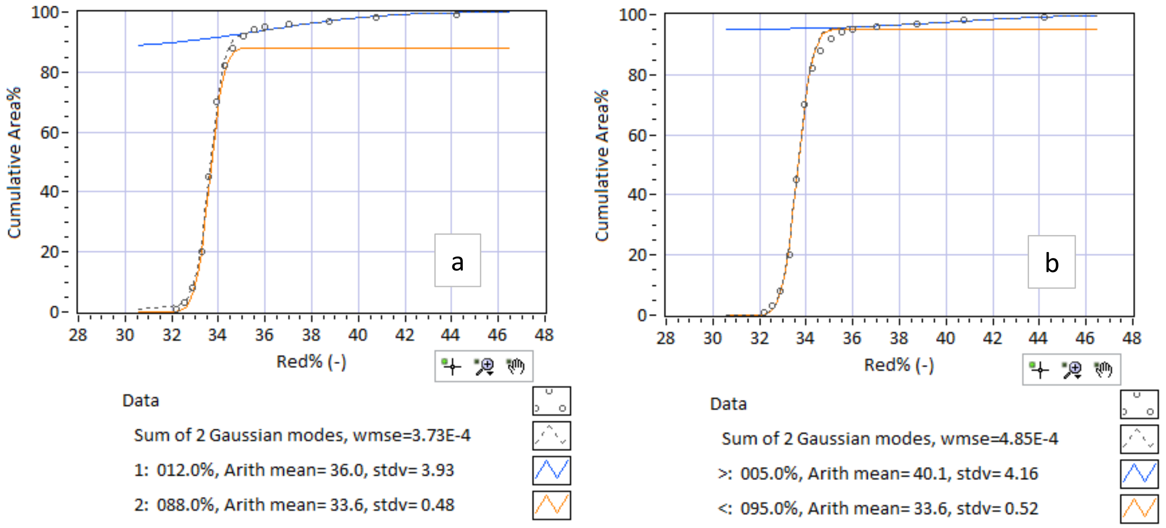

Figure 8. Particle color analysis: a) multimodal analysis using the methodology discussed herein; and b) threshold analysis to split the distribution by an independent feature, in this case, particle color.

A different granular sample is used to illustrate the use of multi-modal fitting for analysis of tails in a distribution. It is often observed that small tail fractions, either fine or coarse, can have significant impacts on processing and product quality. Yet these tails are not always evident in sensor analysis or in models. In the example, the overall distribution is well represented by a single-mode log-normal fit; in fact, the fit looks very good when viewed on a cumulative or even frequency plot (9 a, b). On the other hand, tails are evident in the linearized cumulative probability scale (9c). The use of multimode fitting (9d) elucidates small tails on both the fine (1.6%) and coarse side (1.3%) of the distribution.

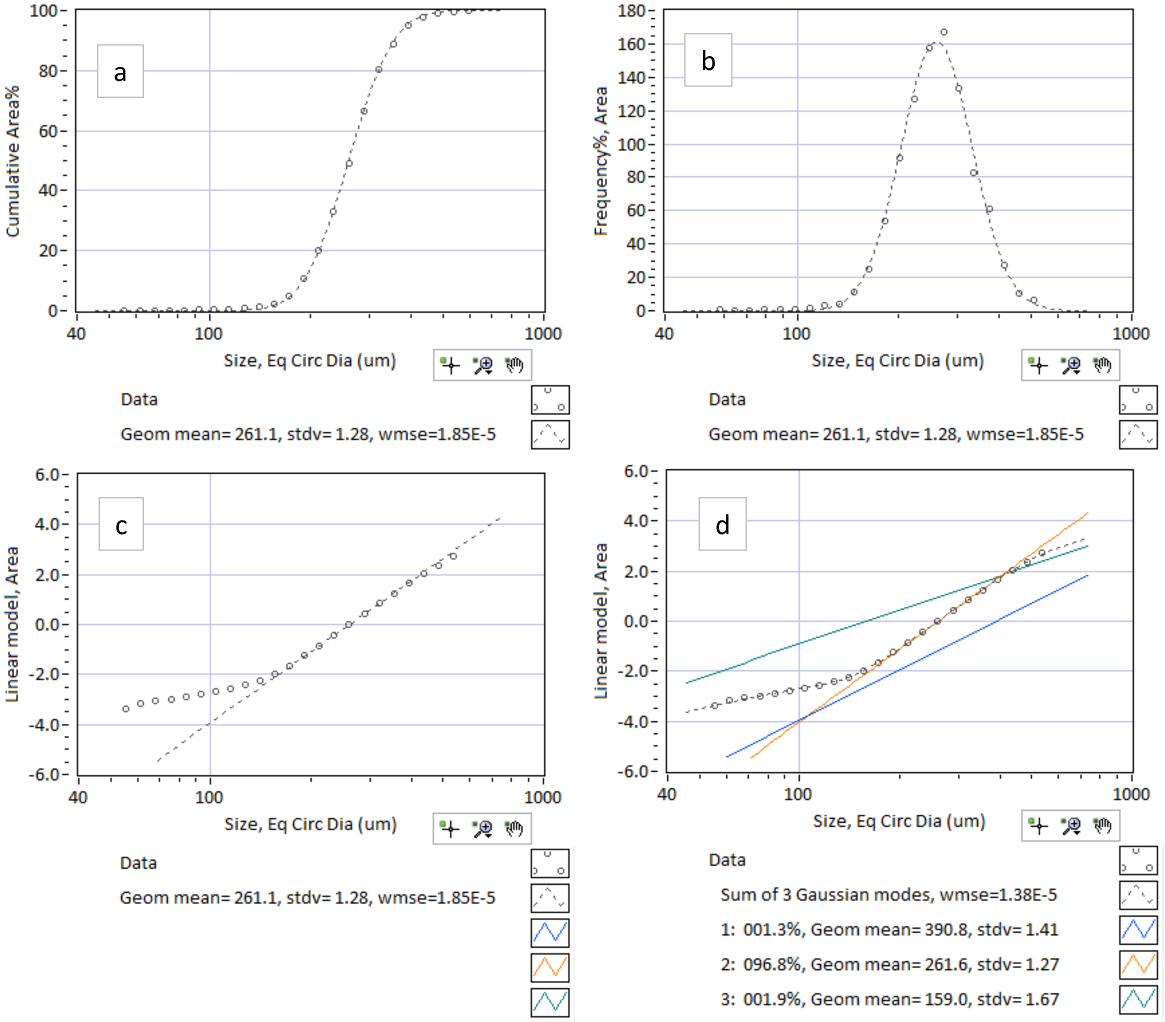

Figure 9. Multi-mode analysis of a granular sample having a distribution with minor minor fine and coarse tails. The single mode distribution look quite good when viewed on cumulative and frequency plots (a, b). The fine tail is more evident from the probability plot (c). Multimode analysis using the resuduals of the single mode regression reveal minor modes on each tail (d).

The final example is based on static sample imaging with back-lit illumination, i.e., dark particles on a light background. The sample data contains 20,000 particles from a milk powder with a substantial fraction of fines.[9] The residual analysis reveals three significant modes (Figure 10).   While the shape factor analysis (Figure 11) shows reasonably good geometric fit of the inverse shape factors to the cumulative stretched-exponential distribution model, we observe a small portion of the Inverse PR distribution having illogical values, $1/PR > 1.0$. Diving deeper (Figure 12), we see there is an apparent correlation between the particle size and the illumination characteristics of the sensor, i.e., larger particles appear darker. Figure 12 is a scatterplot with each point representing a particle. The blue points have a logical $PR >= 1$; the orange points are illogical ($PR < 1$). It appears that for a given illumination characteristic, smaller particles are more likely to be under-biased in their perimeter measurement. Bottom line, for shape analysis, there appears to be a need to re-bias perimeter measurements and re-scale their derivative shape factors.

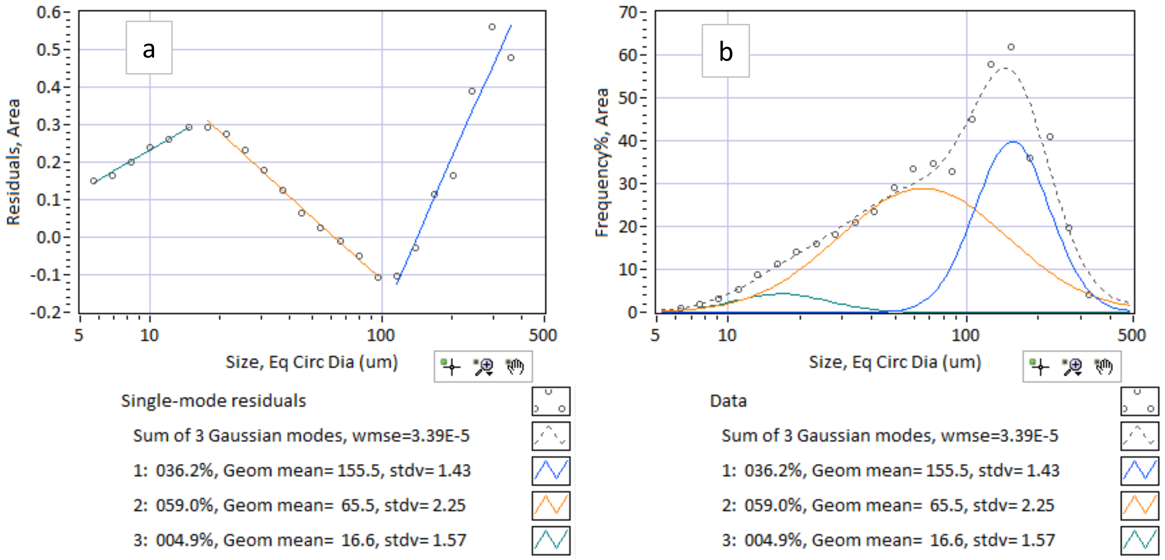

Figure 10. Multi-mode analysis of a milk powder sample. Residual analysis (a) indicates three significant modes, albeit overlapping (b).

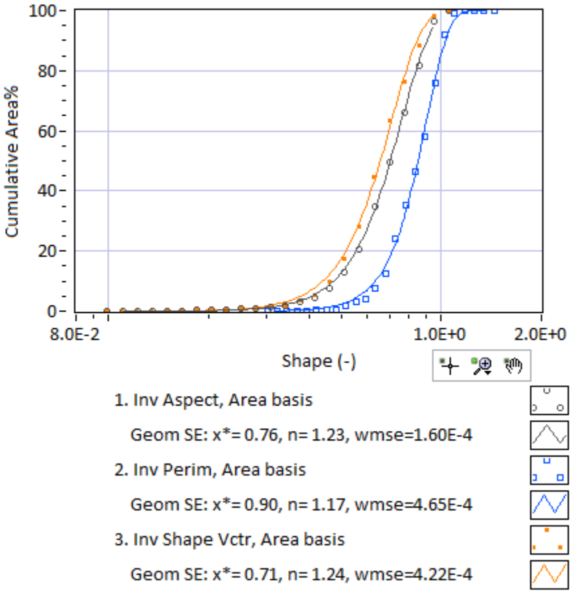

Figure 11. Shape factor analysis suggests that while AR is the stronger component of the overall shape vector distribution, the perimeter ratio (i.e., the irregularity of the perimeter) may be more of a factor with the milk powder compared to the prevous granular samples. Notice the PR distribution has an apparent bias toward low perimeter measurements resulting in higher inverse PR values, some of which are mathmatically illogical (about 15% of the cumulative area distribution, higher on a number distribution).

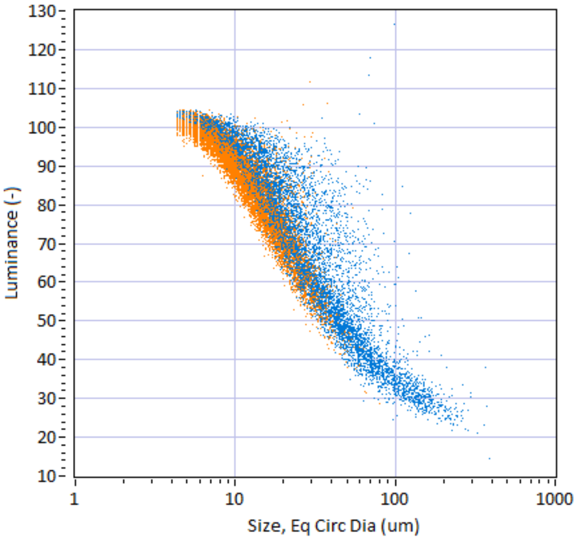

Figure 12. Scatterplot of image data, each point representing one of 20,000 particles. The threshold for image analysis edge detection is at a luminace value of ~104. The blue data have logical perimeter ratios, $PR > 1$; the orange data are mathematically illogical.

Conclusion

Consider Table 1 as an outline for the review, with the content expressed in the above Product/Process Framework, Process Flowsheet, and Sensor Model sections as examples of more detailed content. Please let me know if you have specific feedback or requests.

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Extension Proposal for Drying of Single Droplets at High Temperatures

Prof. A.E.Bayly, University of Leeds, 19th December 2018

Summary

This proposal builds from the work done in the first three years of the project and seeks to maximize its value, and impact, for industries that are developing spray dried materials and formulations. To do this it will focus on three areas: 1> establishing a best practice work process for prediction of product morphology from laboratory experiments and material characterization. It will include experimental work on the influence of temperature history on morphology and an evaluation of quantitative prediction by validating versus as large a scale dryer as possible. 2> Assessment, evaluation, and where possible development, of material property characterization techniques which are capable of making measurements at boiling conditions i.e. high temperature and low moisture content. 3> Extension of the material types investigated to crystallizing and colloidal systems.

Background and rationale

The final droplet morphology is due to the complex interaction between the droplet material, transport and thermodynamic properties and the drying history. The regime maps and models developed in the first phase of the project will give insights into the final particle morphology, the key drivers behind the morphology and how these might be altered to change morphologies. However, as the behaviour of the systems chosen in the first phase of the project has shown, the distinct phase behaviour of a material leads to regime maps which are material specific. The reapplicability of regime maps across other materials is therefore relatively limited.

Even for materials that can be clustered in terms of their phase behaviour, and for which models might be expected to provide reasonable predictions, the challenge in measuring material and thermodynamic properties to predict drying kinetics and morphologies *ab initio* makes this a complex and time consuming challenge. Consequently, when accessing new formulations or materials the effort required to characterize the phase behaviour and material properties will be significantly more than running drying experiments. That being the case if we want to learn about the predict morphology, estimate drying rates and predict dryer performance, rather than *ab initio* models, the most efficient product and process development process will be to use experimental techniques, interpreted through models.

The key opportunity therefore is how best to predict product properties and process performance for a high temperature system from small scale experiments; this is reflected in the first theme of the proposal outlined below. In addition, the time we have had to focus on measurement techniques has a been limit so there is the opportunity to take this further and to test systems for quantifying the material property evolution during drying. Work in this area will help refine models and to quantify mechanistic understanding. Where beneficial we will look to foster collaborations with experimental expertise and apparatus to help with measurement technique development

Finally, the work has focused on three systems HPMC, sodium silicate and sucrose which were chosen to be representative of the amorphous, skin forming/polymeric class of materials. The work over the next year is also likely to be primarily focused on this class of materials. There is therefore an interest in extending the work to other classes of material namely crystallizing systems and colloidal systems

Proposal

T the following three themes are proposed for a continuation of the project, the focus on each theme would be open for feedback and discussion:

1. **Best practice work process for the prediction of morphology**
   The first phase of the project has shown that mechanistic and qualitative understanding of morphology development can be obtained from filament drying.   Work is underway to establish if drying models can capture the behaviour across the range of conditions tested , *e.g.* do the approaches in the models capture the physics of the system well enough to allow material properties parameters to be calibrated.   Here we will build on this work and use it to propose and evaluate methodologies, combining experimental and modelling techniques, to estimate the morphology and intra-granular porosity for a product from a spray drier. These methodologies would range in accuracy from the more qualitative to the quantitative. The quantitative approaches would use CFD and/or zonal models to predict drying histories. Further single particle drying experiments are anticipated to look at the influence of the temperature history on the particle morphology, a potentially important factor for some systems.
   Testing and validation of the methodology would be done versus as large scale experiments as possible, at minimum the method would be tested versus a well characterized lab scale dryer.
   Challenges/Risks: 1> Validation: The challenge with attempting this for large scale dryers is typically the work required to establish the geometry and boundary conditions and validate the airflow model are considerable unless these have already been established. 2> The optimum method and accuracy of the methods are likely to be may be material dependent.

2. **Material characterization**
   The key challenge in material property characterization and measurement is the ability to do this at the temperatures and moisture contents seen during the droplet boiling events. These relatively extreme conditions are a challenge for both standard and advanced techniques. Consequently, existing techniques are not capable of making the measurements required. New methods or modifications to existing methods will therefore be identified, assessed and developed to measure material, transport and thermodynamic properties during the drying history of the droplets or at the equivalent conditions. A key aim will be to get these methods as simple and robust as possible and to provide tools for qualitative assessment as well as quantitative evaluation.   A collaborative approach will be taken for this theme, with the aim of bringing in complementary expertise where synergies exist. A more detailed discussion of some

of the methods is appended to this document. *Challenges/risks:* The effort and cost involved in developing these techniques may be prohibitive, consequently a key milestone in the project will be the decision on which routes to take.

3. **Extension to other material classes**
   Extending the methods to suspension/ colloidal systems, and crystallizing systems (or others that are a priority for IFPRI) rather than the skin/polymer systems that have been the focus to date.

Draft work plan:

Year 1:

Theme 1: a) Establish influence of temperature history on morphology and drying behaviour of HPMC, silicate and sucrose; b) testing and evaluation of single drop models with aim of establishing right to succeed with methodologies; c) identification of initial development methodologies; d) scale-up system assessment and characterization e.g. atomization measurement, inlet temp checking etc;

Theme 2: a) Viscosity/elasticity technique review and assessment. b) Identification and establishment of collaborations; c) experimental rig development

Theme 3: No action

Year 2:

1: a) test system runs at scale; b) characterization of products; c) CFD/zonal model development d) comparison of predictions to results; e) methodology refinement

2: a) method development; b) validation of technique

3: System selection and test runs

Year 3:

1: a) testing of methodology on new material system; b) consolidation and write-up

2: a) characterization of key systems; b) consolidation and write-up

3: a) full characterization of target systems; b) development of regime maps and evaluation of modelling framework

Appendix 1: Material Property Measurement

The characterization of material properties, e.g. viscosity, elasticity, diffusivity, etc for the systems investigated is challenging as they need to be measured at or near boiling point and at low moisture content. Properties such as diffusivity and viscosity also span many orders of magnitude and are therefore challenging to measure. These temperature and conditions are out of the range of most of the techniques available at collaborators or potential collaborators (Reid, Bristol; Schutyser, Wageningen; Murray, Leeds) who have advanced methods for measuring viscosity and diffusivity at low moisture contents. Consequently to move forward, new techniques need to be developed. Potential techniques fall into two categories: in-situ techniques where the properties are measured, during a drying experiment or ex-situ techniques where the properties are measured using alternative apparatus.

In-situ techniques

The advantage of these techniques is that the materials are at the conditions of interest, all be it for a typically limited period of time, and the structures formed, and consequently their material properties, are those of relevance to the puffing droplets. Visco-mechanical properties can be potentially estimated by perturbing the system, and measuring its response. This could be via movement, oscillation e.g. in a Newtonian systems the surface tension and viscosity of a droplet can be estimated by oscillating a droplet; inflation using injected gas; or by passive measurement looking at the bubble expansion dynamics during drying or driven via an external heat source. The use of microwaves as an external heat source was evaluated during the first phase of the project, unfortunately it was found to be ineffective at heating droplets. However IR-lasers have potential and have been used in heat transfer studies on droplets

Diffusivity – this can be estimated from drying curves, if boiling does not occur, and it is also most value to the models in the period before boiling..

Ex-situ techniques

These techniques span well established techniques such as rotating rheometers and more complex systems/geometries such the study of emulsion systems. The challenges in these cases are: stopping the material boiling and drying, an establishing the same material phase and structure as would be seen in a dryer.

For materials that remain liquid like for a period under the conditions of interest, 'standard' rheological methods can be used. To prevent drying a closed system will be necessary, and to prevent boiling a pressurized system is required. For more solid like materials DMA methods may be possible, all be it with the same issues as the rheological experiments, but with the additional complexity of how to make the sample of the material to be tested.

More speculative techniques could involve the use of emulsions to stop drying. For example, an emulsion of the solution of interest in a silicone oil, could be made and the droplets allowed to dry slowly overtime via diffusion of water through the oil. The rheological properties of the material could then be evaluated by using a vacuum system and/or heat to drive bubble nucleation and growth.

Microscopy could be used to look at inflation dyanamics and models used to interpret and quantify the droplet characteristics. The applicability of this type of approach is likely to be material dependent.

A Holistic Approach for the Model-based Control of Crystal Size, Shape and Purity in Integrated Batch and Continuous Crystallization-Wet Milling Systems

Zoltan K. Nagy
Purdue University

1. Introduction. Importance of the topic

The prediction and control of crystal size, shape and purity distributions are necessary for product design, quality control and economical operation point of view. The desired crystal size, shape distributions and purity, largely depend on the application (Lovette et al., 2008). For example, needle-shaped (i.e., high-aspect-ratio) crystals are usually undesirable in pharmaceutical and fine chemical applications, due to difficulty in processing (Variankaval et al., 2008), while they are vital in applications such as synthesis of ZnO nanowires for solar cells (Law et al., 2005). Similarly, while generally in the production of active pharmaceutical ingredients (APIs) high purity is required, for certain food or consumer products (e.g. brown sugar) additives, in precisely controlled proportions, are included in the crystals by design. Moreover, some properties of the crystals such as catalytic activity, dissolution rate, hydrophobicity can be specific to certain crystal faces (Snyder et al., 2007) therefore additives can have a complex effect on crystal size, shape and purity.

This project is focused on the application of process systems engineering methods for the investigation of possibility of shape control of high aspect ratio crystals during solution crystallization. Remarkable results have been achieved in the first two years of the project, which will be further developed during the third year. However, given the process engineering knowledge accumulated so far by process simulations and model-based control implementations, it is evident that there is high potential, from both academic and industrial perspective, for designing and operating efficient, simple and high-performance crystallization processes for simultaneous crystal size and shape control.

2. Key achievements in the first two years

The following list of key achievements summarize the scientific output of the first two years of the project:

- Development of a portable, high performance (GPU accelerated) generic 1D and 2D PBM solver for batch and continuous (MSMPR) crystallization processes with primary and secondary nucleation, growth and dissolution mechanisms,
- Development of a fast, deep-neural network powered approximate 1D/2D CSD to CLD and ARD transformation for real time model-based control applications,
- Development of a NMPC algorithm for batch cooling crystallization processes involving CLD and concentration measurements and high accuracy full 1D PBM solution,
- Implementation of the aforementioned control algorithm for L-ascorbic acid, for which the state-of-the-art direct nucleation control (DNC) was not suitable, therefore, more advanced control strategy was required,
- Model development and GPU acceleration for an integrated crystallizer and wet-mill system for crystal size control (1D PBM) and combined crystal size and crystal shape control (2D PBM)
- Optimization based process synthesis for crystal size and combined size and shape control in integrated crystallizer – external wet mill using the afore described accurate models

These achievements have been disseminated in the following publications as measurable deliverables of the first two years of the poject:

(1) Szilágyi, B.; Borsos, Á.; Pal, K.; Nagy, Z. K. Experimental Implementation of a Quality-by-Control (QbC) Framework Using a Mechanistic PBM-Based Nonlinear Model Predictive Control Involving Chord Length Distribution Measurement for the Batch Cooling Crystallization of l-Ascorbic Acid. *Chem. Eng. Sci.* 2018. in press

(2) Szilágyi, B.; Agachi, P. Ş.; Nagy, Z. K. Chord Length Distribution Based Modeling and Adaptive Model Predictive Control of Batch Crystallization Processes Using High Fidelity Full Population Balance Models. *Ind. Eng. Chem. Res.* 2018, 57 (9).

(3) Szilagyi, B.; Nagy, Z. K. Optimization-Based Process Synthesis for Integrated Crystallizer-Wet Mill System for Improved Crystal Shape Control; *Computer Aided Chemical Engineering*, Vol. 43, 681-686, 2018.

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3. Projected results for the third year

Although the presentation of third year research plan is not the main subject of this proposal, a general summary will be given to provide an overall overview of the achievements of the entire three years period of the project and to put the proposed research directions for the project extension into better context. The third year will be focused on the shape manipulation of crystals during crystallization process. Three major objectives will be investigated:

- **2D MPC crystallization simulation**. A feasible, full 2D population balance model (PBM) based nonlinear model predictive control (NMPC) for cooling crystallization process will be developed, which will use experimental data coming from commercially available process analytical technology (PAT) tools, like concentration measurement, chord length distribution (CLD) and image analysis based mean aspect ratio. According to our best knowledge, there is no implementable full 2D PBM based NMPC system reported for crystal size and shape control yet.
- **2D crystallizer-wet mill configuration analysis**. Suring the first three years of the project it has been demonstrated that the integrated batch crystallizer – external wet mill system has high potential in simultaneous crystal size and shape control. The dynamic optimizer revealed an unexpected and interesting mode of operation, which, besides the clear application-oriented advantages, has high scientific value. However, there are numerous practical challenges for experimental implementation of the approach, associated mainly with the operation of pump and transfer lines. Therefore, at this stage it is reasonable to evaluate the relative performance of crystallizer-only, crystallizer with internal (immersion) milling and crystallizer with external mill for different operation modes (i.e. simultaneous size and shape control in seeded and unseeded crystallization).
- **IMED for spherical agglomeration.** Applying the correct kinetic model structure and finding its correct parameters is essential in model-based design. There are numerous, well analyzed methods to separate and investigate the kinetics of primary crystallization mechanisms (nucleation and growth), significantly less research effort was focused on the secondary crystallization mechanisms, such as agglomeration and breakage. Hence, the iterative model based experimental design (IMED) will be applied for a combined crystallization and spherical agglomeration process. In the first step a preliminary optimization will be applied to find the best kinetic model structure based on the available experimental data, then, in the second step, a precise parameter estimation will be carried out by executing additional experiments with maximal information content for minimizing the parameter uncertainty.

Projected publications for the third year:

1. European Symposium on Computer-Aided Process Engineering (ESCAPE) proceeding paper: “Real-time feasible model-based crystal size and shape control of crystallization processes”
2. Journal paper: “Iterative Model Based Experimental Design for Spherical Agglomeration Process”
3. Journal paper: “Model based analysis and optimization of crystallization of high aspect ratio crystal in the presence of immersion wet-milling and external wet-milling on the product particle size and shape”

4. Proposed project extension

In this section, a brief description of the project extension will be given, including the specific aims, list of deliverables and work plan. The “leverage into the PIs existing projects”, “Broader impact” and “Collaboration with IFPRI member sections” form the original proposal are not repeated here.

Specific aims

This project extension aims to develop and provide the first proof-of-concept simulation and experimental demonstration of a full 2D PBM based NMPC approach for batch and continuous crystallization processes integrated with wet milling system, in order to achieve desired crystal size and shape distribution. Additionally, the effects of impurity/additive mixtures on the size, shape and crystal purity distribution will be incorporated in the model and control design to provide a system that is highly relevant to industrial crystallization where the existence of impurities is rather the norm than the exception. To achieve this aim, the ***specific measurable objectives*** of the project are:

1. Extension of the recently developed, novel and highly efficient numerical solution platform for the 1D and 2D PBM using a parallelized discrete high resolution finite volume method (HR-FVM) solved on graphical processing units (GPUs) with fragmentation and agglomeration algorithms to provide a generic tool for high fidelity simulation of crystallization processes in presence of agglomeration and breakage mechanisms as well as basic level simulation of breakage only (e.g. milling) and agglomeration only (e.g. granulation) processes.
2. Develop a first-principle 2D PBM of the integrated continuous crystallization-wet milling system (C-CWM) with multiple MSMPRs and recirculation streams to optimize the MSMPR network structure and find the required recirculation scenario (recirculation configuration and recirculated amount).
3. Evaluate multiple input multiple output (MIMO) systems for advanced real time model-based crystal size and shape control, including the crystallizer+internal/external wet mill and crystallization in presence of impurities/growth rate modifiers.
4. Develop an imaging-based sensor for *in-situ* crystallization monitoring, for real time control applications. Compare the performance of the custom-probe with the standard imaging tools (e.g. Mettler-Toledo’s ParticleView) and a novel tool (BlazeMetrics probe) for model-based crystal size and shape control applications.
5. Kinetic parameter estimation for the crystallization of a model compound in the most promising crystallization platform for crystal size and shape control and implementation of a full 2D PBM based NMPC.

Task 1. Include agglomeration and breakage into the portable, high performance finite volume based PBM solver. The portable 1D and 2D PBM solver, working based on fully-discretized serial and GPU accelerated HR-FVM, was developed for batch and MSMPR systems for primary and secondary nucleation, growth and dissolution. However, the solver does not consider agglomeration and breakage, which is a drawback for numerous industrial crystallization processes. Beyond advanced crystallization simulations, the agglomeration and breakage would also enable to simulate milling and granulation processes. The most typical empirical breakage and agglomeration kernels will be added to the portable solver and a generic PBM tool will be developed, which will be able to simulate all potential crystallization mechanisms and perform parameter identification and process optimization.

Task 2. Process synthesis and intensification of integrated continuous (MSMPR network) and wet mill system for simultaneous crystal size and shape control. The effectiveness of integrated crystallizer-wet mill system for both crystal size and combined crystal size and shape control has been shown, but the potential of wet milling in combination with an MSMPR network has not been exploited yet, even though MSMPR networks are widely used at industrial scale. In this study, the number of MSMPRs to add (up to three) to one wet mill, the position of wet-mill (pre-milling, intermediate milling or post-milling), mean residence times and circulation flowrates in the streams will be designed by optimization.

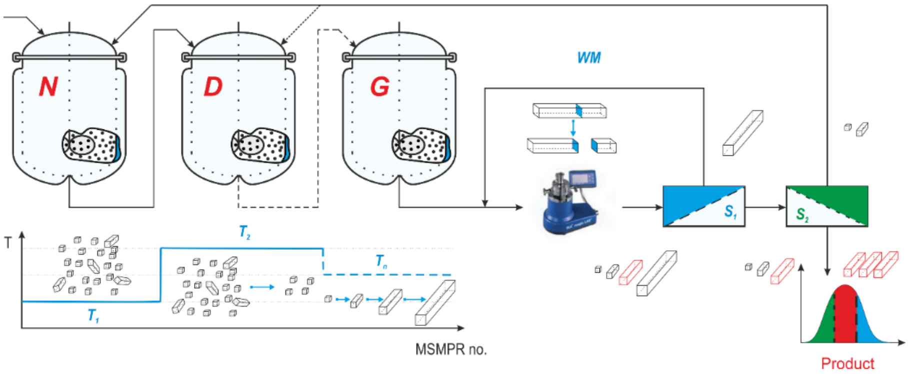

Fig. 1. Integrated continuous (cascade) of crystallization and wet mill system (C-CWM) with fine and course classification units and recycles. Optimizing the operating temperatures in the crystallizers enables to achieve spatially distributed controlled growth and dissolution cycles for improved control of CSD and ARD.

Task 3. Multi-impurity model and its possible application for model-based shape control. The effectiveness of external wet milling systems has been demonstrated by simulation, the powerful impact of growth-rate modifiers (GRM) were not profoundly investigated yet. GRMs with facet-specific effects is a very promising crystal shape modification technique. The practical problem associated with the application of GRMs is that in batch system the GRM concentration can be increased in time, but there is no straightforward solution to decrease it. Therefore, dosing the sufficient amount of growth rate modifier, without overshoot, is essential for effective control, which requires model based techniques for their predictive feature. Here the bottleneck is to capture the effect of growth rate modification well, using the most appropriate kinetic models and apply the required numerical acceleration techniques to make it suitable for real-time control applications.

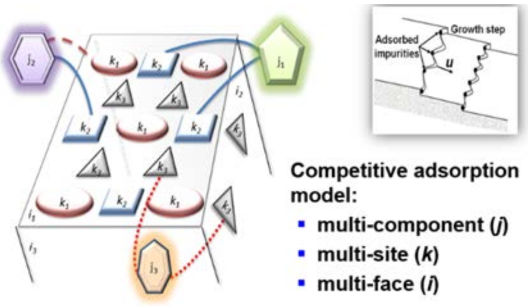

Fig. 2. Schematic representation of the modified crystal growth model using a multi-impurity multi-adsorption model (MIAM).

Task 4. Evaluation of various configurations and development of a model predictive control algorithm for crystal size control in crystallizer/(internal or external)wet mill system. The integrated crystallizer/wet mill system has high potential for crystal size control. The computational time with the current GPU acceleration may enable real-time control, which is required for efficient operation due to the highly uncertain nature of nucleation happening in the wet mill. The moving horizon estimator (MHE) will be tuned to account for the uncertainties (nucleation kinetics, effective breakage rate) and disturbances (temperature, concentration) raised under the milling conditions.

Task 5. Development of a low-cost imaging sensor for on-line crystal size and shape monitoring. The wider acceptance of the developed CSD and ARD control approach will depend on the availability of cost-effective image-based measurement systems, hence the development of a novel in situ stereo video probe, exploiting the recent progress in miniaturization, speed and quality of image processing hardware technologies. Initial proof of concept experiments was carried out in the PI's lab for the development of the dual imaging probe (Fig. 3) and the flexible budget provided by this grant would enable to development of a robust device for broader applications and potential commercialization.

Fig. 3. Schematic representation and preliminary designs of the mono- and stereo-CrystalEyes systems. A1 represents the gap for suspension (suspension flows through the gap in front of the camera lenses), and A2 represents the lens for the backlight (for more homogeneous background on images).

Task 6. Comparison and evaluation of *in-situ* imaging-based tools for on-line control applications. The real time model-based control has numerous application-specific requirements with respect to the measurement systems. The most typical limitations of the imaging probes, that are considered highly performant for system monitoring/off-line system analysis are the lack of real-time, flexible communication, lack of real-time running image analysis algorithm that enable the extraction of relevant particulate information for the NMPC and the high computational need for the image analysis, which overloads the CPU, slowing then down the machine, which is a significant limitation of calculation intensive NMPC algorithm. A control-oriented comparison of three probes, including our custom-designed, low-cost probe (CrystalEyes), the widely used imaging tool (Mettler-Toledo's ParticleView) and a state-of-the-art imaging probe (BlazeMetrics probe), that most recently appeared on the market, will be carried out for model-based crystal size and shape control applications. In addition to providing a recommendation and workflow for the use of imaging based crystallization measurements for 2D PBM model identification and model-based control, this task will also deliver a useful outcome by reporting the results of a detailed comparative investigation of several key imaging systems on the market for real-time quantitative crystallization monitoring and control, which will make the broader adoption of these systems across multiple process industries.

Task 7. Parameter estimation (nucleation, growth/dissolution along the specific axes), using the IMED procedure, for a 2D crystallization system. A critical piece of the NMPC is the process model, that can describe the dynamics of the process variables of interest accurately enough. The parameter estimation of high dimensional PBMs is challenging, because the multidimensional CSD cannot be directly measured with commercial PAT tools, which are typically available in an industrial environment. Subsets of information, such as liquid concentration, mean aspect ratio and FBRM count variation as well as equivalent spherical volume based CSD can be used for the parameter estimation. This, however, often transforms the optimization into an ill-conditioned problem, which requires the two-step IMED based parameter estimation to provide sufficiently accurate kinetic constants for the NMPC.

Task 8. Implementation of a 2D PBM based model predictive control for simultaneous crystal size and shape control. The most promising configuration from the simulation studies of Task 3 and Task 4, using the best shape measurement tool identified in Task 6 will be chosen to implement on a real crystallization system. The implementation is associated with numerous engineering challenges, from the significant effect of plant-model mismatch (PMM), through the uncertain and noisy nature of real time size and shape measurement to high computational power requirement to achieve real-time feasibility. These are the mean reasons why, to our best knowledge, there is no such an industrially relevant NMPC system implemented yet. We propose to develop the first such proof-of-concept experimental implementation of such a comprehensive advanced control approach.

Work plan

Detailed work plan and milestones are proposed in Table 1 and Table 2.

Table 1: Work Plan

Task	**Activity**	**Years 1-3 (4-6 in overall)**					
		6	**12**	**18**	**24**	**30**	**36**
1	Add agglomeration and breakage models into the high performance, portable 1D and 2D PBM solvers	▨					
2	Process synthesis of integrated continuous (MSMPR cascade) and wet mill system for simultaneous crystal size and shape control.	▨	▨				
3	Multi-impurity model and it's possible application for model-based shape control			▨	▨		
4	Evaluation of various configurations and development of a model predictive control algorithm for crystal size control in crystallizer/(internal/external)wet mill system.			▨	▨		
5	Development of a low-cost imaging sensor for on-line crystal size and shape monitoring	▨	▨	▨	▨		
6	Comparison and evaluation of *in-situ* imaging-based tools for on-line control applications.			▨	▨	▨	

7	Parameter estimation of the crystallization of a model-compound for simultaneous crystal size and shape control				▨	▨	
8	Implementation of a 2D PBM based model predictive control for simultaneous crystal size and shape control						▨

Table 2. Main milestones of the project

Month	Milestones
6	**(1)** Agglomeration and breakage functions in the portable PBM solver
12	**(2)** Process synthesis of integrated continuous (MSMPR cascade) and wet mill system for simultaneous crystal size and shape control.
24	**(3)** Multi-impurity model and it’s possible application for model-based shape control **(4)** Evaluation of various configurations and development of a model predictive control algorithm for crystal size control in crystallizer/(internal/external)wet mill system. **(5)** Development of a low-cost imaging sensor for on-line crystal size and shape monitoring
30	**(6)** Comparison and evaluation of *in-situ* imaging-based tools for on-line control applications. **(7)** Parameter estimation of the crystallization of a model-compound for simultaneous crystal size and shape control
36	**(8)** Implementation of a 2D PBM based model predictive control for simultaneous crystal size and shape control

Main deliverables:

- A high performance, GPU accelerated portable 1D and 2D PBM solver extended with agglomeration and breakage.
- An optimized MSMPR/wet mill network for crystal size and shape control.
- Model based comparison of crystallizer with internal and external mill and crystallization in the presence of growth rate modifiers for real time model-based crystal shape control.
- Image analysis-based parameter estimation of multidimensional crystallization kinetics for a model-system.
- Implementation of a full 2D PBM based NMPC for crystal size and shape control.
- High quality journal and conference publications.

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Grinding Aid Additives for Dry Fine Grinding Processes

Review Article

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It is well known that attractive particle-particle interactions become more decisive with decreasing particle size. Especially in dry fine grinding processes, where small particles are produced within a dry environment by different types of mechanical stress, these forces lead to a variety of challenges, such as a complicated control of the powder behavior, a decrease of grinding efficiencies and production rates as well as obtaining high product finenesses. In order to control these forces, chemical liquid or solid additives – so called grinding aids – are added to the process in many industrial dry fine grinding applications. Even though the benefits of grinding aids have already been shown in various experimental studies and industrial applications, their selection and application is still mostly based on empirical knowledge. As shown in this review article, the variety of applied substances, ground materials and target finenesses, but also available mill types, process designs, mill and process parameters as well as analysis methods complicate the development of a comprehensive understanding. Within this article, we present the basic mechanisms of action of various liquid, gaseous and solid grinding aids. Subsequently, it is shown how grinding aid molecules interact with the solid particle surface, leading to decisive changes of the particle and bulk behavior. Based on various scientific studies it is shown, how this may affect the micro- and macro-processes inside the mill as well as the whole grinding plant operation. Finally, the current gaps of understanding are identified and critically discussed with a special regard towards a more efficient selection and application of grinding aid additives for future dry fine grinding processes.

1. Introduction

The history of grinding aids in dry grinding processes starts in the late 1930s with the application of the first commercial grinding aids in the cement industry [1]. Since that time, the importance of grinding aids in industrial dry fine grinding processes has strongly increased; so did the number of scientific papers dealing with this topic. Nowadays, grinding aids are widely established in the cement industry, but also in other industrial sectors such as in the field of ceramics or filler materials. The main objectives of a grinding aid application are either: a) increasing the production capacity, b) decreasing the specific energy consumption to achieve a certain product quality, c) achieving finer particles or d) improving the product quality in terms of enabling the use of lower-quality feed materials [2]. However, even though more than 100 scientific papers on that topic can already be found in the literature and a variety of grinding aids are currently applied in industrial processes, a comprehensive understanding of grinding aids is still missing. Despite the fact that their basic mechanisms of action are known nowadays, the application of grinding aids is still mainly based on empirical knowledge. Especially a time efficient grinding aid selection is still almost impossible, as several aspects come together making the derivation of the appropriate selection criteria very complex. Therefore, this review gives a comprehensive overview on the state-of-the-art technology and methods regarding grinding aids in dry grinding processes. The mechanisms of action for liquid but also gaseous and solid grinding aids are presented; dissolved chemicals, which are often used as a surface active compound in commercial liquid grinding aid blends, are hereinafter assigned to the group of liquid grinding aid additives. Furthermore, it is shown how these additives may influence the particle and bulk behavior in the case of different products. Subsequently, a variety of studies dealing with grinding aids in grinding processes are reviewed. The article distinguishes between different ground materials, fine and ultrafine grinding, a number of mill types as well as batch and continuous operated grinding processes. Also, an overview of the variety of substances as well as their impact on the grinding result is given. In addition to that, findings from industrial processes are evaluated. Simultaneously, the above-mentioned lack of understanding is discussed critically.

2. Mechanism of action

2.1. Liquid grinding aids

As mentioned above, the history of grinding aids in dry grinding processes starts in the late 1930s with the application of the first commercial grinding aid in the cement industry [1]. At the same time, the first studies concerning grinding aids in dry grinding processes appeared in the literature [3, 4]. In a first instance, it was assumed that grinding aids may act by bringing static charges of the same sign to the surface of the product particles [3]. However, this idea was soon abandoned again for various reasons, such as the fact that also non-ionic grinding aids cause very good grinding results. Already prior to these studies, Rehbinder [5] as well as Rehbinder and Kalinkovaskaya [6] created the basis for a later and more lasting, but also controversial theory. In fact, they investigated the impact of the adsorption of surface active substances on the mechanical properties of solid particles. By using sclerometer tests they showed that adsorbed surfactants reduce the surface hardness of different materials. They concluded that an adsorption-induced lowering of the particles surface energy reduces the fracture resistance of the solid matter. Also, they categorized these substances into two groups, namely (A) dissolved inorganic salts and (B) organic molecules with polar groups. Within the following decades, a variety of studies dealt with the investigation of the impacts of surface active substances on the mechanical properties (such as fracture, compressive and tensile strength) of particles and rocks. A detailed review of these papers was already presented by El-Shall and Somasundaran [7]. In the year 1958, Rose and Sullivan [8] were the first to extend the findings of Rehbinder to grinding processes in tumbling ball mills in order to explain the mode of action of grinding aid molecules in technical mills; making the “Rehbinder effect” also very popular in the field of grinding.

Simultaneously, a growing number of authors started to question the relevance of the Rehbinder effect for dry grinding processes, as they presented studies that revealed further aspects. For instance, Kennedy and Mark [9] observed an increase of dust formation when applying grinding aids, which was one of the first indicators regarding the fact that grinding aid effects are connected to a better particle dispersion. Furthermore, the reduction of ball-coatings by those additives was monitored, leading to a controversial discussion as to whether this may be the primary grinding aid mechanism [10]. In 1961, Mardulier [11] showed that polar additives are more effective than nonpolar molecules. He explained this finding by attributing higher affinities of the polar groups within the grinding aid molecule to the high energy sites on the surface of those particle which possess unbalanced valence force. In contrast to Rehbinder, he connected the reduction of surface energy by grinding aid molecules to a decrease of the inter-particle adhesion forces; instead of to a change of the fracture behavior. Also, he considered ball coatings as an extreme case of agglomeration. Thus, the prevention of ball coatings indeed contributes to the grinding aid mechanisms especially at high finenesses, but it is not considered as the major effect. Moreover, influences of grinding aids on the material recirculation in closed circuit grinding plants were shown by this author, indicating further impacts of these additives on the flow behavior of the material. At the end of the 1960s, von Seebach [12] showed that adhesion forces between cement particles can be reduced significantly by exposing the particles to vapors of liquid chemicals, namely ethylene glycol (see Figure 1). His work confirmed that grinding aids primarily act by reducing the adhesion forces between the particles. During the same period, Westwood [13-15] as well as Westwood and Goldheim [16] found that surfactants only reduce the particle strength, if the plastic deformation is important for the particle fracture. They thereby presented a further indirect disproof for the validity of the Rehbinder effect in dry grinding processes, because mostly brittle fractures are important for the technical grinding of inorganic materials in tumbling ball mills. Following, they introduced a completely new idea on grinding aid mechanisms. They suggested that the adsorption of grinding aid molecules leads to a hindered motion of the dislocations near the particle surface, thus, decreasing the plasticity of the material. The authors highlighted this effect as the main grinding aid mechanism, because this would lead to a more brittle character of the material. From the beginning on, this theory was doubted though since plastic material behavior would be required to explain this effect, which is actually not the case for most of the grinding processes in tumbling mills.

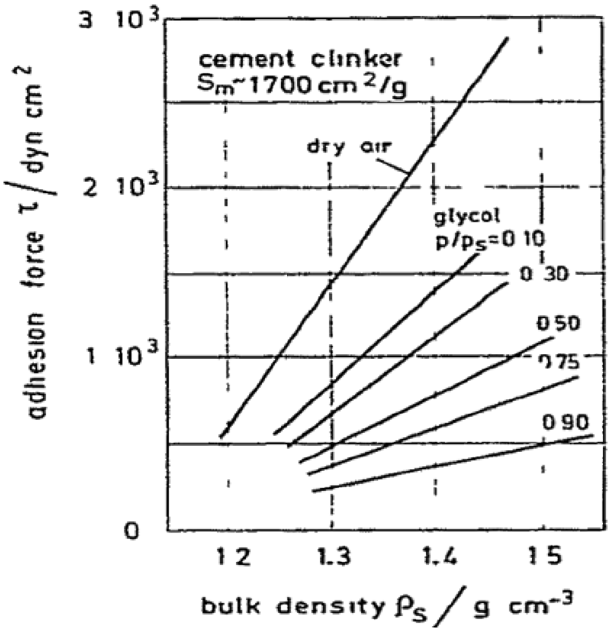

Figure 1: Impact of ethylene glycol vapors on the adhesion force of cement clinker particles [12].

In the 1970s, the relevance of both the Rehbinder as well as the Westwood effect for dry grinding applications was finally disproved. It started with the measurements of crack propagation velocities, as it was done by Schönert [17]. Even though Schönert actually did not focus on the investigation of grinding aids, he also lastingly changed the understanding of the particle breakage in the field of additive application. Studies like this indicated that the crack propagation velocities while particle stressing in technical mills are substantially greater compared to the spreading velocities of additive molecules over the particle surface. Thus, any surface active molecules are not able to follow the crack propagation fast enough in order to maintain those mechanisms proposed by Rehbinder and Westwood. Locher and von Seebach [18] directly showed that vapours of (liquid) chemicals do not improve the actual breakage event for brittle fractures. They also showed that grinding aids promote comminution by abrasion as the molecules prevent the (re)agglomeration of the fine abraded particles. Further detailed statements against the relevance of both effects, Rehbinder or Westwood, were also given by Somasundaran and Lin [19] and Ocepek and Eberl. [20]. Graichen et al. [21] as well as Graichen and Müller [22] showed experimentally that no impact on the breakage probability is seen when stressing single particles which were pre-treated with different chemicals. They also illustrated that this finding is valid for both compression and impact stressing. After those studies, it was widely accepted that grinding aids act by reducing the adhesive forces between the particles, and thus, by changing the agglomeration behavior of the powder as well as improving its state of dispersion and flow behavior [23]. Schubert [24] concluded, that thereby the micro-processes of the stressing events inside the mill are improved, leading to a decrease of energy losses especially for those mills in which particles are stressed as particle beds. Also, he attributed an improvement of the transport behavior in grinding plants as well as the prevention of material coatings on the milling equipment to the reduction of the particle-particle interactions.

In the middle of the 20th century, also the aspect of "stress corrosion cracking" was discussed to be responsible for the observed grinding aid effects [25]. This phenomenon describes the growth of crack formation along grain boundaries for certain kinds of materials which are exposed to tensile stresses within a corrosive environment. Several authors showed that especially materials such as stainless steel, aluminum or magnesium alloys and brasses are sensitive towards stress corrosion cracking when being placed in certain chemical environments (e.g. saturated vapors of ammonia or corrosive aqueous solution) [26]. However, whether this phenomenon is responsible for grinding aid effects in industrial dry grinding operations has not been clarified yet. Most likely, it can be neglected due to the same points that were made for disproving the relevance of the Rehbinder effect.

In the 1970s and 80s, a great number of authors dealt with the investigation of grinding aid impacts on dry grinding processes. Among the literature especially the works by Scheibe et al. [27] as well as Dombrowe et al. [2, 23, 28, 29] deserve to be highlighted. They performed several systematic investigations of various grinding aids within industrial grinding processes, but also regarding the basic grinding aid mechanisms. For instance, Dombrowe et al. [23] investigated the impact of grinding aids on the grinding limit of clinker grinding in laboratory ball milling. They showed that agglomeration and product adhesion are significantly reduced by grinding aids especially in the range of very fine particles in the lower micron range, leading to a shifting of the grinding limit towards higher product fineness. They also attributed these effects to the material transport inside the mill, which is strongly affected by the fine particle fraction (0 – 5 µm), and can thus be increased by grinding aids. Moreover, they showed that grinding aids are not only efficient in the lower micron range, but already increase the size reduction rate at the beginning of the grinding process. However, coarse grinding of clinker was found to be independent of the addition of grinding aids [28].

Several years later, Mishra et al. [30] as well as Weibel et al. [31] found by means of molecular simulations that the agglomeration energy between cement particles is strongly reduced by adsorbed grinding aid molecules. Thus, this finding indirectly confirmed that the surface energy of particles is in fact reduced by the adsorption of surface active compounds.

The authors also verified, that the polar parts of the additive molecule adsorb on the particle surface while the non-polar compounds further shield the particles (see Figure 2). The corresponding adsorption mechanisms are specifically discussed in a later chapter.

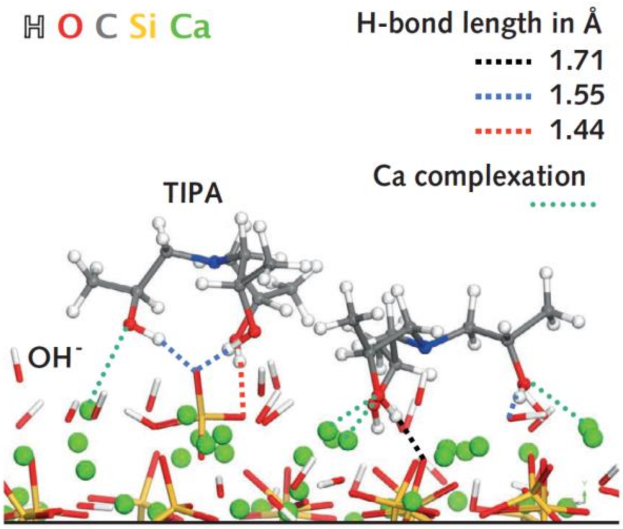

Figure 2: Adsorption mechanism of triispropanolamine molecules on a clinker particle surface, determined by molecular simulation [31].

The final experimental evidence, proving that liquid grinding aids truly decrease the surface energy of the product particles, was recently presented by Prziwara et al. [32] by means of inverse gas chromatography measurements. On the one hand, they showed that the reduction of the surface energy of ground limestone particles depends on both the kind and the concentration of the applied grinding aid. On the other hand, they confirmed the relation of surface energy and adhesion forces by presenting a very good correlation between the surface energy values and different powder properties like the agglomerate sizes as well as the powder flowability (see Figure 3).

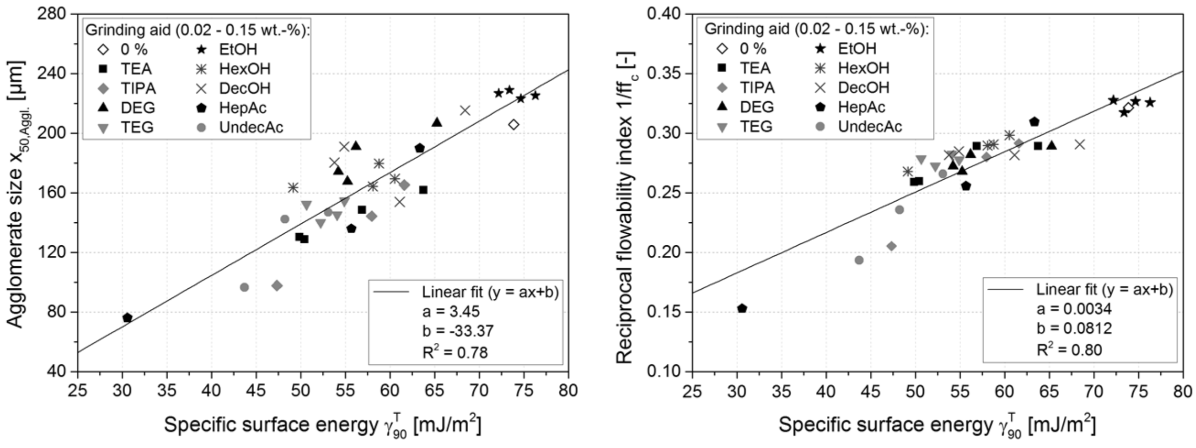

Figure 3: Relation of specific surface energy of the particles (measured by inverse gas chromatography) and agglomerate size (left, optical image analysis) as well as powder flowability (right, ring shear tester) for different grinding aids and additive concentrations [32].

2.2 Gaseous grinding aids

The mechanisms discussed above are in particular valid for all liquid as well as dissolved grinding aids. In both cases, the surface active compounds are present in the form of separated and freely movable molecules which are able to form adsorption layers on the product particles, and thus, decrease the adhesive forces between the particles. Generally, it can be assumed that similar mechanisms determine the grinding aid performance also for gaseous additives or vapors of liquid chemicals. For instance, the aforementioned study by von Seebach [12] clearly showed that also the adsorption of gaseous surface active compounds onto the particle’s surface leads to a decrease of the adhesion forces between the product particles. In general, these effects can only be obtained as long as a sufficient number of molecules finally adsorb onto the particle surface, which is not necessarily the case for highly volatile gaseous compounds. Furthermore, the adsorbed grinding aid molecules are in equilibrium with their surrounding gas phase, meaning that adsorption capability also depends on ambient conditions like temperature and vapor pressure. For example, Buczek et al. [33] placed coal in an atmosphere of saturated surface active vapors for more than 24 h prior to grinding. Due to a sufficient adsorption under these conditions, they were subsequently able to show that even very volatile compounds like methanol and acetone but also ammonia and chloroform can act as grinding aids when dry grinding the coal. However, most of the industrial dry grinding processes are performed in open systems or even in air supported grinding plants, where high concentrations of additive molecules in the gas phase are hard to maintain. Also, high milling temperature (e.g. 80-120 °C for cement grinding) may impair the adsorption mechanism [31]. Thus, even conventional liquid grinding aids do partly desorb from the particle surface and are subsequently removed from the system with the mill air: For instance, Rechenberg [34] detected 2-13 % of the total additive amount in the exhaust air, while the higher values were measured in the case of higher product surface related grinding aid concentrations. The fact that high additive amounts inside the exhaust air are occurring especially at high applied concentrations may be the reason why Dombrowe et al. [23] only detected smaller amounts of approx. 2 % inside the exhaust air within their studies. These studies clearly show that the use of gaseous substances is principally possible, but often not applicable as the main part of the grinding aid amount is exhausted from the process without having brought its stabilizing effect. This may also be the reason why exclusive studies on gaseous grinding aids are hard to find in the literature.

2.3 Dry particulate grinding aids

A reliable description of the mode of action of dry grinding aids is more complicated compared to liquid (or gaseous) additives, since only a low number of corresponding studies are available in the literature. The situation is aggravated by the fact that different types of dry grinding aids may follow different mechanisms. Thereby, it needs to be distinguished between certain substances:

- Dry organic compounds with melting points slightly above room temperature, such as medium-chained alcohol amines and carboxylic acids
- Dry (mainly inorganic) particulate grinding aids having significantly higher melting points, such as inorganic salts
- Colloidal sub-micron particles

Chemicals with melting points slightly above room temperature do probably follow the same mechanisms as liquid and gaseous additives since the mill temperatures and especially short-term temperature peaks are often significantly higher. In combination with the aforementioned aspect, the intense stress and mixing inside the mill may help to break the initial particulate structure of the grinding aid and to spread the molecules within the particle bulk, respectively. Despite the initially restricted mobility of the molecules, the formation of adsorption layers similar to a liquid/gaseous additive may therefore be possible. The most famous of such compounds is stearic acid, which was shown to cause beneficial effects in dry grinding processes of both inorganic (e.g. cement [35], aluminum [36] or brass powder [37]) and organic products (e.g. chitosan [38]). Another important representative is triisopropanolamine, which is solid at room temperature but often leads to similar effects as liquid alcohol amines such as triethanolamine (see Figure 4). Such solid chemicals are often added in dissolved form, which further helps to dose the additive to the process and distribute the single molecules within industrial mills.

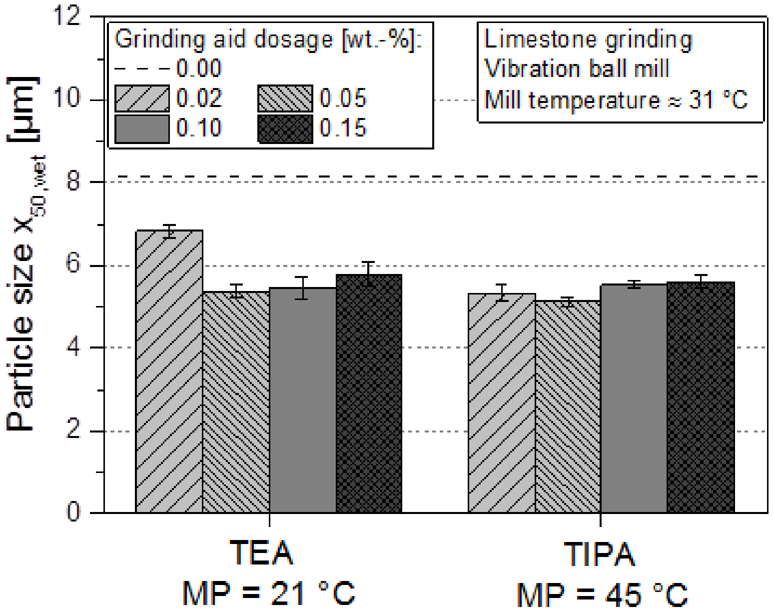

Figure 4: Grinding aid effects of Triethanolamine (TEA, melting point below room temperature) and Triisopropanolamine (TIPA, melting point above room temperature) for dry fine grinding of limestone (values taken from [32]).

In contrast to that, the mode of action of those dry particulate grinding aids, which have significantly higher melting points (e.g. salts), may be completely different. Unfortunately, a comprehensive understanding of these additives is missing, as only a few studies deal with this topic. For instance, Pollmanns et al. [39] and Pollmanns [40] investigated the impact of high concentrations (20 wt.-%) of sodium chloride on the ultrafine (submicron) grinding of various inorganic materials (see Figure 5). They found that this additive leads to a strong increase of the product fineness for zinc oxide and zirconia, while it only causes medium and negligible effects for alumina and calcite, respectively. Thereupon, the authors assumed that the salt ions are incorporated into the solid surface, whereby free valence electrons are saturated, and thus, the tendency of agglomeration is reduced. However, they were not able to present evidences for this thesis. Similar effects were achieved by Ikizaki et al. when adding large quantities (≥ 8 wt.-%) of solid nitrates to dry ultra-fine grinding of either soda glass [41] or sericite [42]. The authors confirmed an exchange of potassium ions from the sericite with ions from the nitrate salts using XRD measurements. Therefore, they rather called this process chemically assisted dry comminution (CADC) instead of applying grinding aids. They also showed that the wet measured particle size and the BET surface of the product particles showed inconsistent trends [41]. This outcome indicates that particle agglomeration still plays a decisive role despite the application of this kind of additives.

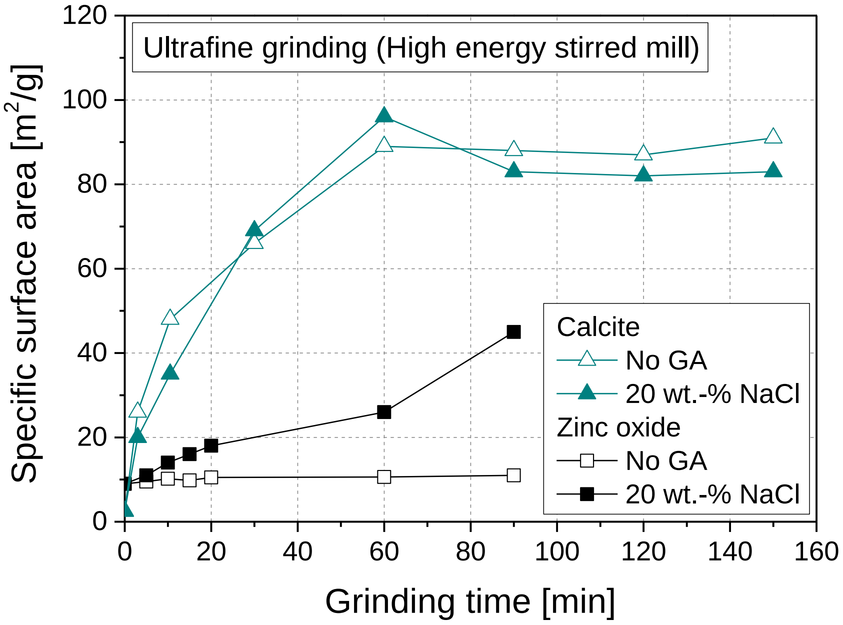

Figure 5: Impact of sodium chloride on dry ultrafine grinding of calcite and zinc oxide (values taken from [39]).

Generally, a different mode of action can be assumed for additives consisting of colloidal sub-micron particles. Here, the mechanisms may be similar to those ones of solid flow additives, which are widely used in many industries in order to control the mechanical properties [44] as well as the flow behavior [45] of fine cohesive powders. These flow additives – mostly ultrafine (guest) particles – are added to the process in order to adhere to the product (host) particles. Thereby, the guest particles act as spacers between the hosts particles, leading to an increased distance between the host particles, and thus, to a reduction of the attractive forces. Consequently, values like agglomeration, powder flowability and further bulk properties are directly affected by these additives. It can therefore be assumed, that solid flow additives – when added in appropriate concentrations – may lead to comparable effects like conventional liquid grinding aids.

Sweitzer and Craig [43] showed that colloidal carbon black increases the fineness of dry ground cement clinker, whereby a maximum increase of 49 % was found for an additive concentration of 1.28 wt.-% (see Figure 6). Also, they observed a sufficient reduction of the ball coating with the addition of carbon black.

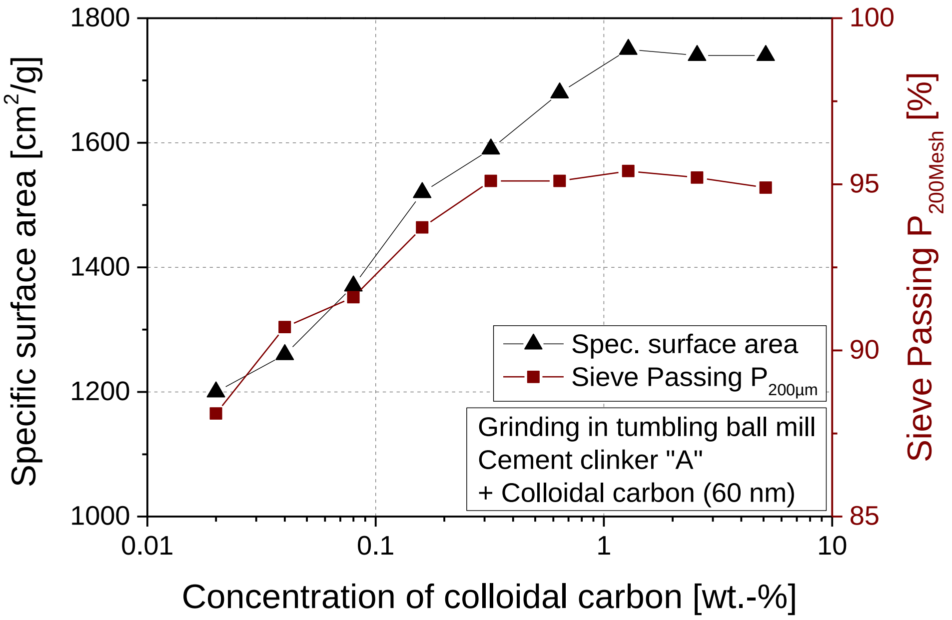

Figure 6: Specific surface area and sieve passing of ground cement clinker for different amounts of colloidal carbon black as a grinding aid additive (values taken from [43]).

In order to control the product behavior, a further special case can be found in the field of “co-milling” where particulate additives are applied to dry grinding processes. Co-milling basically describes the addition of solid additives to dry grinding processes in order to enable micronization and a simultaneous dry coating of the product particles. Nowadays, most of these applications can be found in the pharmaceutical industry where such additives are mainly added in order to decrease the cohesiveness of fine pharmaceutically active ingredients (APIs). Thus, the purpose of co-milling is rather to control the product behavior for subsequent process steps than to improve the grinding process. However, similar mode of actions as discussed above may lead to a reduction of the adhesive forces of the product particles. For example, Mullarney et al. [46] used different types of sub-micron silicon dioxide particles as additives for dry fine grinding of various active pharmaceutical components (APIs) in a “comil”. They showed that this kind of co-milling strategy is very effective in terms of a simultaneous dispersion of the nanoparticles as well as their dry coating onto the host particles, leading to an improved flow behavior of the APIs. Similar results were presented for co-milling of KCl particles in a continuous fluid energy mill using silica, alumina and titania nanoparticles as coating material [47]. Vogt et al. [48] presented that the co-milling of various poorly soluble drugs in a jet by using different excipients also leads to positive effects regarding the drug dissolution behavior. In other studies, Ibuprofen was successfully dry-coated in a fluid energy mill with both amorphous hydrophilic silica particles as well as water-soluble polymers as coating components [49, 50]. Here, it was also proven that dry coating does not only improve the flow and bulk properties of the ground drug particles, but also their later dissolution behavior. Han et al. [51] further showed that dry coating with nanosilica by co-milling leads to a reduced cohesion and improved flowability of the guest particles not only by creating nanoscale surface roughness, but also by passivating high-energy surface sites, and thus, reducing the surface energy of the milled material. Wang et al. [52] showed that excessive amounts of wax as coating material may also lead to negative effects on the particle size and the dissolution behavior of co-milled ascorbic acid particles. Even though no conclusions can be derived regarding the impact of those nanoparticles on the grinding process, accompanying and maybe less regarded effects on the grinding step are also possible. Thus, these studies may indicate further potentials especially regarding the optimization of dry fine grinding processes within the pharmaceutical industry.

2.4 Dispersion and adsorption of grinding aids

In industrial processes, grinding aids are commonly added to the material by dropping the chemical either onto the feed conveyor belt or directly into the milling chamber [53]. Scheibe et al. demonstrated that different addition strategies such as dropping, injecting or vaporizing have no significant impact on the grinding aid performance in tumbling ball mills, mainly because of the good mixing effect within this mill type. Weibel et al. [31] reported that the dispersion of the grinding aid within the product happens in particular via a) gas phase transfer and/or b) surface contact transfer. They affirmed this assumption with different observations: On the one hand, they found that the dry grinding of cement was significantly increased using various alcohols with boiling points below grinding temperature. At the same time, the authors noticed the characteristic odour of the alcohols coming from the cold cement, which indicates a high volatility of the chemicals as well as a weak adsorption. However, since the additives still increased the grinding performance significantly, they assumed that the grinding aid is distributed partially via the gas phase. On the other hand, the authors successfully applied polycarboxylate ether (PCE) as a grinding aid, which only evaporate under irreversible decomposition. This occurence is therefore a strong indicator for a surface contact transfer of the polymer. The authors concluded that conventional grinding aids such as glycols and alcohol amines have low but sufficiently high vapor pressures, so that their dispersion probably happens via both mechanisms. It can further be assumed, that chemicals having a lower boiling point are distributed via the gas phase to a higher extent than high-boiling compounds. However, the ratio of the gas phase and the surface contact transfer is difficult to characterize, not at least because of the overlapping impacts of the mill and the grinding conditions [31].

Different information can be found in literature regarding the optimum point of time of the additive addition. As mentioned above, Scheibe et al. [28] reported that positive grinding aid effects were not seen for coarse grinding processes. At the same time, they did not detect any negative effects when already adding the additive to the coarse grinding chamber either. In contrast to that, Nair and Paramasivam [54] found a slight increase of fines for the delayed adding of calcium stearate to ball milling of limestone. Hasegawa et al. [55] also achieved better results for a step-wise addition of the grinding aid during the ultrafine grinding limestone in a vibration rod mill. The inconsistencies of these studies may be explained by a study of Prziwara et al. [56] on the impacts of grinding aids on the dry stirred milling of limestone: The authors found that the strategy of adding the grinding aid only influences the grinding result, if an early (or delayed) addition of chemicals influences the flow behavior of the product in such a way, that the micro-processes inside the mill, and thus, the grinding conditions are changed. A detailed discussion of the impact of the additive on the stress behavior inside the mill is given in a later chapter.

Furthermore, Weibel et al. [31] discussed the impact of the surface energy of the solid as well as the surface tension of the grinding aid on the wetting and spreading behavior of the chemical on the solid surface. They stated that liquids with a low surface tension easily spread out on solid surfaces of high surface energy, as it is normally the case for grinding aids in combination with inorganic particles such as cement clinker. At the same time, the grinding aid molecules need to be adsorbed on the solid surface sufficiently, which is reflected by a low interfacial energy between additive and solid surface. Thus, chemicals with a low surface tension do not necessarily lead to the best performance. For instance, non-polar liquids spread out rapidly on polar surfaces due to their low surface tension. However, they are not applicable as grinding aids, because they do not adsorb adequately in order to form a stable adsorption layer on the solid surface.

Dombrowe et al. [2] had a closer look into the optimum grinding aid concentration range. They characterized the coverage of cement particles with different primary alcohols by means of adsorption/desorption experiments. Thereby, they found that the amount of molecules within a monomolecular adsorption layer is rather a function of the number of hydroxyl groups than of the molar mass of the additive, indicating that grinding aid molecules adsorb onto the particle surface with their polar parts. Moreover, the authors showed that the adsorption energy is not an exclusive measure for the grinding aid performance.

By means of molecular simulations, Mishra et al. [30] showed that grinding aids like triisopropanolamine (TIPA), triethanolamine (TEA), N-methyl-diisopropanolamine (MDIPA) and glycerin orientate to a polar surface with the polar parts of the molecule, while the non-polar rest shields the particle. They found that adsorption onto cement surfaces happens by coordination of Ca^{2+} ions, hydrogen bonds as well as other polar interactions. Thereby, they determined higher adsorption energies on dry, non-hydroxylated surfaces. However, they further assumed that the adsorption of grinding aid molecules does not happen on freshly cleaved surfaces, since those surfaces can be assumed to relax immediately after breakage. The adsorption energy turned out to rather depend on molecule-solid interactions than on the volatility of the grinding aids. Thereby, they found the adsorption strength follows the order glycerin > MDIPA > TEA ≈ TIPA. In contrast to that, the reduction of the agglomeration energy, which was computed from the simulation results, turned out to follow MDIPA > TIPA > TEA > glycerin. On the one hand, the authors concluded that the adsorption strength is an important parameter regarding the formation of a stable adsorption layer. On the other hand, they stated that the agglomeration energy actually correlates with the experimental grinding efficiency rather than the adsorption energy. They also assumed that the binding geometry including the thickness of the adsorption layer leads to the better results obtained by the amines compared to glycerin. In agreement with that, Prziwara et al. [32] found that the surface energy of the limestone particles, which correlates with their tendency to agglomerate, is also reduced stronger by applying alcohol amines compared to glycols. Possible impacts of the molecular structure of the grinding aid are discussed in chapter 3.2.

2.5 Impact of grinding aids on particle and bulk properties

As described above, the reduction of the surface energy by grinding aids was recently proven experimentally by Prziwara et al. [32]. It was shown that the surface energy of limestone particles decreases with an increasing amount of grinding aid, as a more complete adsorption layer on the particles is achieved with sufficiently high grinding aid concentrations. Generally, the strongest reduction of > 50 % was achieved by carboxylic acids followed by alcohol amines, poly alcohols and mono alcohols. Simultaneously, both the cohesiveness of the powder as well as the state of agglomeration decreased with the reduction of surface energy. The authors attributed this to the relation of surface energy and adhesion forces between the particles. The first studies aiming to characterize the impact of surface active compounds on the adhesion forces between the particles were already presented much earlier [12, 29]. A further important study was presented by Spindler et al. [57] who measured the adhesion forces between limestone particles by an ultra-centrifuge method as a function of the amount of added hexanoic acid as a surface active compound (see Figure 7). On the one hand, they showed that the adhesion forces are reduced with a certain amount of hexanoic acid, leading to an optimum concentration at which minimum forces are obtained. The adhesion forces were shown to increase again above this concentration. On the other hand, they presented a very good correlation between adhesion forces and the powder flowability, which in turn reached maximum values in the range of low adhesion forces. They showed that the adhesion force, and thus, the grinding aid have a significant impact on the bulk behavior of the powder. In general, minimum adhesion forces are assumed to be achieved in the range of a mono-molecular adsorption layer which leads to best stabilization effect. At higher concentrations, excessive amounts of molecules cause capillary effects which again lead to an increase of the adhesion forces [31].

As the powder flowability is easier to measure than the adhesive forces between the particles, various authors have examined the impact of grinding aids on the flow properties of the ground material. Furthermore, the investigation of the powder flowability is of higher application-oriented importance, because the knowledge of this property helps to understand the impact of grinding aids on flow and transport processes inside the mill on both micro as well as macro levels. The relation of grinding aid, powder flowability and milling process is discussed separately in chapter 3.3.

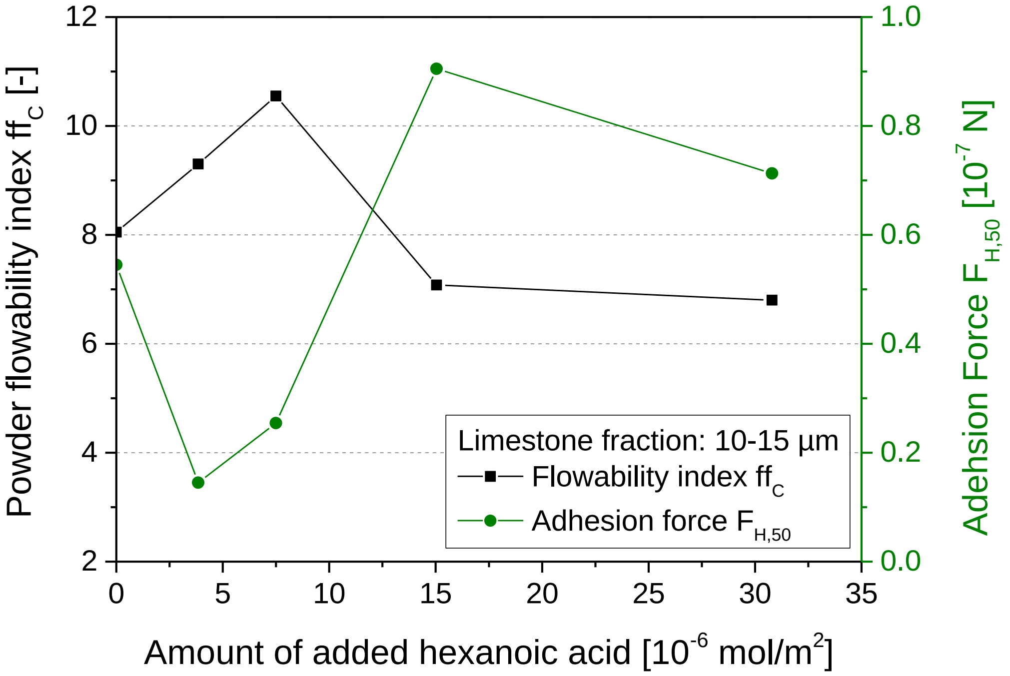

Figure 7: Impact of the amount of hexanoic acid on a) the powder flowability index ff_C of limestone particles and b) the corresponding adhesion forces between the single particles (data taken from [57]).

Unfortunately, there is still a very limited understanding to how far the powder flowability of a certain product is influenced by different types of grinding aids as well as grinding aid concentrations. The lack of comprehension may especially be caused by the complexity of overlapping parameters: Besides the chemical structure of the additive as well as the actual (and usually unknown) surface coverage, the flowability is also determined by a variety of partly unknown particle properties (e.g. particle size distribution, particle shape, particle roughness, moisture content or chemical surface properties). Also, the variety of used testing methods, like ring shear tests (e.g. [32, 56, 58]), Imse flowability tests (e.g. [23, 59]), Jenike shear tests (e.g. [54]), simple measurements of the static angle of repose (e.g. [60-62]) and recently also powder rheometry (e.g. [50]), make the development of universal rules even more difficult. Some of these studies indicate that a larger non-polar part within the grinding aid molecule may support positive effects on the powder flowability [23], possibly due to steric stabilization effects. However, molecules with a high fraction of non-polar to polar parts may require significantly higher concentrations: Larger non-polar parts reduce the density of anchor groups within the molecule, which is why a higher number of molecules is required to saturate the solid surface [32]. Other studies indicate, that carboxylate acids often lead to a stronger increase of the flowability especially for inorganic minerals (e.g. [32]). Recently, it was also shown that polymer-based grinding aids such as polycarboxylate ethers are very effective regarding the flowability enhancement, especially of cement powders [60]. Nevertheless, the specific interactions between the solid surface and the additive molecules may cause deviations from these trends.

Furthermore, grinding aids may cause further effects on other bulk properties like the compaction behavior [63, 64] or bulk density [63], which may also be relevant to optimize grinding operations. Unfortunately, only limited information on these aspects can be found in the literature.

3. Grinding aids in batch-wise grinding processes

3.1. Grinding results from laboratory investigations

Nowadays, grinding aids are mainly established in continuously operated industrial grinding processes. However, as laboratory mills are often seen as the more convenient tool for an efficient grinding aid screening, most of the present studies were carried out in batch-wise operated grinding devices on laboratory scale. Thereby, a variety of different mill types have been used so far. The majority of the investigations were done in mills containing loose grinding media such as tumbling ball mills, vibration ball and rod mills, stirred media mills, planetary balls mills or even more exotic devices like box mills. Batch-wise laboratory studies using mills based on differing stress mechanisms like high pressure grinding or (single particle) impact stressing are very rare.

Table 2 in the appendix summarizes a variety of chemicals that have successfully been tested as grinding aids in batch-wise operated laboratory mills. It is distinguished between the physical state (liquid/dissolved and solid) and the kind of grinding aid, the ground material as well as the used mill type. Also, results from studies dealing with ultrafine (uf) grinding into the sub-micron particle size range are specifically marked. In order to give an impression of the grinding aid performance, the relative increase of the product fineness ϕ_{GA} which was achieved by applying grinding aid application is calculated based on data from the present studies. The calculated values are listed together with the corresponding grinding aid concentration. The relative fineness increase ϕ_{GA} is defined as the ratio of the specific product surface area $S_{m,GA}$, that was achieved using a grinding aid, and the specific surface area $S_{m,ref}$ obtained from the reference comminution without any grinding aid under identical grinding parameters as well as similar grinding times or specific energies (see Eq. 1). The used values of the specific surface areas were mostly obtained from either BET or Blaine measurements.

$$\phi_{\mathrm{GA}} = \frac{S_{\mathrm{m,GA}}}{S_{\mathrm{m,ref}}} \qquad [1]$$

In many studies, only particle sizes or sieve residues instead of the specific surface area are used for quantifying the grinding aid success. In such cases, the fineness increase ϕ_{GA}* was calculated based on these alternative fineness characteristics. Thus, a direct comparison of the values ϕ_{GA}* with the surface-based values ϕ_{GA} needs be done with caution.

As seen in Table 2, a high number of researchers have already dealt with the investigation of grinding aids in laboratory experiments. Thereby, a variety of over 100 chemicals were successfully tested as additive for different particulate products. Naturally, the majority of the studies are located in the field of construction materials, especially because these materials are produced in large quantities while often demanding comparatively high specific energy inputs. However, also other inorganic products like alumina and quartz were investigated intensively. Other products like graphite, zirconia or zinc oxide and in particular organic materials like chitosan are in the minority among the tested materials. Independent of the ground material, mostly chemicals from the groups of mono alcohols, poly alcohols (mainly glycols), alcohol amines and carboxylic acids as well as their salts are suitable as grinding aids. In contrast to scientific laboratory studies, which often focus on the investigation of single grinding aid components, commercial grinding aid are usually provided as blends of these chemicals [65]. Recently, substances with a more complex chemical structure or chemical composition have succesfully been tested as grinding aids. For instance, waste products such as soapstock [66], sulfite waste liquor [67], waste cooking oil [68] and fly ash [69] were tested especially for economic reasons. Also, polymer-based grinding aids such as polycarboxylate ethers, which are already established as superplasiticizers in the concrete industry, are currently becoming more popular as grinding aids [31, 60, 70-72]. Schrabback [72] as well as Heller et al. [73] found that those complex molecules are in particular beneficial, when being applied together with common grinding aids.

Table 2 also indicates that it is hardly possible to derive any universal rules on mill- or solid-specific grinding aid effects based on these studies, even though the total scope of experimental results is very large. The reasons for the difficulty regarding a direct comparison of these various studies are very divers:

- The **diversity of ground products** including their mostly unknown surface properties makes the development of a comprehensive understanding even more difficult, especially regarding solid-specific grinding aid effects. This aspect is made even more complicated, as a variety of studies from the sector of construction materials do not focus on the grinding of a single material, but on the multi-component grinding of material mixtures. For instance, Teoreanu and Moanta [74] showed that different alcohol amines will lead to varying effects, depending on the content of granulated blast furnace slag within the cement blend. Moreover, the grinding aid performance can be influenced by the state of the material (fresh vs. aged) as shown by Dressel and Stark [71]. Thus, only a few studies indicate clear trends. For instance, the results of both Dombrowe et al. [23] and Sohoni et al. [67] show that alcohol amines are most effective for grinding cement while monocarboxylic acids are favorable for grinding limestone.
- **Grinding equipment:** Both of the aforementioned studies investigated grinding aids only in tumbling ball mills. To what extent the grinding aid performance may be related to the grinding mechanism as well as stressing conditions inside the mill, is nowadays still not really understood. The corresponding aspects are discussed separately within the next chapter, because this relation seems to be underestimated in most of the grinding aid application.
- **Measurement equipment:** In general, the usage of different measurement devices to quantify grinding aids effects on the product fineness makes a reliable comparison of these different studies partly very difficult. Especially values characterizing the specific surface areas, which are often obtained from Blaine measurements, can be seen critical. As shown by Graichen and Müller [22], significant differences between the particle size distribution and the Blaine surface are observed after applying grinding aids, because the adsorbed molecules tend to change the packing structure of the particle bed as well as its permeability, which directly affects the Blaine measurement. It was also shown that BET measurements are inaccurate when the samples are not prepared sufficiently by thermal conditioning prior to the measurement. This is due to the still adsorbed grinding aid molecules changing the nitrogen adsorption onto the particles, and thus, the measurement result [23, 75]. Dombrowe et al. [23] also assumed that grinding aids may affect wet particle size measurements, as they change the wetting properties of the particles. Therefore, they recommended to only use dry particle size analysis like sieving and air classification methods. Unfortunately, those methods are hardly appropriate for characterizing fine particle systems as well as fine fractions in particulate product.
- **Test evaluation:** In the field of industrial production, the specific energy demand, thus the amount of energy that is needed per product mass to obtain the desired

product fineness, is one of the most important parameters. Therefore, it should also be considered as the most important value to describe grinding aid benefits in batch-wise operated grinding experiments. However, a lot of studies are only based on grinding times as the measure to characterize the grinding success. Of course, some studies rather aim to describe basic phenomena, such as determining the impact of grinding aids on the particle and powder behavior (see e.g. [32]). Nevertheless, the universal illustration of the product fineness as a function of the specific energy demand would help to develop a comprehensive understanding of the grinding aid impacts on batch-grinding processes.

- **Fineness range:** The investigated product finenesses differ a lot among the presented studies, making a comparison of the results very difficult. A comparison of these studies indicates that grinding aid effects can be fineness-specific, which is not surprising as the adhesive particle forces become more decisive with increasing product fineness. As seen in Table 2, the relative increase of the product fineness is generally in the range of ϕ_{GA} = 1.0-1.5 for usual fine grinding (independent of the physical state of the grinding aid). In contrast to that, the benefits of grinding aid applications are much higher in the case of ultrafine grinding (uf), leading to ϕ_{GA} values of up to approx. 15. For instance, ϕ_{GA} values of 1.5 are achieved for the fine grinding of limestone, while in ultrafine grinding values of up to 2.7 are obtained. These results clearly show that the actual product fineness needs to be taken into account when comparing different studies. Moreover, these “fineness-effects” may also depend on the nature of the applied grinding aid. As an example, Figure 8 shows the grinding progress of cement clinker as a function of the specific energy consumption. When adding an amine-based grinding aid, ϕ_{GA} increases with the product fineness from initially 1.08 (≈ 2000 cm^2/g Blaine) to 1.5 (≈ 7500 cm^2/g Blaine). In contrast to that, ϕ_{GA} stays almost constant in the range of 1.2 while using a glycol-based additive.
- **Grinding aid concentration:** It is widely known that the grinding aid performance rather depends on the degree of particle surface coverage with grinding aid molecules than on the gravimetric grinding aid concentration (see e.g. [32]). In general, this value is not only affected by the grinding aid concentration itself, but also by the specific surface area of the product particles as well as other aspects like the purity of the added grinding aid or its molecular structure which determines the space requirement of each molecule on the particle surface. Obviously, finer products possess a larger specific surface area, which is why they demand a higher amount of grinding aid in order to be stabilized sufficiently. A similar trend can already be seen in Table 2: For instance, ultrafine grinding processes demand a significantly higher grinding aid concentration up to several percent related to product mass to achieve the desired grinding aid effects. In contrast to that, lower concentrations between 0.005-0.2 wt.-% are common for usual dry fine grinding processes within the lower micron range. However, as the aforementioned aspects

are not included in most of the studies, it is difficult to develop a comprehensive understanding of the optimum grinding aid concentrations. Moreover, several studies investigate excessively high concentrations, which certainly lead to certain grinding aid effects, but do not help to understand the selection of optimum concentrations (see e.g. [76]).

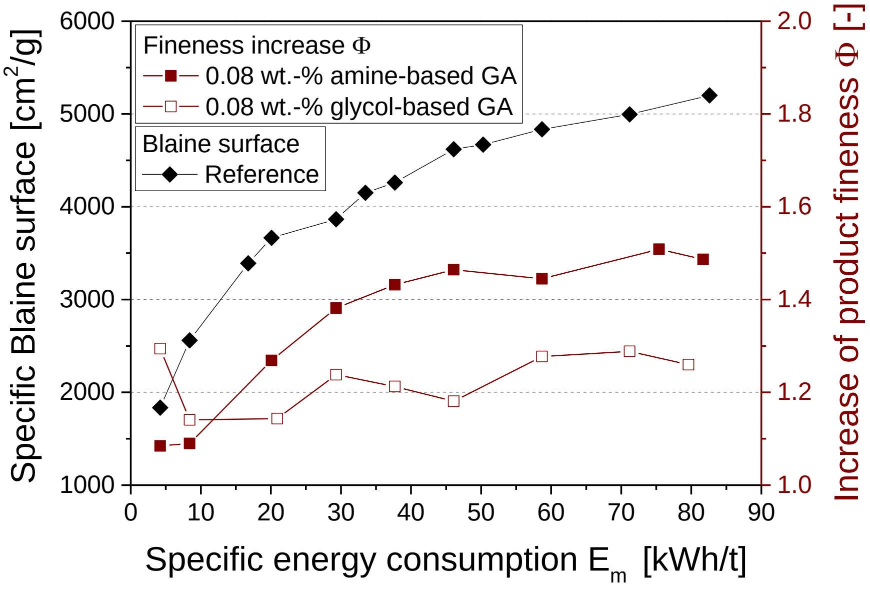

Figure 8: Evolution of the specific Blaine surface of cement as a function of the specific energy input, including the relative increase of the product fineness when applying amine- and glycol-based grinding aids (data taken from [77]).

3.2 Impact of the molecular structure on grinding performance

In order to enable an efficient grinding aid selection, many researchers addressed the question to which extent the grinding performance is correlated with certain chemical-physical properties of the additive. Scheibe et al. [27] carried out an extensive investigation of various grinding aids on the batch-wise grinding of cement clinker, quartz and limestone in the 1970s. They found that the impacts of the applied chemical on parameters like the product fineness or the material adhesions inside the mill depend on a complex relation between the ground material itself and the properties of the chemical. Thereby, they did not see a significant impact of neither the dipole moment of the grinding aid nor its solubility. In contrast to that, Paramasivam and Vedaraman [63] concluded that a high dipole moment, a high surface tension and a low vapor pressure (for low grinding aid concentrations) as well as a low viscosity (independent of the grinding aid amount) lead to higher product finenesses in the case of grinding limestone. Based on the results of grinding quartz, Hasegawa et al. [78] suggested that the product of dipole moment and molar mass may be a good indication for the grinding aid effectiveness. However, both approaches are not satisfactory for an efficient grinding aid selection, because the chosen properties do not include solid-specific grinding aid effects as shown by Scheibe et al. [27]. Also, the impact of the molecular geometry and further physico-chemical parameters are thereby not considered appropriately. Other studies revealed that even the adsorption energy is not an exclusive measure for the grinding aid performance [2].

Dombrowe et al. [23] also summarized a number of criteria for selecting grinding aids with a special regard on their molecular structure. They summarized that the chemical structure has a decisive influence on the grinding aid performance; this includes the kind and number of functional groups as well as the chain length of nonpolar parts within the molecule. They also showed that an asymmetrical arrangement of the polar groups within the molecule favors the effectiveness. However, they concluded that it is hardly possible to derive selection criteria based on these properties, also due to the fact that grinding aids may act solid-specific. They further showed that a high concentration of functional groups does not guarantee a high stabilization success, even though this may lead to a high surface coverage at the same time. For instance, the investigation of different carboxylic acids at a constant gravimetrical concentration revealed that the best effects on the grinding of limestone are obtained with medium-chained molecules (see Table 1). The authors also mentioned that the small effects of long-chained carboxylic acids (C_{12} and higher) at usually applied concentrations can be compensated by applying uncommonly high concentrations. It clearly shows that different additives demand other optimum concentrations.

Table 1: Impact of the concentration of carboxylic groups within monocarboxylic acids on the product fineness (undersize at 40 and 17 µm) as well as Imse powder flowability of ground limestone for different chain lengths (data taken from [23]).

Chain length	Conc. [mmol/kg]	Passing D_{40} µm [wt.-%]	Passing D_{17} µm [wt.-%]	Imse powder flowability [%]
C_2	8.3	88.5	67.2	85
C_3	6.8	87.6	67.3	87
C_6	4.3	89.2	68.4	98
C_8	3.5	88.6	66.1	87
C_{12}	2.5	84.6	68.5	85
C_{14}	2.2	74.4	63.0	40
C_{18}	1.7	73.0	58.0	38

Prziwara et al. [32] showed that the number of grinding aid molecules per solid surface (N_{GA}) is a better measure to describe the grinding aid performance than the gravimetric concentration. They also found that molecules with a high ratio of polar to non-polar molecules demand lower N_{GA}-values to achieve their maximum effects than molecules with a longer non-polar chain. The authors concluded that the number of polar groups determines the number of anchor groups for the adsorption. They stated that molecules with more than one anchor group lead to a more “flat” adsorption, and thus, to a higher surface coverage at a constant number of added molecules. However, it was also shown that these molecules do not necessarily achieve the best effects. Instead, the molecules leading to the strongest reduction of the surface energy of the particles turned out to be the most effective grinding aid additives regarding the prevention of agglomeration and the increase of powder flowability. Unfortunately, no method to approximate the reduction of the surface energy based on the chemical grinding aid parameters is known until now.

3.3. Importance of stress conditions inside the mill

Similar to the aspects discussed above, it is also almost unknown how the grinding aid performance is influenced by the selected mill and process parameters, and thus, by the stress conditions inside the mill. It may appear obvious that the micro-processes of the individual stress events inside the mills are affected by the grinding aids, since those additives are well-known to influence decisive product properties like the powder flow behavior and agglomeration. Therefore, it seems more than likely that the product reacts differently to certain stress situations, depending on its bulk and flow properties. However, only a very low number of authors have dealt with this question so far.

A reason for this may be the predominant role of tumbling ball mills in the cement industry especially within the last century. Thus, most of the grinding aid studies focus on this mill type, which makes it difficult to compare the grinding aid performance for different grinding mechanisms. Also, tumbling ball mills are usually operated within a narrow range of process parameters, since the choice of parameters like mill speed and ball size is strictly limited. This also restricts the stress conditions to certain boundaries. Within one of these studies, Dombrowe et al. [23] showed that the efficiency of grinding aids in tumbling ball mills is not affected by parameters such as mill speed, ball filling ratio, ball size, product filling and temperature. In contrast to that, Deckers and Stettner [79] revealed that the grinding ball size as well as the ball filling ratio influence the grinding aid effects.

A further hint regarding the change of friction and stress conditions as a consequence of the grinding aid application is given by the results of Moothedath and Ahluwalia [61]. They operated a lab-scale tumbling ball mill specifically at two completely different process conditions in order to comminute limestone predominantly by either breakage or attrition. Even though the experimental set-up of this paper is not always comprehensible, the results clearly indicate that grinding aids may have significantly different impacts on the grinding result depending on the stress conditions inside the mill. For instance, grinding aids like TEA and oleic acid showed different influences in attrition mode, while grinding in the common breakage mode was almost identical for both grinding aids.

A much clearer indication is given by Allahverdi and Babasafari [80], who investigated the effect of TEA on the comminution of cement in both a tumbling ball mill as well as vibrating disc mill. Therefore, they first identified those process parameters, which resulted in an identical Blaine value for both mills when grinding without any additive. Subsequently, they added TEA under the selected parameters. They found, that the use of TEA led to a stronger increase of the Blaine value in the case of the tumbling ball mill in comparison to the vibration disc mill (see Figure 9). This result clearly shows that the grinding aid efficiency is indeed a function of the stressing conditions provided by the mill. Similar to that, Nair and Paramasivam [81] found that the extent of enhancement within the grinding performance to grind calcite with calcium stearate as an additive varies for different media mill types.

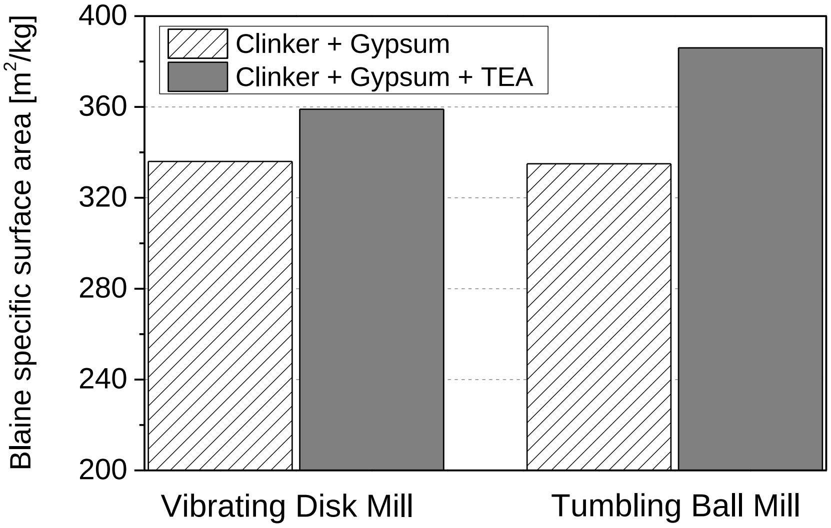

Figure 9: Impact of TEA on the grinding of clinker in vibration disc and tumbling ball mill, when grinding with mill parameter that lead to identical Blaine values without any additive (data taken from [80]).

Hoffmann and Bernhardt [82] showed that different carboxylic acids do not only improve the batch-wise high pressure grinding of limestone in a vertical rolling ball mill, but also reduce the power draw of the mill drive. The authors stated that the reduction of the adhesion forces by applying grinding aids leads to a decrease of the friction between the particles, which in turn, leads to an easier slipping and sliding of the particles within the bulk. They also assumed that this may further increase the grinding efficiency, because the increased particle movement may bring the particle bed closer to the more efficient conditions of single particle layer beds. This statement seems inappropriate for continuous processes, since it does not include the production capacity: In such cases, high transport velocities along the mill and low power draws of the mill drive may lead to low production rates, simultaneously. In comparison to roller mills, the power draw of a tumbling ball mill is only slightly affected by the adhesion forces of the ground particles, while the milling parameters play a larger role [82].

Oettel and Husemann [64] observed similar effects when they investigated the impact of the powder flowability on the comminution of limestone particles (40-50 µm) which were stressed batch-wise by high pressures within a force-controlled press. They specifically adjusted the powder flowability of the limestone by using different amounts of caproic acid and found that the particle stressing is significantly influenced by the powder flow behavior. Especially for only partially confined particle beds, the mass of particles that is captured beneath the piston decreases with an increase of powder flowability (see Figure 10). Depending on the geometry of the confinement, this increased product transport may also lead to a higher specific energy adsorption but a lower energy utilization at the same time. The authors clearly showed that the micro-processes are strongly influenced by the powder flow behavior while stressing, and thus, the applied grinding aid. In general, these finding indicate that the flowability does not only affect high pressure grinding, but also all of those grinding processes where the particles are stressed as particle beds.

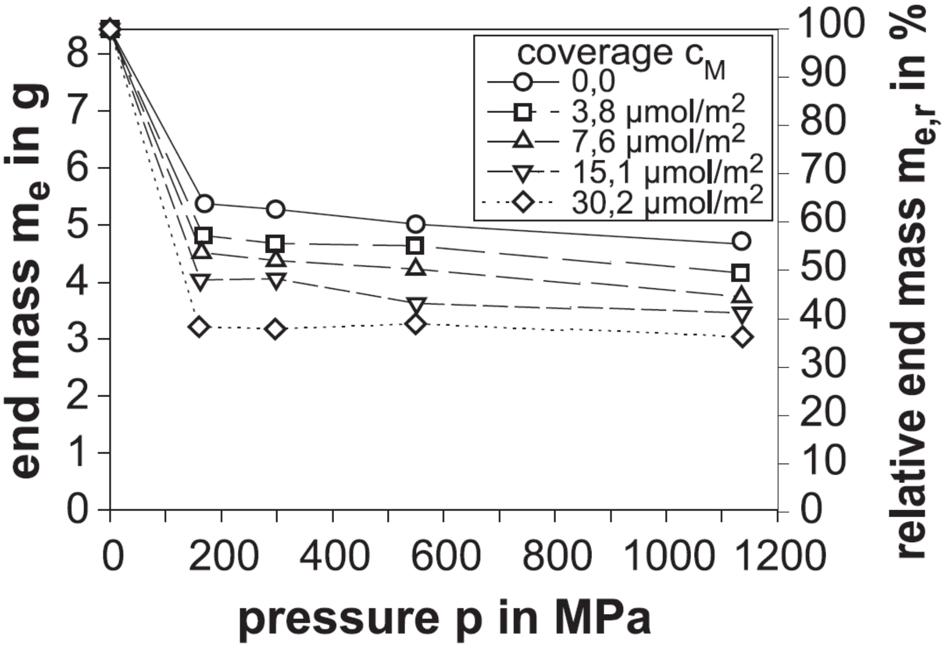

Figure 10: Impact on the amount of caproic acid on the capturing behavior of fine limestone particles in a high pressure grinding test (force-controlled press) using a partially confined particle bed [64].

Moreover, Recchi et al. [53] reported that traditional grinding aids such as ethanolamines, glycols or inorganic salts are surprisingly inefficient in vertical roller mills (VRMs), where grinding is also caused by high pressure stresses. Within this study, the authors achieved much better results by adding an innovative grinding aid containing high-boiling compounds and thickening agents by means of a new grinding aid dosing system. They assumed that the addition of the usual grinding aids directly inside the mill in combination with the higher mill ventilation of VRMs facilitates the early evaporation of the additive as well as its removal from the mill with the ventilation air. Indeed, mill ventilation is different in VRMs and may cause overlapping impacts on the grinding aid performance. However, since also traditional grinding aids have comparatively high boiling points (partly above 300 °C), it is doubtful that this mechanism alone causes the observed effects. Accordingly, Rechenberg [34] showed that the content of TEA or propylene glycol in the exhaust air of tumbling ball mills was independent of the temperature even up to clinker temperatures of 150 °C. In the case of Recchi et al. [53], the optimization of the VRM performance by adding high-boiling compounds and thickening agents may be an indication for a further aspect: It is conceivable that those kind of additives cause a more cohesive powder, leading to both a higher product retention time on the grinding table as well as an improved particle capturing under the grinding roll achieved by a more stable particle bed (compare high flowability investigated by Oettel and Husemann [64]). This would also explain why VRMs often demand the additional injection of water, which is usually assumed to “stabilize the particle bed”. Unfortunately, there is a lack of studies on grinding aid effects in high pressure grinding systems, which is why this explanation should rather be seen as a thesis.

For batch-wise operated dry stirred milling, Prziwara et al. [56] found that the grinding result also depends on the product flowability which was specifically adjusted by different grinding aids. In contrast to VRMs, high flowabilities generally appeared to be more favorable in the batch operated stirred mill. The authors also showed that the powder flowability may have completely different effects depending on the process parameters of the mill and concluded that the flow behavior of the product powder determines the amount of particles that are captured between the colliding grinding beads (see Figure 11). Thus, the stress intensity as well as the product-related stress frequency inside the mill does not only depend on process parameters, but also on the applied grinding aid. The results indicate, that the grinding aid needs to be selected with a special regard to the stress conditions inside the mill, especially for those mills that enable very variable grinding conditions.

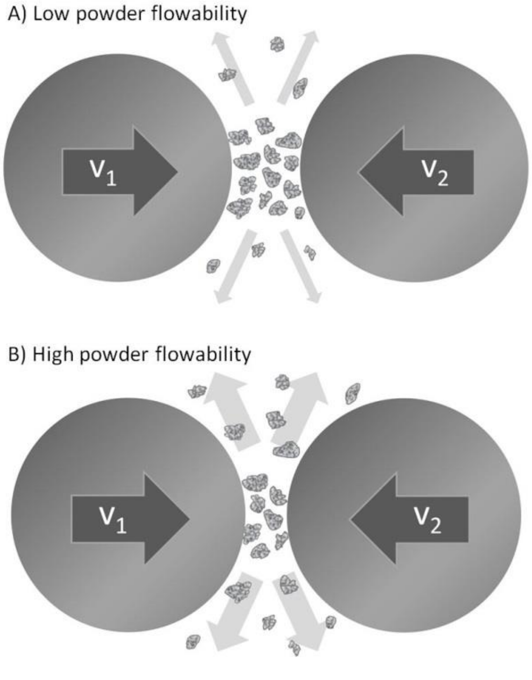

Figure 11: Influence of the powder flowability (specifically adjusted by diethylene glycole, DEG and heptanoic acid, HepAc) on the capturing of limestone particles between colliding grinding beads [56].

4. Grinding aids in industrial grinding processes

4.1. Transfer from batch to continuous processing

Laboratory experiments based on batch-wise operated mills are still the most common measure for selecting grinding aids and grinding aid concentrations. However, a reliable transfer of results obtained by batch-wise laboratory milling to continuously operated processes is hardly possible, as a number of overlapping parameters cannot be included in batch-wise experiments. Thus, remarkable differences regarding the grinding performance between laboratory experiments and industrial scale operations are very common. Assaad [83] showed that laboratory trials strongly underestimate the grinding aid effects in comparison to industrial grinding for cement grinding. Thereby, energy savings of 7-9 % were achieved in laboratory grinding, while doubling the amount of saved energy (13-18 %) in the industrial scale. Also, the particle size distribution varied between the different scales.

Results of different papers (see e.g.[2][58]) and own experience show that the most important impact is caused by the additive-induced change of the product flow behavior, which alters the retention time of the product material inside the mill. For example, Figure 12 shows that the concentration of TEA during the milling of cement in a continuously operated tumbling ball mill changes the transport behavior; among others by increasing the non-axial flow rate as well as the width of the residence time distribution (seen by the Bodenstein number which is equivalent to the Peclet number). By the combination of these effects on both the micro and macro level, a maximum product fineness is obtained at medium TEA concentrations [23]. In the worst case, high powder flowabilities may lead to an insufficient number of stress events on the material on its way through the mill. Obviously, such effects cannot be observed in batch-wise operated mills. Prziwara et al. showed that grinding aids causing high powder flowabilities are beneficial to batch-wise grinding of limestone in a dry stirred mill [56], while the same additives lead to an inferior process in the continuous single-passage grinding mode [58]. In contrast to that, Scheibe et al. [28] showed that grinding aid effects seen in laboratory tumbling mills can be transferred to industrial processes, at least in its tendency. However, they only investigated small concentrations of TEA, whereby the impact on the flow properties of the product is assumed to be very low. In a later paper, Scheibe et al. [2] clearly showed that higher amounts of TEA indeed lead to a reduced retention time within a passage-wise operated tumbling ball mill, especially due to the additive-induced increase of the powder flowability. They also stated that the addition of excessive grinding aid amounts above the optimum concentration leads to a decreasing grinding performance.

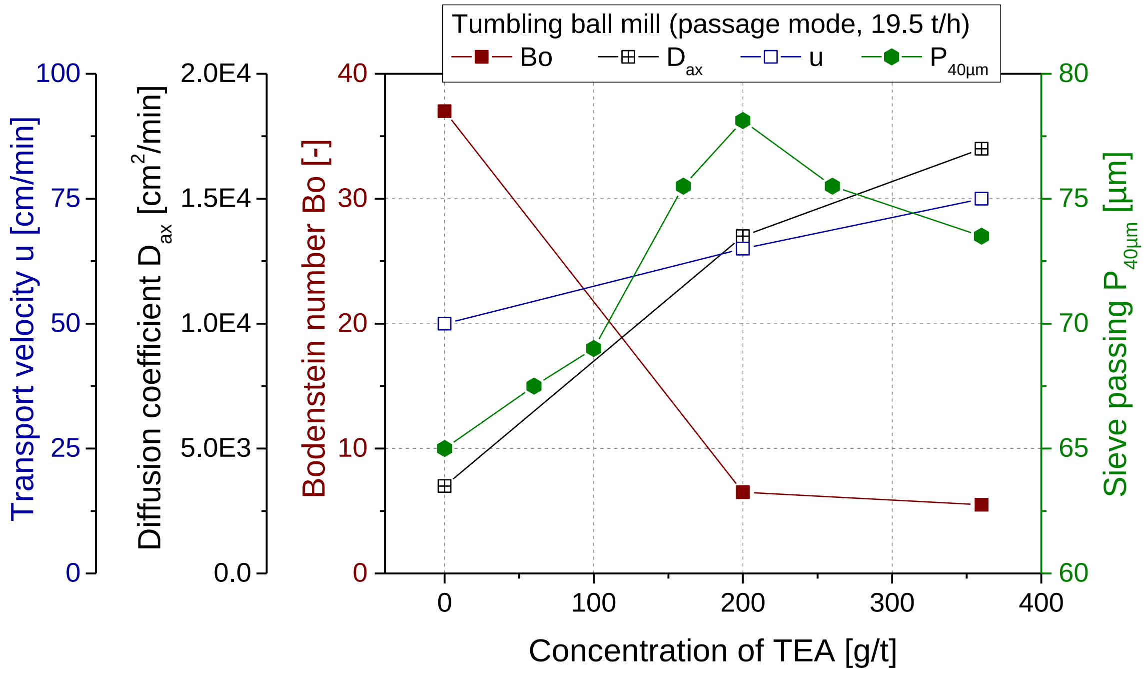

Figure 12: Impact of the TEA concentration on transport characteristics and grinding performance for milling cement in a passage-wise operated tumbling ball mill (values taken from [23]).

Besides the retention time inside the mill, further important aspects are the scale-dependent stress conditions inside the mill, the additional ventilation within continuous mills, the varying grinding temperature as well as the additional use of screening or classification devices [83]. Especially the use of screens and classifiers (especially when grinding in closed circuits) prevents the accumulation of very fine particles inside continuously operated mills. This in turn is an important issue within batch-wise milling experiments, because especially the fine particle fractions have a strong impact on the micro-processes inside the mill (see chapter 2.1). On top of that, grinding aids often have more decisive impacts on fine particles than on coarse particles. Thus, it is not surprising that the Bond Work Index (BWI) is often independent of the grinding aid [28], as the bond test includes the removal of fine particle fractions from the mill as well as its replacement with fresh material. Inspired by Bond, Assaad [84] developed a new laboratory method which aims for mimicking the industrial closed-circuit mode. The method also includes the periodic screening of the mill content in order to remove and analyze the fine particles. By repeating this procedure and balancing the fine and coarse fractions, the material circulation of a closed circuit process is simulated. The author found that the method gives a higher consistency of the grinding aid impacts obtained from laboratory and industrial grinding. However, it needs to be noted that this method does not consider impacts of retention time, classification efficiency or temperature, either. In a further study, Assaad [85] therefore investigated the impact of the grinding temperature on the performance of alcohol amine grinding aids in a laboratory tumbling ball mill. At least for these grinding aids, he did not find a significant influence of the temperature in the range of room temperature to 100 °C. How far this observation may be valid for other grinding aid types is difficult to say.

In addition to the actual grinding process, the classification step in closed-circuit mode may cause overlapping grinding aid effects, which are not considered by laboratory grinding tests. Especially grinding aids, which cause a strong reduction of the particle agglomeration, can bring further positive effects in closed-circuit processes. The impact of grinding aid additives on the classification process is discussed separately within the next chapter.

Altogether, it is still difficult to say in how far the grinding aid effects obtained from laboratory mills can be transferred to industrial-scale processes. The present studies indicate that the transferability probably depends on various material-related aspects (e.g. the impact of the grinding aid on bulk, flow and agglomeration behavior) as well as process parameters (e.g. process mode or differences of the milling conditions).

4.2. Further grinding aids effects in closed-circuit processes

As closed-circuit processes consist of different process units such as milling, classification, separation but also bulk and pneumatic conveying, grinding aids may lead to very divers and complex impacts on these industrial processes [2]. Besides milling, the classification step is assumed to be the most decisive process unit, because it determines the quality of the fine product. In addition to that, a bad classification performance may result in a high recirculation factor by increasing the reject flow of (agglomerated) fines to the mill, which in turn, directly affects the milling performance. Since grinding aids are known to influence the agglomeration behavior of the product, it seems obvious that these additives do also cause overlapping impacts on the classifier performance.

Scheibe et al. [2] were one of the first to show that grinding aids can also have positive influences on the air classification. For instance, the authors had a closer look to the classifier bypass, which is a measure to quantify the amount of fine particles that are mistakenly rejected by the classifier and led back to the mill. They demonstrated that this parameter is significantly reduced once a grinding aid is added to the process. For a constant product throughput, the material load of the mill is reduced, which results in both more efficient grinding conditions as well as a lower material recirculation. This in turn further increases the classifier performance. Sottili et al. showed that these aspects enable an increase of the overall production rate of 19 %, when applying 0.02 wt.-% of a commercial grinding aid blend in a closed-circuit tumbling mill cement plant. Simultaneously, the specific energy demand decreased of about 16 %. Due to the fact that the mean mill retention time decreased from 6 to 4.6 minutes with the addition of the additive, lower amounts of fine particles were produced in each grinding passage which is why the material recirculation almost doubled. Despite the higher resulting classifier load, they still detected higher separation efficiencies in the case of the grinding aid addition. As illustrated in Figure 13, grinding aid cause even greater improvements of the classification process (represented by higher yields of fine particles within the fine product) for higher specific material loads in the classifier chamber [23]. This clearly shows that especially the grinding operations with high material loads of the grinding plant can benefit from grinding aids.

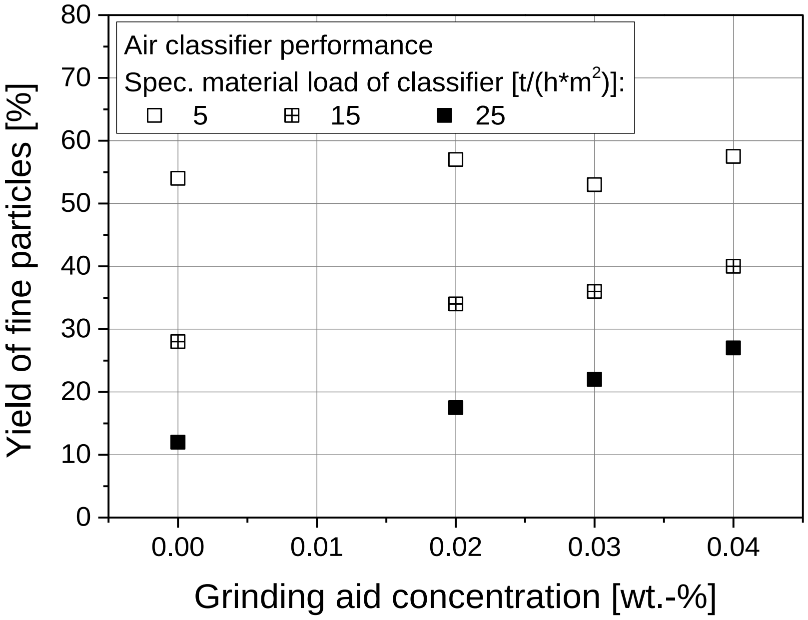

Figure 13: Yield of fine particles as a function of the grinding aid concentration for different specific material loads in the classifier chamber (data taken from [23]).

Toprak et al. [86] also showed that different grinding aids have a positive impact on the classifier bypass. Within their study, in particular grinding aid blends containing alcohol amines and hydroxyl amines caused a significant decrease of the bypass from initially 22.6 % to 15.7 % and 15.6 %, respectively. Toprak et al. [87] repeatedly identified a reduction of the by-pass through the addition of grinding aids in a further study, while they did not observe a significant change of the separation sharpness. Unfortunately, they did not give any information on the material loads of the classifier air. Therefore, it cannot be excluded that the experiments were carried out in an operating range, where grinding aid effects are rather low (compare Figure 13). Other mixtures containing modified amines or PCEs only caused medium effects. However, it is difficult to evaluate the impacts of these chemicals on the classifier performance solely based on these results, since the applied concentration was not held constant for the different additives. Furthermore, no information about the concentration of the active component within the used additive blends was given. This may explain opposing trends presented by other authors.

For instance, Mishra et al. [88] found that – in contrast to batch-wise milling – PCE containing grinding aids are favorable in closed-circuit grinding compared to TEA, which they attributed to superior effects of PCEs on the classification process. However, no evidence for this assumption is presented. In a recent study it was also shown that TIPA is more effective regarding the reduction of by-pass values compared to TEA and diethylene glycol, whereas the separation sharpness only slightly changed with the grinding aids [87]. In the case of ultrafine classification of limestone, Husemann et al. [75] showed that the addition of 0.7 % of stearic acid increased the mass of fine particles < 1 µm inside the fine fraction significantly.

Moreover, Scheibe et al. [2] stated that bulk conveying may be more difficult when grinding aids are applied, especially for a resulting increase of the powder flowability in combination with a steep conveyor belt. In contrast to that, pneumatic conveying is usually easier when grinding aids are added. Sottili and Padovani [89] also mentioned that the use of grinding aids can lead to a higher filter load as well as a lower grinding media wear, but without presenting experimental data for that.

4.3. Results from continuously operated grinding processes

Most of the available studies on the investigation of grinding aids in continuously operated grinding plants focus on closed-circuit operations with tumbling ball mills. For instance, Sottili and Padovani [90] showed that industrial closed-circuit grinding of cement clinker using a tumbling ball strongly benefits from grinding aid applications. Within their study, the use of grinding aids led to a decrease of the medium retention time of the material inside the mill by 25 %, which in turn, resulted in a 100 % increase of the product recirculation. Nevertheless, the overall process performance was not negatively affected by that, as the production rate was increased by 10-30 % [90] or even 25-40 % [89] at a constant product quality. For a comparable closed-circuit tumbling mill grinding plant, Lai et al. [91] achieved enhancements of the cement production rate of up to 23.5 % by adding PCE-based grinding aids. Similar enhancements up to 20 % were also reported by Schrabback [72]. Toprak et al. [86] were able to increase the production capacity of a 4500 cm^2/g Blaine cement up to 24 % with the addition of appropriate grinding aids containing either alcohol amines, hydroxylamine or mixtures of PCEs and amines. The authors also reported that the material circulation load significantly decreases as a consequence of the grinding aid additive addition. Similar results were demonstrated by Dombrowe et al. [23], where the addition of grinding aids led to a decrease of the circulation factor from 5 to 2-3.

An investigation on VRMs was carried out by Pohl et al. [92]. They achieved an increase of the production capacity from 70 to 90 t/h for the production of CEMII-32,5 cement by applying glycols as a grinding aid. Thereby, a simultaneous reduction of the specific energy consumption from 19,7 to 18,5 kWh/t (exluding energy demand for the pneumatic transport) was accomplished.

Grinding aids were also investigated in continuously operated dry stirred mills in open-circuit mode (passage grinding). Altun et al. [93] showed that triisopropanolamine-based (TIPA) grinding aids leads to a higher reduction of the specific energy demand for clinker grinding than additives based on glycols or TEA. They achieved the best effects with grinding aid concentrations of 0.1 wt.-%, which is comparatively high for the obtained Blaine surface < 3000 cm^2/g. Whether dry stirred mills generally demand higher grinding aid concentrations than conventional ball mills is difficult to say, as the author only described “TIPA-based” grinding aids without giving further information about the content of the surface active component within the used grinding aid blend. Furthermore, the authors showed that the material load inside the mill decreased with increasing grinding aid concentration for a constant product throughput. Thus, grinding aids also affect the ball-to-powder ratio inside the mill, which may be a further positive effect at higher additive concentrations. According to calculations done by the authors, the lower mill hold-ups also indicate reduced mean mill retention times, which normally counteract a high size reduction. Nevertheless, the best grinding performance was achieved with high additive concentrations. Prziwara et al. [58] investigated the impact of the powder flowability, which they specifically adjusted with comparatively high concentrations of different grinding aids, on the open-circuit grinding of limestone. In contrast to the aforementioned study, they used a special stirrer design, which is equipped with an additional classifier wheel in order to hold back the grinding beads inside the mill. As mentioned before, they found a significantly higher grinding efficiency in the case of low powder flowabilities. Surprisingly, higher mill hold-ups were found for the powders with high powder flowabilities, which the authors attributed to additional impacts of the internal classifier wheel. The comparison of the two studies indicates, that grinding aid effects may also depend on certain constructive elements of the mill, such as the design of the mill outlet.

Further grinding aid studies on continuous grinding processes were carried out for jet opposed mills. For instance, Schwarzwälder et al. [94] presented a reduction of the specific energy demand of 83 % and 62 % by applying grinding aids in the ultrafine jet milling of a ceramic pigment and a metal oxide, respectively. For the fine grinding of a hydraulic bonding agent they still found a decrease of the specific energy by 56 %. Unfortunately, the authors do not give any information on the ground materials, the kind of grinding aids or their concentration. Thus, it is hardly possible to obtain any important information on grinding aid effects in opposed jet mills from this study. This is also the case for a study on jet mills by Miranda and Yilmaz [95], who determined a strong increase of the product throughput (up to several 100 %) when grinding a ceramic oxide by means of an additive, but without giving important information on the product, grinding aid or process parameter. Results presented by Godet-Morand et al. [96] demonstrated, that the grinding aids success also depends on the product particle size. In the best case, they also obtained very high production rate increases of 88 %. Husemann et al. [75] showed that the product particle size is not significantly affected by the addition of 0.7 % stearic acid as additive for the ultrafine grinding of limestone in a jet opposed mill. Unfortunately, the authors did not present any data regarding the impact of the stearic acid on the resulting product throughput or energy efficiency. Altogether, it can be seen as a kind of predicament that three out of four present studies reveal huge potentials of grinding aid applications in jet opposed milling, but without paying more attention to this topic; such as performing further systematic investigations or just giving more information on the used additives. Since other studies on grinding aid effects in jet mills are hard to find, future systematic investigations on this topic would be highly appreciated.

5. Influence of grinding aids on product properties

As surface active grinding aids mainly stay adsorbed on the product particle surface even after grinding, further impacts of the additives on the final product properties or processing properties of the ground material are not surprising. These effects are especially well-known in the field of construction materials. However, they are not the main focus of this review paper. Thus, the most important of these aspects are summarized briefly within the following chapters, since they may limit the choice of appropriate grinding aids but also cause significant benefits regarding the product quality.

5.1. Construction materials

Especially in the field of construction materials, the effects of remaining grinding aid molecules on the handling properties of the ground materials along the further processing as well as on the final product characteristics are crucial. The reason is that they may exclude even those additives, which lead to promising grinding results. Therefore, a variety of studies have already investigated the impact of grinding aids on these aspects. The most important effects may be roughly divided in three different groups:

a) Processing properties: As shown in various studies, grinding aid molecules maintain their stabilizing effects even after mixing the ground particles with water. This of course significantly influences the rheological properties of the particulate paste, such as the viscosity and the spreading behavior as well as the water demand (e.g. [97-99]).
b) Chemical hydration reaction: In the field of cement chemistry, the influence of chemical additives on the chemical hydration reaction when mixing a fine particulate binder (such as cement clinker) with water and other filling materials as well as fine and coarse aggregates is of major interest. The kinetics of these reactions primarily determine the setting behavior of the paste, and thus, its processability especially in terms of time for mixing, transporting, placing and compacting. The impact of remaining grinding aid molecules on the hydration reaction and the subsequent

setting behavior was already investigated and discussed within a variety of studies (e.g. [70, 71, 100-102]).

c) Hardening of the paste as well as strength development and final strength of the building component: As a consequence of influencing the hydration reaction as well as the reaction products, grinding aids may also change the strength of the final building component. In fact, the majority of those scientific papers, which investigate grinding aid impacts on the dry grinding of cementitious materials, evaluated the influence of the additives on the strength development simultaneously (see e.g. [93, 100, 103].

5.2. Other examples

Other impacts of grinding aid molecules on the product properties, apart from the construction sector, are only reported sporadically. For instance, Toraman et al. [104] showed that color properties like the lightness, the total color difference or the whiteness index of ground calcite are influenced by certain grinding aids. These effects are also independent of the obtained product fineness. Badjena [37] also reported that grinding aids influence properties like shinning and leafing characteristics in the case of brass particles and pigments. Here, smaller concentrations (0.1 %) of stearic acid led to the best results. The author also observed changes of the particle shape, while more equiaxed shapes were obtained with stearic acid. For the grinding of graphite particles, Hayashi [105] showed that certain grinding aids like tri-sec-butylaluminate and octofluoropentanol cause a thinning of the flaky graphite particles (see Figure 14). The authors attributed this to chemisorption of the grinding aid molecules on the broken bond planes, which in turn may facilitate the fracture of particles along cleavage planes. However, evidence for this assumption was not presented.

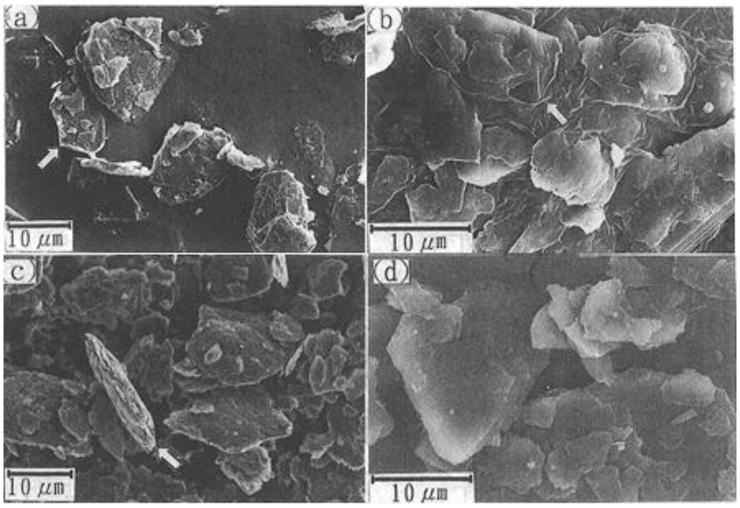

Figure 14: Shape of graphite particles after processing with different grinding aids; a: raw material, b: grinding without additive, c: grinding with tri-sec-butylaluminate and d: grinding with octofluoropentanol (pictures taken from [105]).

Moreover, Hasegawa et al. [55] observed dependences of the particle crystallinity on the grinding aid for the ultrafine grinding of limestone. As already mentioned above, further effects were reported in the field of co-milling, where the applied additives did not only result in an improved powder flowability of the micronized pharmaceuticals, but also in a beneficial dissolution behavior of these compounds [48-50].

6. Conclusion

Even though the benefits of grinding aids have already been shown in various experimental studies and industrial applications, the selection of appropriate chemicals and concentration is still mostly based on empirical knowledge. As shown in this review article, it is still hardly possible to derive a comprehensive understanding regarding the additive impacts on the grinding performance, even though more than 100 papers on this topic can be found in the literature.

On the one hand, there is a lack of understanding towards how the additive molecules interact with the solid surface. In particular, it is not yet understood how the molecular structure of the additive influences the adhesion forces between the particles, and thus, the particle and bulk behavior of the product. It is also hardly known why many grinding aids act solid-specific and which particular chemical parameters are relevant for this relation. On the other hand, it is also only partly known how the changes of the particle and bulk behavior may affect the micro- and macro-processes inside the mill as well as the whole grinding plant operation. This may especially be critical when transferring findings on grinding aids to other processes, as the impact of grinding aids may be completely different depending on the technical equipment or process mode. Altogether, common rules for selecting appropriate grinding aids do not exist. The high difficulty in the selection and the efficient application of grinding aids gets also clear by considering a further aspect: The variety of applied chemicals, ground materials and target finenesses, available mill types and process designs, mill and process parameters as well as analysis methods complicate the development of a comprehensive understanding based on the present studies.

This review article reveals that further extensive scientific work has to be done to develop such a comprehensive understanding. In a first instance, more investigations on the "particle-scale" need to be carried out to understand the specific interactions between the applied chemical and the solid product surface. It needs to be determined which physical-chemical properties of both, the additive as well as the solid surface, determine the mode of action of the grinding aid; especially regarding the adsorption strength, the reduction of the surface energy, the adsorption geometry or further steric stabilization effects. In a second step, a more comprehensive understanding is needed to which degree these aspects change the adhesions forces between the particles, and thus, properties like the agglomeration behavior of the particles, their dispersability, flow and fluidization properties or the compaction behavior of the powder. Finally, these findings are fundamental to estimate how the product reacts to the stressing conditions inside the mill, how the material is transported and how its behavior within air streams is changed or whether important product qualities of the powder are affected by the additives. Only if these very complex relations are understood, an efficient predictive selection of grinding aid additives will be possible for industrial processes in the future.

7. Appendix

Table 2: Examples of applied chemicals that showed positive impacts on dry grinding in different mill types (TBM = tumbling ball mill, BBM = box ball mill, VBM = vibration ball mill, VDM = vibration disc mill, VRoM = vibration rod mill, PBM = planetary ball mill, SMM = stirred media mill, VRM = vertical roller mill) in the case of various ground materials, including ultrafine grinding (UF) to the submicron range. Grinding success is characterized by the fineness factor (*fineness factor calculation based on sieve residue or mean particle size instead of specific surface area).

	Ground material	Grinding aid	Mill type	Fineness factor [%]	Related conc. [wt.%]	Ref.
Liquid / dissolved	Cement and cement clinker	Water	n/a	1.17	n/a	[31]
			TBM	1.20*	1.0	[76]
		Hexane	n/a	1.14	n/a	[31]
		Paraffin oil	n/a	1.18	n/a	[31]
		Mixture of aromatics	n/a	1.18	n/a	[31]
		Rape seed oil	n/a	1.20	n/a	[31]
		Dioxan	n/a	1.21	n/a	[31]
		Acetone	n/a	1.20	n/a	[31]
		Ethyl acetate	n/a	1.23	n/a	[31]
		Isopropanol	n/a	1.28	n/a	[31]
		Ethylene glycol	TBM	1.21	0.05	[59]
		Water + ethylene glycol (50/50)	TBM	1.10	0.04	[67]
		Diethylene glycol	n/a	1.27	n/a	[31]
		Water + diethylene glycol (50/50)	TBM	1.07	0.04	[67]
		Propylene glycol	TBM	1.24	0.05	[59]
		Polypropylene glycol	TBM	1.18	0.05	[59]
		Lignin-based	TBM	1.12	0.03	[11]
		Mixture of fatty acids	TBM	1.07*	0.3	[76]
		Polyethylene glycol 6000	TBM	1.03*	0.5	[76]
		Fatty acid salts	TBM	1.23*	0.5	[76]
		Base of titanate + phosphite	TBM	1.40*	0.75	[76]
		Butylacrylate	TBM	1.07*	0.5	[76]
		2-Ethylhexylacrylate	TBM	1.07*	0.5	[76]
		Acetate	TBM	1.07*	0.5	[76]
		Triethanolamine	TBM	1.18	0.0175	[27]
			TBM	1.08	0.06	[80]
			VDM	1.16	0.06	[80]
			TBM	1.03	0.03	[106]
			TBM	1.7*	0.1	[76]
			TBM	1.1	0.1	[60]
		Modified triethanolmine	TBM	1.06	0.03	[106]
		Water + triethanolmine (50/50)	TBM	1.06	0.04	[67]
		Water + triethanolmine (60/40)	TBM	1.40	0.10	[73]
		Water + polycarboxylate ether (60/40)	TBM	1.26	0.10	[73]
		Water + dodecylbenzene sulphonic acid (50/50)	TBM	1.07	0.04	[67]
		Water + sulphite waste liquor (70/30)	TBM	1.03	0.065	[67]
		Phenyl polyglycol ether	TBM	1.25	0.0175	[27]
		Heptanoic phosphonic acid	TBM	1.21	0.0175	[27]
		Decanol	TBM	1.14	0.0175	[27]

		Potassium ethyl xanthate	TBM	1.13	0.0175	[27]
		Lignosulfonate	TBM	1.11	0.0175	[27]
		Dipotassium phosphate	TBM	1.07	0.0175	[27]
		Organophosphate	TBM	1.06	0.0175	[27]
		Methyl silicon oil	TBM	1.04	0.0175	[27]
		Oleic acid	BBM	1.05	0.025	[107]
			TBM	1.06	0.1	[98]
		Sunflower oil	BBM	1.04	0.1	[107]
		Amine-based	TBM	1.19	0.096	[108]
			TBM	1.51	0.08	[77]
		Glycol-based	TBM	1.07	0.128	[108]
			TBM	1.29	0.08	[77]
		Acid-based	TBM	1.03	0.042	[108]
		Polymer-based	TBM	1.1	0.1	[60]
	Cement raw meal	Soapstock (sunflower oil)	TBM	1.46	0.5	[66]
		Soapstock (corn oil)	TBM	1.38*	1.0	[66]
		Triethanolamine	TBM	1.24*	1.5	[66]
	Limestone	Water	SMM	1.1	0.25	[104]
		Triethanolamine	SMM	1.3	0.25	[104]
			TBM	1.15	0.03	[61]
			TBM	1.13	0.1	[67]
			VBM	1.44	0.1	[32]
		Triisopropanolamine	VBM	1.48	0.1	[32]
		Ethylene glycol	SMM	1.3	0.25	[104]
			TBM	1.09	0.1	[67]
			VRoM	2.0^{uf}	3.6	[55]
		Diethylene glycol	VBM	1.34	0.1	[32]
		Triethylene glycol	VBM	1.26	0.1	[32]
		Propylene glycol	VRoM	2.1^{uf}	3.4	[55]
		Methanol	VRoM	2.7^{uf}	4.2	[55]
		Ethanol	VRoM	2.5^{uf}	4.2	[55]
			VBM	1.48	0.1	[32]
		1-Propanol	VRoM	2.0^{uf}	4.3	[55]
		1-Hexanol	VBM	1.43	0.1	[32]
		1-Decanol	VBM	1.24	0.1	[32]
		1-Heptanoic acid	VBM	1.48	0.1	[32]
		1-Undecanoic acid	VBM	1.51	0.1	[32]
		Oleic acid	TBM	1.11	0.005	[67]
		Poly-acrylic-acid-based	SMM	1.3	0.2	[109]
		Water + sulfite waste liquor (70/30)	TBM	1.02	0.05	[67]
	Quartz	Water	VRoM	1.1^{uf}	5.6	[78]
			TBM	1.05	0.025	[67]
		Methanol	VRoM	1.9^{uf}	4.6	[78]
		Ethanol	VRoM	2.0^{uf}	4.6	[78]
		2-Propanol	VRoM	1.8^{uf}	4.5	[78]
		1-Butanol	VRoM	1.6^{uf}	2.8	[78]
		1-Hexanol	VRoM	1.7^{uf}	4.3	[78]
		Cyclohexanol	VRoM	1.7^{uf}	5	[78]
		Ethylene glycol	VRoM	1.8^{uf}	6	[78]
			TBM	1.06*	0.0175	[27]
			TBM	1.02	0.05	[67]
		Propylene glycol	VRoM	2.0^{uf}	6	[78]
		Glycerol	VRoM	1.8^{uf}	6.8	[78]
		Benzene	VRoM	1.2^{uf}	3.1	[78]

		Hydroxamic acid	TBM	1.08*	0.0175	[27]
		Sodium stearate	TBM	1.08*	0.0175	[27]
		Heptanoic phosphonic acid	TBM	1.07*	0.0175	[27]
		Methyl silicon oil	TBM	1.07*	0.0175	[27]
		Triethanolamine	TBM	1.06*	0.0175	[27]
			TBM	1.03	0.05	[67]
		Cetyl sulfate	TBM	1.05*	0.0175	[27]
		Tributyl phosphate	TBM	1.05*	0.0175	[27]
		Sodium cetyl sulfate	TBM	1.03*	0.0175	[27]
		Dipotassium phosphate	TBM	1.01*	0.0175	[27]
		Lignosulfonate	TBM	1.02*	0.0175	[27]
		Potassium ethyl xanthate	TBM	1.06*	0.0175	[27]
	Feldspar	Water	VRoM	1.2^{uf}	4.8	[62]
		Methanol	VRoM	2.1^{uf}	6.2	[62]
		Ethanol	VRoM	2.5^{uf}	6.2	[62]
		2-Propanol	VRoM	2.1^{uf}	6.2	[62]
		1-Butanol	VRoM	2.8^{uf}	6.	[62]
		1-Octanol	VRoM	1.7^{uf}	3.9	[62]
		Cyclohexanol	VRoM	2.4^{uf}	7.3	[62]
		Tetraethoxysilane	VRoM	2.5^{uf}	7.1	[62]
		Various commercial blends	SMM	1.33*	0.2	[110]
	Blast Furnace Slag	Mix of water/PCE/TIPA	TBM	1.14	0.2	[71]
		Mix of water/PCE/TEA	TBM	1.09	0.2	[71]
		Mix of water/PCE/DEG	TBM	1.08	0.2	[71]
	Fly ash	Triethanolamine + ethylene glycol (1:1)	TBM	1.14	0.05	[111]
	Alumina	Methanol	VRoM	15.6^{uf}	4.6	[112]
		Ethanol	VRoM	12.2^{uf}	2.9	[112]
		2-Propanol	VRoM	13.9^{uf}	2.9	[112]
		Ethylene glycol	VRoM	12.2^{uf}	6.3	[112]
	Calcined black talc		PBM	1.17	n/a	[113]
	Silicon carbide pigment	Polyethylene glycol ether	VBM	2.0^{uf}	1.0	[75]
	Silicon carbide	Polyethylene glycol ether	VBM	2.3^{uf}	1.0	[75]
	Silicon nitride	Polyethylene glycol ether	VBM	1.18	0.5	[75]
	Iron oxide pigment	Polyethylene glycol ether	VBM	1.1^{uf}	1.0	[75]
	Graphite	Tri-sec-butylaluminate	n/a	2.7	1.6 mole/kg	[105]
		Octafluoropentanol	n/a	3.0	1.6 mole/kg	[105]
		1-pentanol	n/a	2.0	1.6 mole/kg	[105]
	Chitosan powder	Polyethylene glycol	PBM	1.75*	10.0	[38]
		Lauryl alcohol	PBM	2.07*	10.0	[38]
Solid	Cement and cement clinker	Carbon black		1.49	1.28	[43]
		Stearic acid	TBM	1.07	0.025	[35]
			BBM	1.09	0.025	[107]
		Lauric acid	BBM	1.06	0.025	[107]
		Myristic acid	BBM	1.07	0.1	[107]
		Sodium stearate	TBM	1.17	0.0175	[27]

		Sodium hydroxamic acid salts	TBM	1.16	0.0175	[27]
	Limestone	Calcium stearate	TBM	1.22*	0.4	[54]
			VBM	1.03	0.05	[63]
		Magnesium stearate	VBM	1.15	0.05	[63]
		Palmitic acid	VBM	1.08	0.10	[63]
		Stearic acid	VBM	1.13	0.10	[63]
	Soda glass	Lithium nitrate	VBM	47.4^{uf}	15.0	[41]
	Sericite	Lithium nitrate	VBM	2.8^{uf}	33.3	[42]
		Sodium nitrate	VBM	3.0^{uf}	33.3	[42]
		Potassium nitrate	VBM	4.2^{uf}	33.3	[42]
		Rubidium nitrate	VBM	4.7^{uf}	33.3	[42]
	Aluminum	Stearic acid	VBM	n/a	2.2-3.1	[36]
		Oleic acid	VBM	n/a	3.2-4.6	[36]
		Aluminum stearate	VBM	n/a	6.4-9.0	[36]
	Brass powder	Stearic acid	TBM	n/a	0.1-0.4	[37]
		Paraffin wax	TBM	n/a	0.1-0.4	[37]
		Oleic acid	TBM	n/a	0.1-0.4	[37]
	Zinc oxide	Sodium chloride	PBM	3.58^{uf}	n/a	[39]
	Nickel oxide	Amorphous carbon	VBM	1.36^{uf}	1.5	[114]
	Zirconia	Sodium chloride	PBM	3.75^{uf}	20.0	[40]
	Alumina	Sodium chloride	PBM	1.42^{uf}	20.0	[40]
	Iron oxide pigment	Nano-disperse silicon oxide	VBM	1.16^{uf}	1.5	[75]
		Nano-disperse alumina	VBM	1.57^{uf}	1.5	[75]
	Chitosan powder	Citric acid	PBM	1.12*	10.0	[38]
		Cholesterol	PBM	2.07*	10.0	[38]
		Lauric acid	PBM	2.43*	10.0	[38]
		Lauryl amine	PBM	2.80*	10.0	[38]
		Sodium lauryl sulfate	PBM	2.55*	10.0	[38]
		Capric acid	PBM	2.33*	10.0	[38]
		Myristic acid	PBM	2.95*	10.0	[38]
		Palmitic acid	PBM	2.95*	10.0	[38]
		Stearic acid	PBM	3.11*	10.0	[38]

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