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Development of Novel Compaction Regimes for Hydrogen Storage Materials

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Project ID # st151

Overview

Timeline and Budget

Timeline

- Project Start Date: 04/09/2018
- Project End Date: 10/08/2018

Budget

- Total Project Budget: $149,751

Barriers

- Barriers addressed:
- A. System Weight and Volume
- D. Durability/Operability

Partners

- No partners currently

Abstract

Fuel Cell Electric Vehicles (FCEV) are an emerging technology for improving energy efficiency and reducing pollution emissions related to transportation. However, improving on-board Hydrogen storage is a key challenge to the advancement of light duty FCEV. Current storage methods utilize composite on-board vessels for high pressure Hydrogen gas. This method is costly and requires large storage volumes which is problematic for light duty vehicles.

Alternative methods of storage using materials that either chemically bind and release hydrogen, or reversibly adsorb hydrogen, have long been investigated as a means to lower the onboard storage pressure, reduce overall system and delivery costs, and lessen safety concerns. However, these materials struggle to meet the system targets for volumetric density due to packing inefficiencies of the storage materials.

This shortfall of hydrogen sorption storage systems can be overcome by densification of absorbent material while maintaining available surface area.

In Phase I, suitable sorbent materials will be chosen for evaluation, and tested for initial material properties and performance characteristics. Based on material properties, material will be densified via compaction processes optimized to the specific material. Materials will be tested for performance properties after densification to quantify improvements in overall performance. Following evaluation of material performance, process refinement will be addressed.

Relevance

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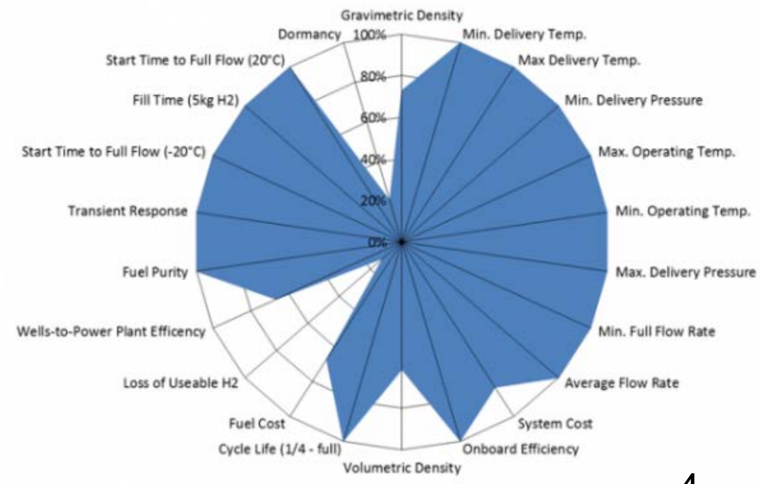
- Objective: To establish novel material densification regimes for sorbent materials utilized in hydrogen storage systems (w/high volume storage of small footprint), and required solids processing methods based on incoming material properties of sorbent powder feeds, using industry standard design principles of single and/or dual stage granulation & compaction processes.

- Anticipated Impact DOE Technical System Targets:
  - System Volumetric Capacity
    - Increase H_2 volumetric uptake
  - Durability/Operability
    - Increase mechanical strength of sorbent form

Projected MOF-5 System Compared Against 2020 Targets
(100 bar, 80-160K, Type I Tank, Hexcell – loose powder)



Approach: Key Objectives (1)

1. Establish likely solids processes:
- Fabricate high-density powder compacts or granulate
- Maintain accessible surface area/pore space to meet volumetric DOE targets
- Review multi-step processes (e.g. wet/dry granulation plus tableting)

2. Assess <u>bulk material properties</u> of MOF and carbon powders:
- Wetting behavior & related stability
- Powder and die/roll/wall friction vs. pressure
- Powder cohesion, bulk permeability, bulk density vs. pressure

3. Evaluate typical, likely process methods:
- Wet solvent-based granulation methods that maintain sorbent stability
- Roll pressing as a dry granulate production method
- Tableting as a dry compaction method (both powder or granulate feeds)
- Evaluate accessible surface area and mechanical integrity

4. Preliminary formulation design:
- Assess the addition of select, non-sorbent materials (excipients, lubricants)
- To improve process operability and product uniformity and strength
- Increase volumetric capacity at reduced footprint

5. Develop a commercialization plan:
- Down select representative sorbent formulations & process methods, w/ costing
- Identify sorbent and processing partners & collaborators
- Establish Phase Two plan

Approach: Key Objectives (2)

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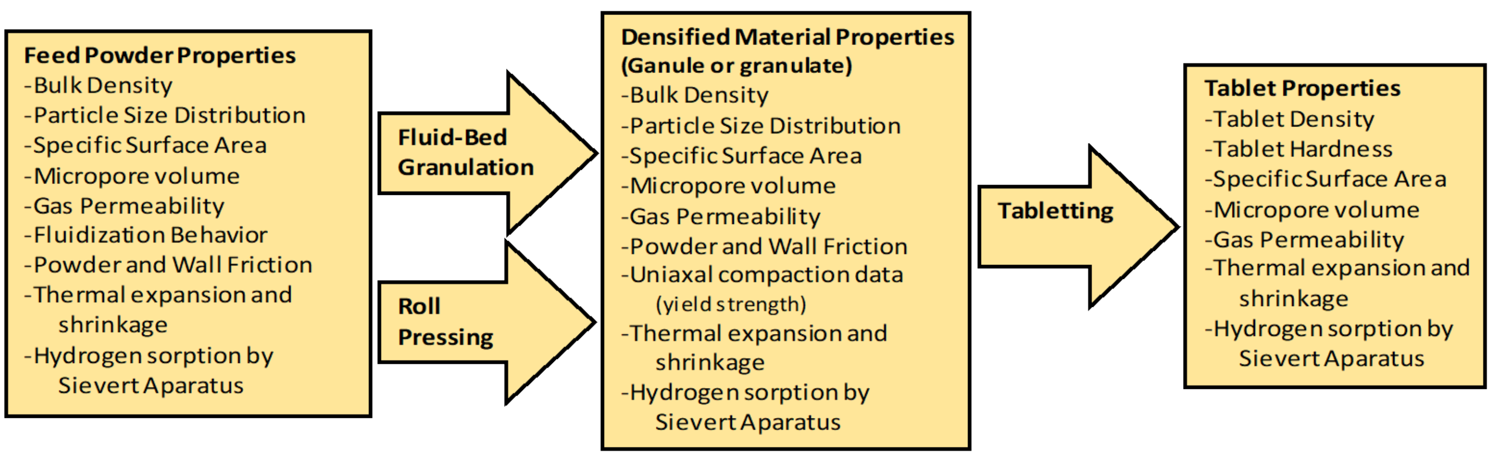
Specific Phase I Activities:

1. Selection of porous carbon and MOF sorbent feed powders.
2. Construction of In-House Sievert
3. Material Property Characterization of Sorbent Feed Powders.
4. Initial Densification Trials by Granulation and Compaction.
5. Material Property Characterization of Densified Material.
6. Down-Selection of Sorbent Materials for Additional Densification Studies.
7. Performance metrics.



Example multistep densification process for H2 sorbent materials, w/ feed powder, granulate and compact characterization.

Approach: Overview

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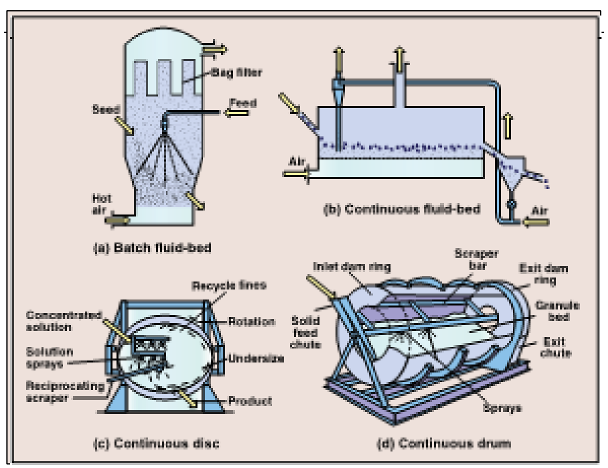
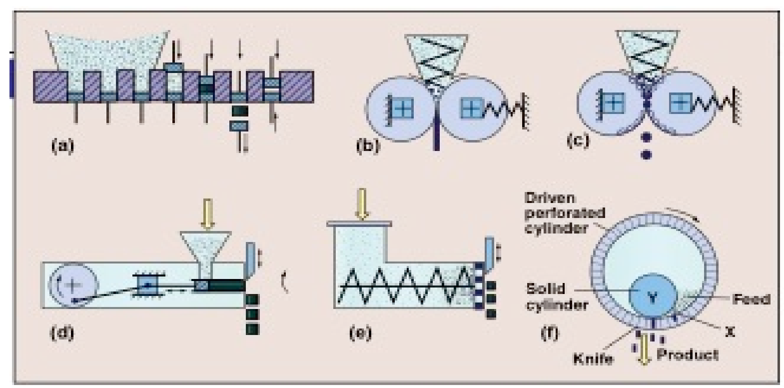
Overview of granulation & compaction:

- To significantly increase bulk density of a feed powder
- With controlled porosity and mechanical strength
- In a free flowing, non-segregating defined meterable structural form
- While maintaining key powder attributes (e.g. accessible surface area)
- Employing industry standards of engineering process-formulation design
- Using often wet granulation, dry granulation, and tableting processes
- PI team has 30 decades of experience in granulation/compaction design





Example processes. (left) Low-shear granulation processes include both batch and continuous choices, such as the batch and continuous fluid-beds, and continuous rotating discs and drums. (right) . Examples of compressive agglomeration include: For dry compaction, (a) tableting, (b) roll pressing, (c) briquetting, (d) ram extrusion; and for paste extrusion, (e) screw extrusion and (f) concentric-roll pelletizing. From Ennis.[9]

Approach: What is Wet Granulation?

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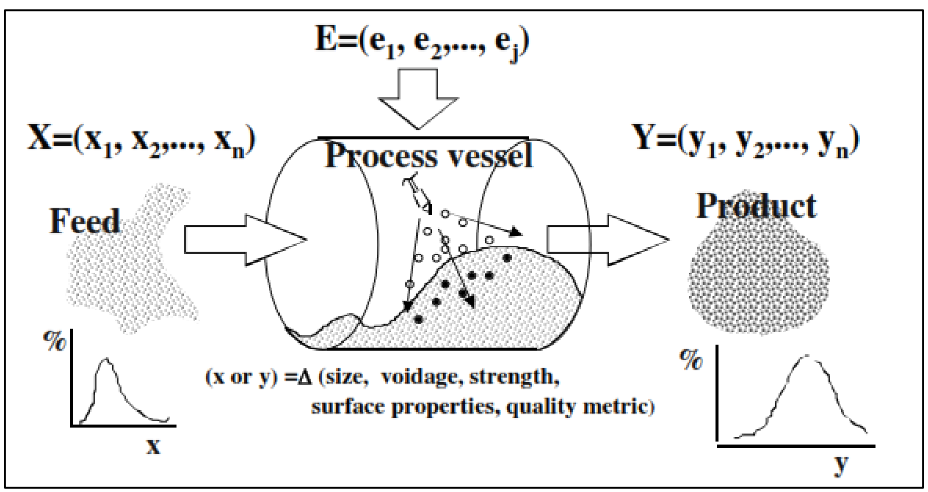
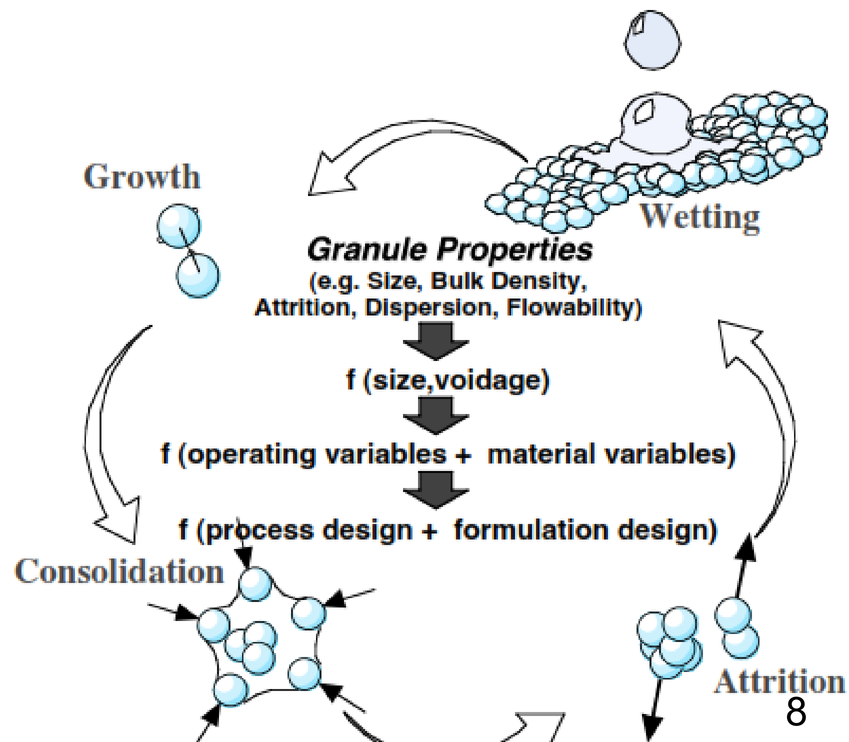
- What is wet granulation?
  - Controlling granule size and internal porosity
- Rate process steps in wet granulation:
  - wetting, growth, consolidation, attrition
- Material properties:
  - wettability, wet mass rheology, permeability, fracture toughness



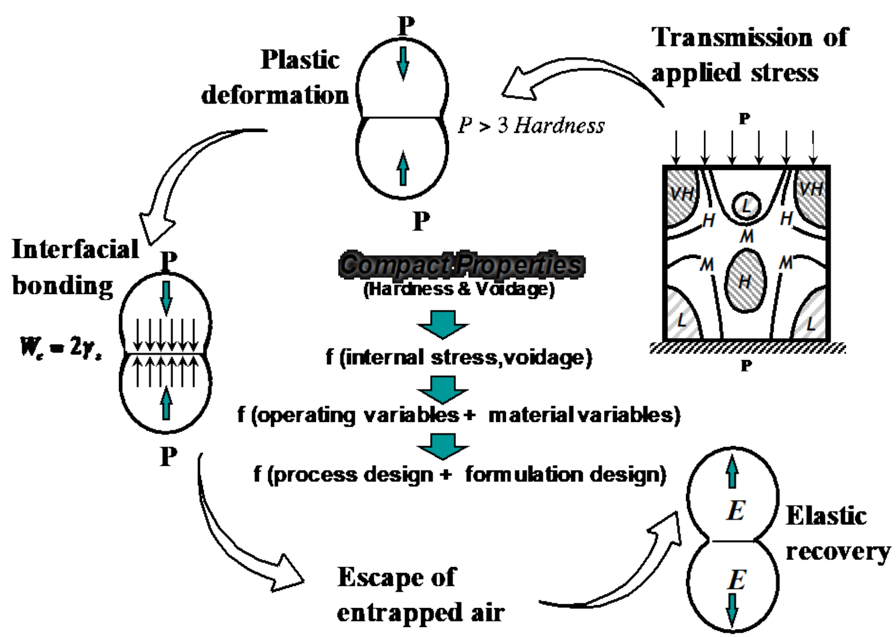


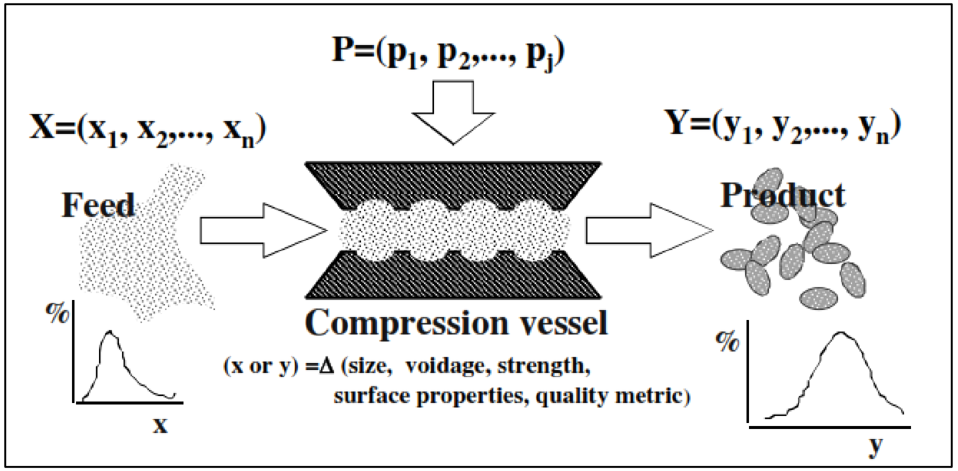
Approach: Wet Granulation

Define desired properties of final granule product	Size distribution, wettability, permeability, powder flowability, powder friction, wall friction
↓	
Material characterization of feed powder properties	Size distribution, wettability, permeability, powder flowability, powder friction, wall friction
↓	
Design formulation to achieve desired granule properties	Surfactants, wetting & dispersants, diluents, binders & lubricants, solvents
↓	
Select granulation process based on formulation and desired granule properties	Tumbling granulators, mixer granulators, fluid-bed granulators
↓	
Select operating variables based on formulation, process, and desired granule properties	

Approach: What is Compaction?

- What is dry granulation and compaction?
  - Controlling compact strength and <u>uniformity</u> of internal porosity
- Mechanical steps in dry granulation & compaction:
  - Zone filling, stress transmission, plastic deformation, bonding, deareation, elastic recovery & flaw/damage
- Material properties:
  - Powder/wall friction, hardness, brittle v. plastic, interfacial energy, permeability vs. load, elastic modulus





Approach: Processes compared

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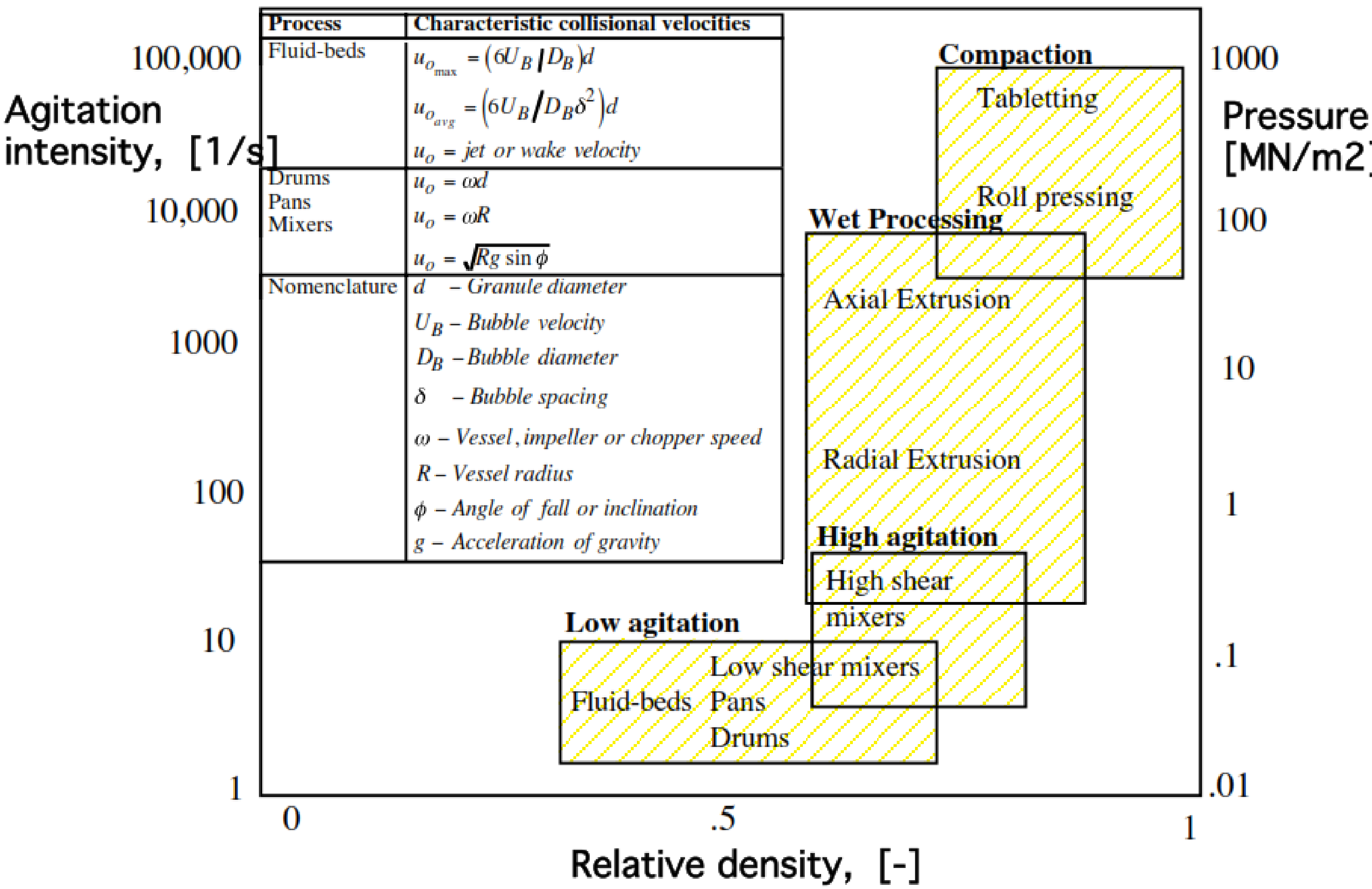
- Density map of granulation/compaction processes



Approach: Processes compared

- Process selection considerations of granulation/compaction processes

Attributes	Process:					
	Batch Fluid Bed	Continuous Fluid Bed	Continu-ous Disc	Continu-ous Drum	Batch Mixer	Continu-ous Mixer
Process Characteristics						
Typical pre/post processing	C	C, R	B,D,C,R	B,D,C,G,R	D,C	D.C,T
Ease of dust/toxicity containment	Y	Y	N	N	Y	Y
Ease of cooling or heating	H	H	L	L	H	H
Typical level of recycle	L	L-M	L	H	L-M	L-M
Heat activated granulation	N	N	N	N	Y	Y
Simultaneous drying / reaction	Y	Y	N	Y	Y	Y
Competing deformable growth	N	N	?	?	Y	Y
Stable non-deformable growth	Y	Y	Y	Y	N	N
Acceptable Feed						
Sensitive to small feed variations	L	L	L	L	M	M
Heat or pressure sensitive	Y	Y	Y	Y	?	?
Able to process induction time	Y	Y	N	?	Y	? (1)
Poor wettability / high viscosity	N	N	N	N	Y	Y (1)
Product Appearance Attributes						
Flowability for metering	M-H	M-H	VH	M-H	M	M
Product form	SG	SG	VSG	SG	IG	IG
Width of size distribution	M	M	L	M	M-H	M-H
Size range, mm	0.2–1	0.1–3	0.5–20	2–20	0.1–3	0.1–3
Production, ton/h or kg/batch	100–900	50	0.5–800	0.5–800	100–500	50
Product density	L-M	L-M	M	M	M-H	M-H

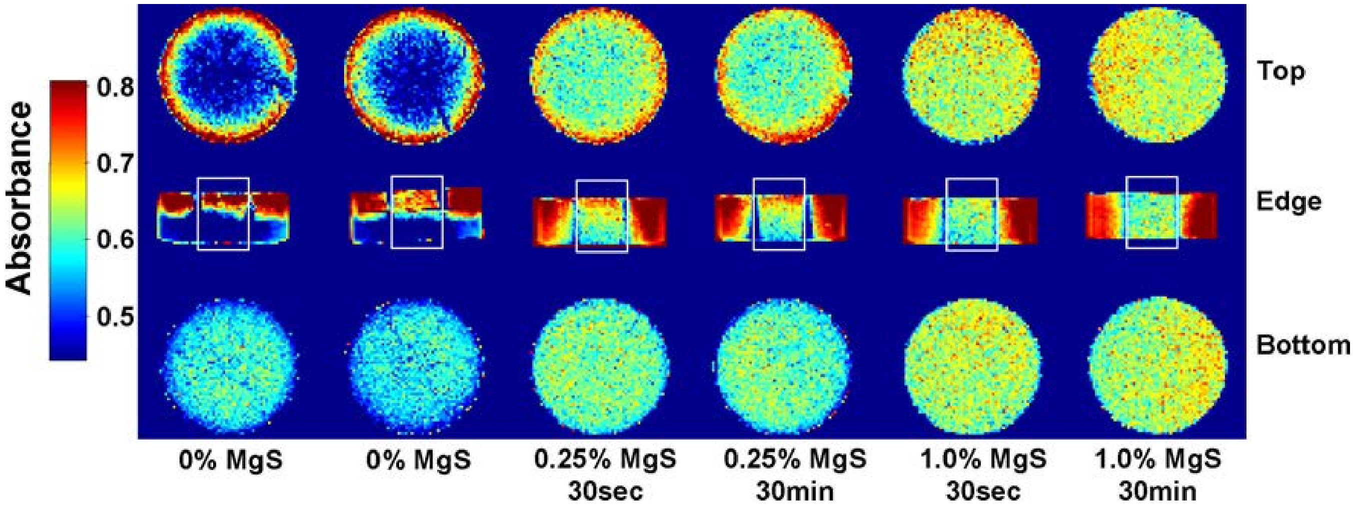
General comments: Binder required. Either solvent required, or in some cases, heat-activated binder. Maximum feed of 500 μm smaller preferred. Moisture no more than 80% pore saturation. Able to process brittle, abrasive, elastic, most plastic materials.
Definitions: Y=yes, N=no, ?=possible
zzΩΩ
Processing: C=Classification, R=Recycle, B=Blending, D=Drying, G=Grinding, T=Two-stage
Notes: (1) Dependent on contact time.

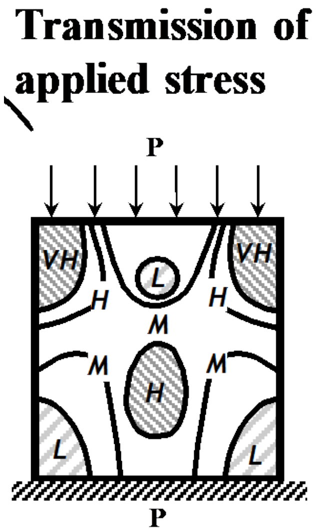
Attributes	Process:						
	Roll Pressing (smooth)	Roll Press-ing (pattern)	Tablet-ting	Ram/ Piston Extrusion	Pelleting Mills	Radial Extrusion	Axial Extrusion
Process Characteristics							
Typical pre/post processing	B,G,C,R,T	T,B	T,B	T,B	B,C,D,R	B,C,D,R	B,C,D,R
Ease of dust/toxicity containment	M	M	H	H	M-H	H	H
Ease of cooling or heating	H	M	L	H	L	H	H
Typical level of recycle	M-H	L-M	O	O	L	L	L
Heat activated granulation	N	N	N	N	N	Y	Y
Solvent	N	N	N	N	Y	Y	Y
Simultaneous reaction	N	N	N	N	N	Y	Y
Acceptable Feed							
Sensitive to small feed variations	VH	H	H	VH	VH	H	VH
Can process hard materials	N	N	N	N	Y	Y	Y
Can process low permeability	Y	?	N	N	Y	Y	Y
Can process low wall friction	N	Y	Y	Y	N	?	?
Product Appearance Attributes							
Flowability for metering	M	M	M	M	M	M	M
Product form	IG	B	T	IT	C-SG	C-SG	C-SG
Width of size distribution	M-H	VL	O	O	L	L	L
Size range, mm	0.2–5	5–50	5–10	5–10	0.5–3	0.5–3	0.5–3
Production, ton/h or kg/batch	50	50	1	5	10	5	5
Product density	H	H	H-VH	H-VH	H-VH	M-H	VH

General comments: Binder not required except for some hard mateirals. Small levels of moisture common; must be low or compaction arrested. Minimum feed of 100 μm, unless deaeration/vacuum provided. Moisture no more than 80% pore saturation. Non-wettable material acceptable.
Definitions: Y=yes, N=no, ?=possible
Product form: L=low, M=medium, H=high, V=very, G=granular, S=spherical, I=irregular, T=tablet form, C=cylindrical
Processing: C=Classification, R=Recycle, B=Blending, D=Drying, G=Grinding, T=Two-stage
Notes: (1) Dependent on contact time.

Approach: Challenges in compaction

- Poor stress transmission and density maldistribution
- Rate limiting deareation (related to low powder permeability, fine powder)
- Leads to unnecessary losses in surface area
- Corrected by lubricants, compact geometry, dwell profile, vacuum feeds





Tablet density profiles by chemical imaging. Comparison of tablet absorbance or density profiles for lactose tablets. Representative images of tablet tops, bottoms, and edges are shown for 0%, 0.25%, and 1.0% MgS blended 30 s or 30 min. Higher absorbance correlates to higher density.

Approach: Challenges in compaction

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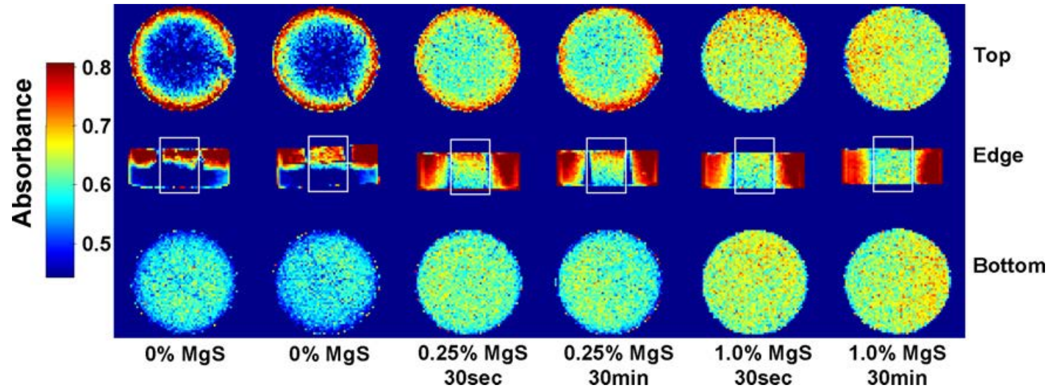

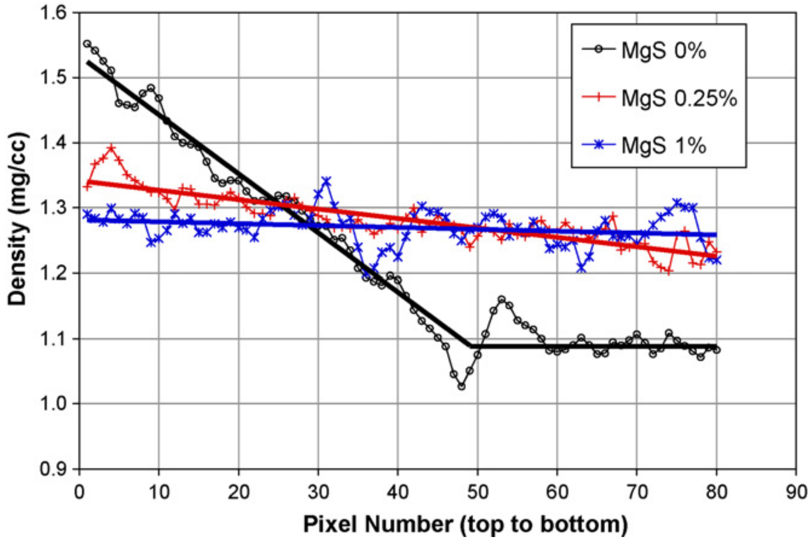

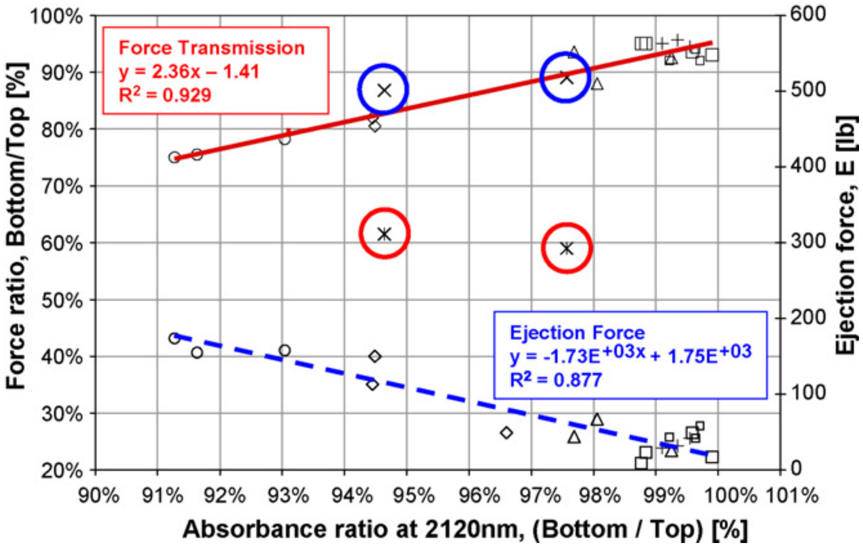

Tablet density profiles & ejection forces. Tablet density profiles (top to bottom), stress transmission ratios (force ratio) and ejection force for varying MgS lubricant for lactose formulations. Higher absorbance correlates to higher density.

Accomplishments and Progress

- Acquisition of MOF-5 and porous carbon samples

- Preparation of equipment for granulation & compaction trials:
  - Fluid-bed granulator
  - Tumble granulator
  - Laboratory roll press
  - MCC Presster™ Tablet Press Simulator

- Preparation of material characterization equipment
  - Sympatec HELOS for particle size distribution
  - Micromeritics Tristar for BET surface area & porosity
  - Micromeritics Accupyc™ for skeletal density
  - Rame-Hart goniometer for contact angle & wettability
  - iShear™ Rotary Shear Cell for powder flowability and friction
  - iFluid™ Permeability Cell for gas permeability and fluidization behavior

Responses to Previous Year Reviewers' Comments

This project was not reviewed last year.

Collaboration & Coordination

- E&G is working to initiate collaborations:
  - NREL for high pressure sorption capacity measurement of granules and compacts produced from this project.
  - Univ. of TN for uniaxial compression characterization and high pressure friction to complement E&G Prester tablet press replicator

Remaining Challenges and Barriers

- Densification of sorbent materials offers several challenges, of which some of the requirements are:
  - Maintaining high active pore volume and high accessible surface area of adsorption, as well as uniformity of these properties, as close as possible to the original raw powder.
  - Achieving sufficient mechanical strength (and related properties such as flex strength) of the form for handling and final end-use, including during repeated, long term operational cycling.
  - Avoiding thermal or chemical degradation of the MOF powder during production.

Proposed Future Work

- Acquisition of porous carbon and MOF sorbent feed powders.
- Material property characterization of sorbent feed powders.
- Initial densification trials by granulation and compaction.
- Material property characterization of densified material.
- Down-selection of sorbent materials for additional densification studies.
- Evaluate final material properties against performance metrics.
- Propose Phase II work based on results of Phase I work.

Any proposed future work is subject to
change based on funding levels

Summary

- For select sorbent materials, characterize particle scale and bulk powder scale properties relevant to granulation and compaction processes.
- Identify granulation formulations and processes that will increase volumetric sorption capacity.
- Conduct granulation trials with sorbent materials
- Conduct compaction trials with granulated sorbent and raw feed powder.
- Characterize hydrogen storage capacity of granules and compacts.