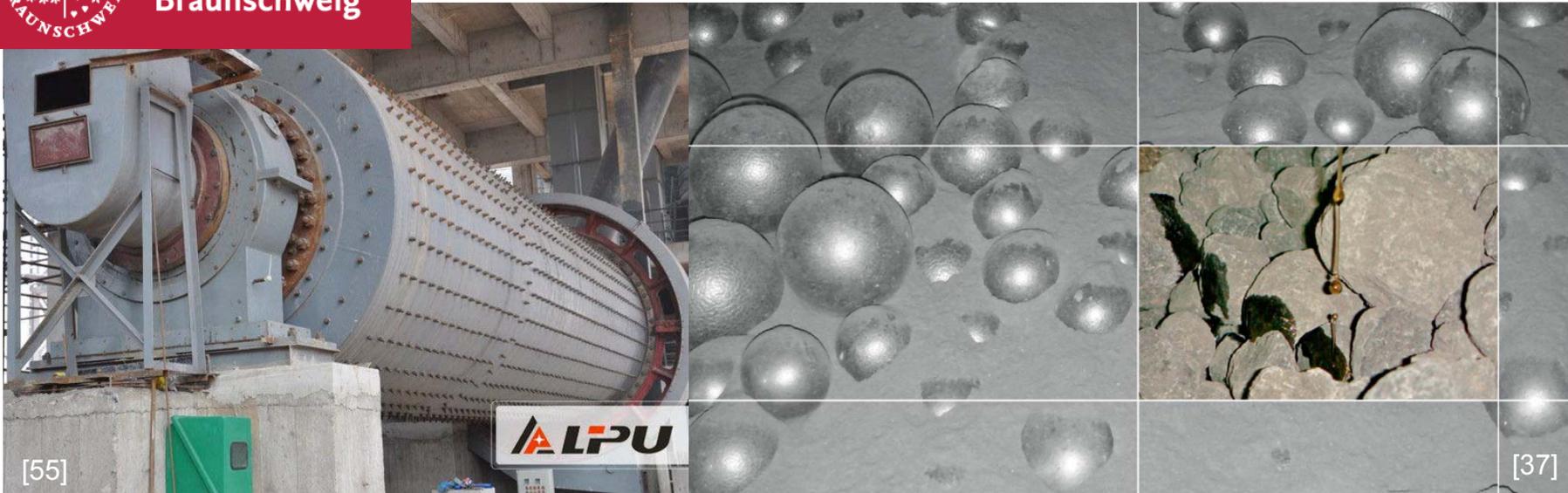




Technische
Universität
Braunschweig



Grinding Aid Review

IFPRI 40th Annual General Meeting

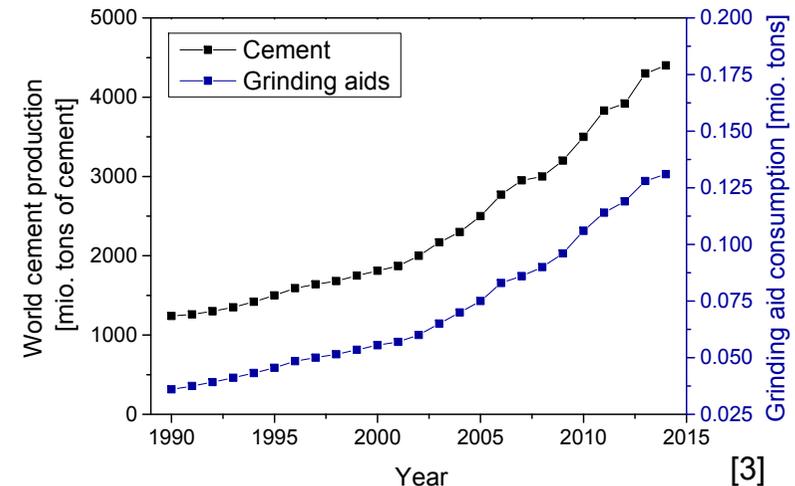
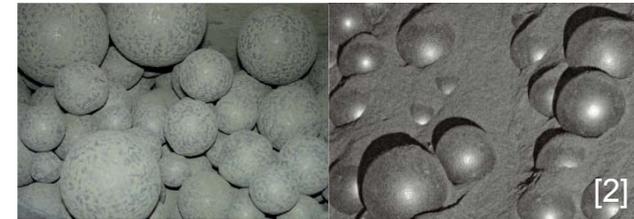
P. Prziwara, A. Kwade

24th June 2018

Introduction

Grinding aids = **Liquid / dissolved / solid additives**

- Application in dry grinding processes to improve the grinding performance
- Originally: Coming from the cement sector (1930's) [1]
- Today: Great importance in many industries
→ But: > 80 % of present papers still have a focus on construction materials

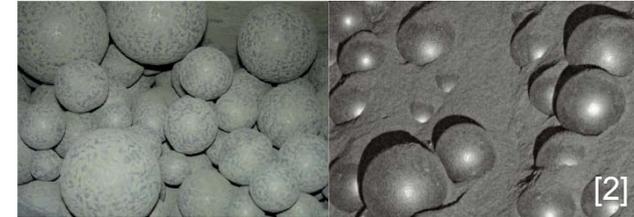


Main objectives [4]

1. Increase of the production capacity
2. Decreasing the specific energy demand
3. Achieving finer products
4. Enabling use of low-quality feed materials

Grinding aids = **Liquid / dissolved / solid additives**

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Main objectives [4]

1. Increase of the production capacity
2. Decreasing the specific energy demand
3. Achieving finer products
4. Enabling use of low-quality feed materials

Despite great industrial importance:

Grinding aid applications are still mostly based on empirical knowledge

Agenda

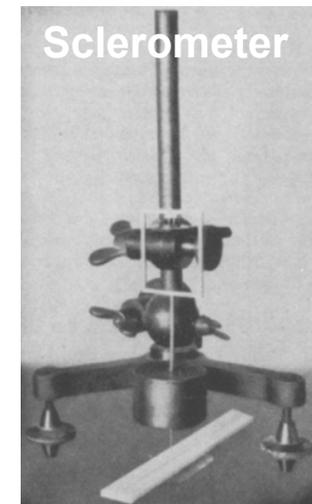
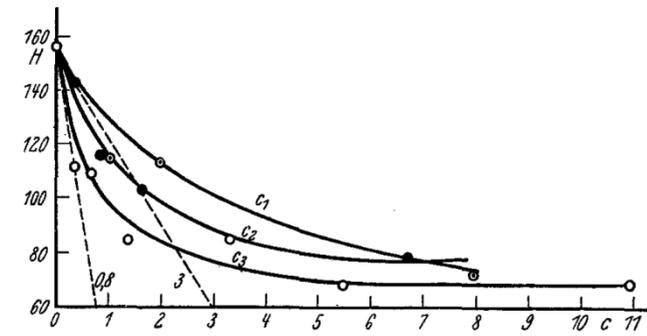
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2. Overview on laboratory studies
 - Liquid, dissolved and gaseous grinding aids
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3. Impact of the stressing conditions on the grinding aid performance
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5. Grinding aids in plant operations
6. Summary and Outlook

Understanding the mode of action

The historical evolution



- **1930's:** First applications of Grinding Aids in the cement industry [1]
- **Rehbinder (1931/32)**^[5,6]: Grinding aids reduce the surface energy of the particles
→ Adsorption-induced reduction of the surface hardness
- **1930s – 1960s:** > 20 studies on impact of surface active substances on mechanical properties of particles and rocks
→ See review by El-Shall^[7]
- **Rose and Sullivan (1958)**^[10]: Extension of Rehbinder theory to grinding in tumbling mills



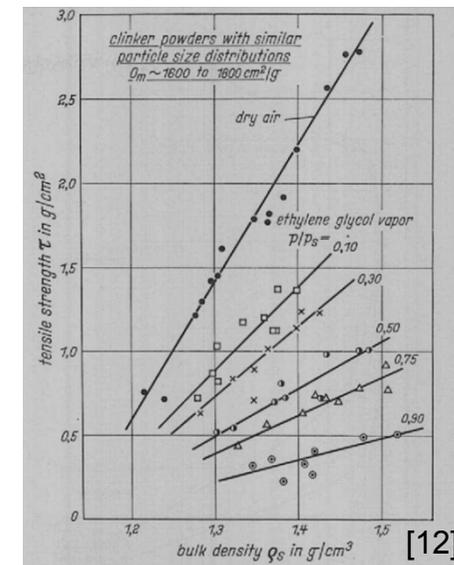
[5]

Understanding the mode of action

The historical evolution



- **Kennedy and Mark (1938)**^[8]: Observation of dust increase by Grinding Aids
→ First suggestion that Grinding Aids effects may be due to particle dispersion
- **1940s**: Effects may be caused by reduction of ball coating^[9]
- **Mardulier (1961)**^[11]: Reduction of surface energy leads rather to a decrease of adhesion forces than to a change of fracture behavior
→ Ball coating solely as an extreme case of agglomeration
- **Von Seebach (1969)**^[12]: Measurement of adhesion forces
→ Reduction by introducing ethylene glycol vapours



Understanding the mode of action

The historical evolution



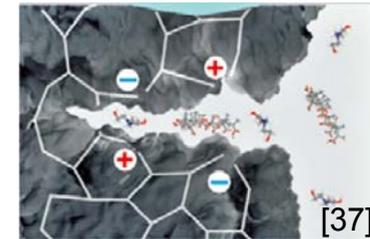
- **Westwood and Goldheim (1970)** ^[13-15]:
The reduction of the material strength by surfactants is only relevant when plastic deformation is important for the fracture
 - Mostly brittle ground products in tumbling mills
 - Thus, further indication against Rehbinder
- New theory: „**Westwood effect**“
 - Adsorption of surfactants blocks the motion of dislocations near the surface
 - Material becomes more brittle
 - Substantial mechanism of grinding aids

Understanding the mode of action

The historical evolution



- **Schönert 1972** ^[16]: Measurement of crack propagation velocities
→ Crack propagation too fast for the grinding aid molecules to „follow“ the crack
- **Locher, Von Seebach 1972** ^[17]:
→ No impact of grinding aids on breakage in the case of brittle fracture
→ Grinding aids promote comminution by abrasion as the molecules prevent the (re)agglomeration of the fine abraded particle
- **Somasundaran, Lin 1972** ^[18]: Statement against the relevance of Reh binder/Westwood
- **Graichen et al. 1974/75** ^[19]: No impact of grinding aids on breakage propability
→ Valid for single particle stressing by both compression and impact



Understanding the mode of action

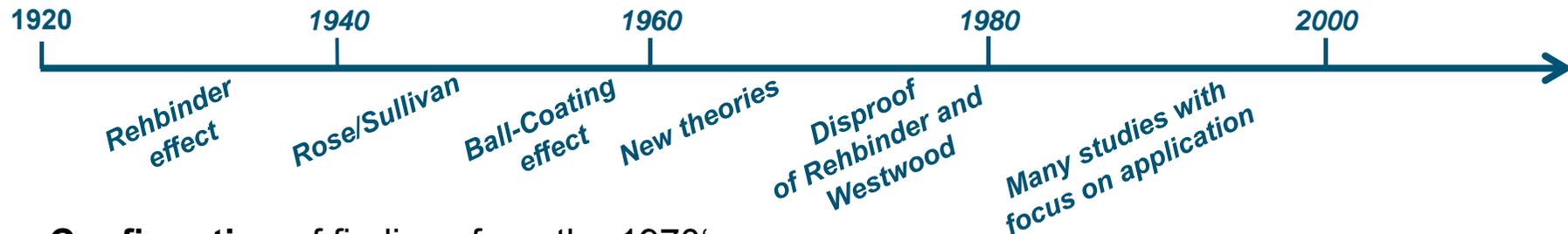
The historical evolution



Disproof of the relevance of both
Rehbinder and Westwood
for technical dry grinding of
inorganic materials

Understanding the mode of action

The historical evolution

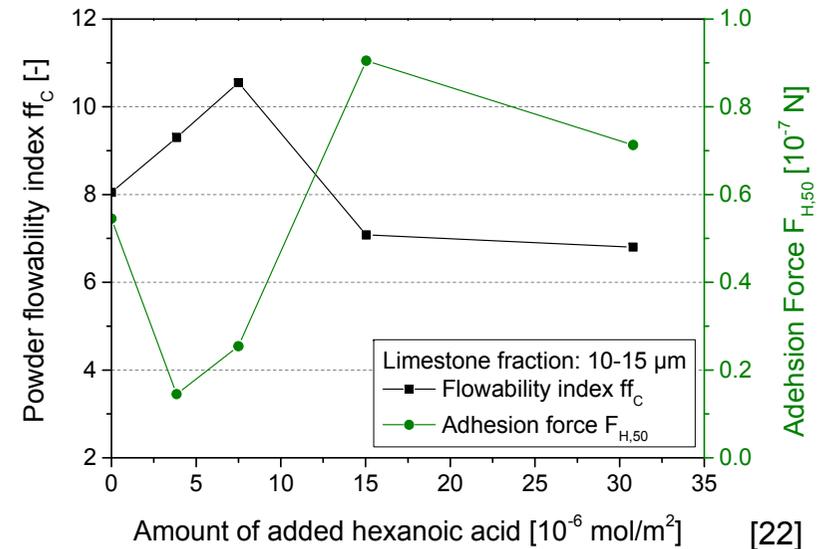


Confirmation of findings from the 1970's:

- Reduction of adhesion forces, thus change of:
 - a) Tendency of agglomeration
 - b) Flow and bulk properties
- Micro-processes inside the mill [20]
- Overlapping impacts on macro-processes [21] (e.g. axial material transport)

Further important results:

- Increasing effectiveness for high product fineness
- Grinding aids may act solid-specific
- The surface coverage of the product particles determines optimum concentration



Understanding the mode of action

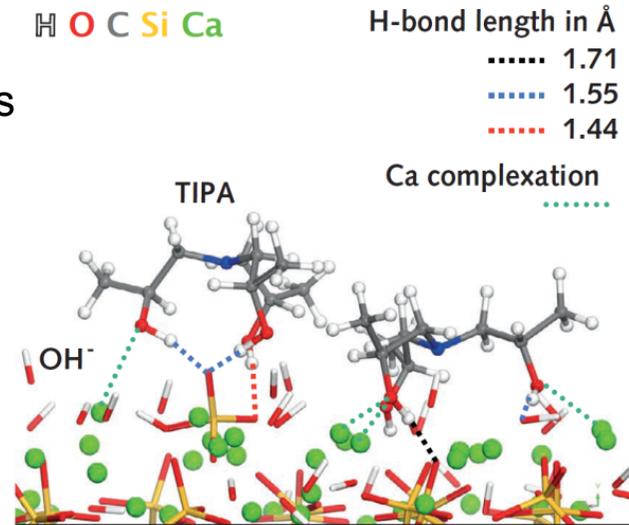
The historical evolution



New insights by **innovative techniques**:

Molecular simulations by **Weibel et al.**^[23], **Mishra et al.**^[24]

- Molecules adsorb on (clinker) surface with their polar parts
- The adsorption strength is important for a stable adsorption layer
 - But: Adsorption strength \neq Reduction of agglomeration energy
 - Overlapping impact of binding geometry and steric effects on stabilization
- Agglomeration energy is more decisive for the grinding result



Understanding the mode of action

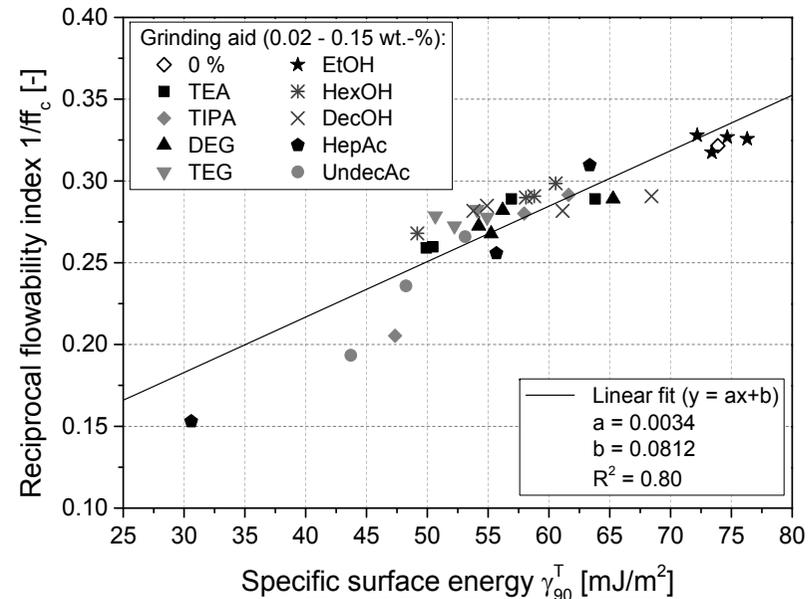
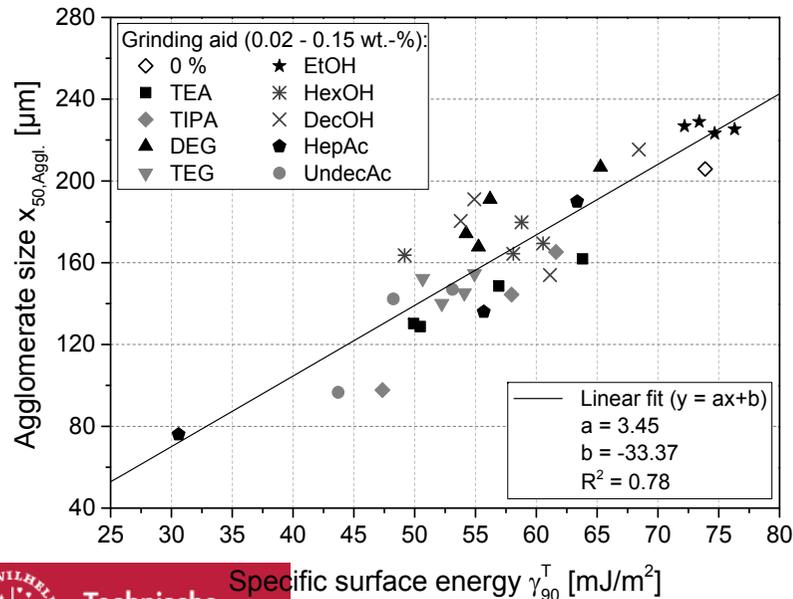
The historical evolution



New insights by innovative techniques:

Prziwara et al. [25]: Surface energy measurement by inverse gas chromatography

→ Final proof: Reduction of surface energy = key parameter for reduction of adhesive forces



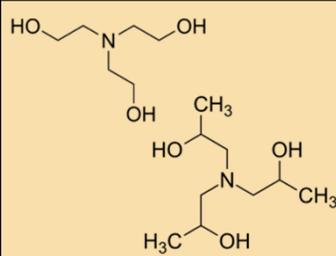
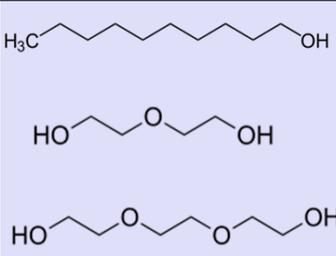
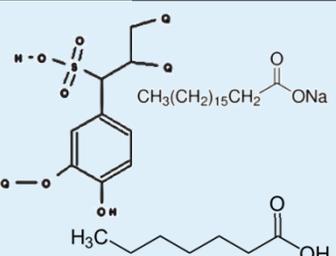
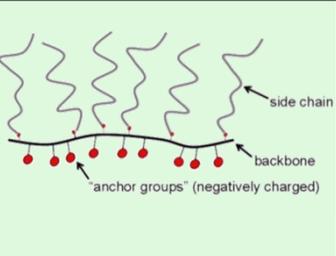
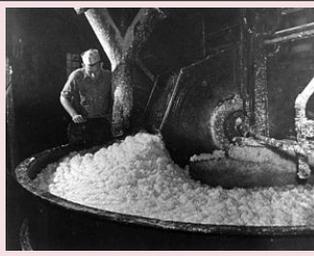
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Types of grinding aids

Liquid / Gaseous / Solid

I. Liquid and dissolved grinding aids (>100 chemicals in the literature)

Alcohol amines	Simple alcohols + poly alcohols	Organic acids + their salts	Poly carboxylate ethers (PCE)	Waste products
				

II. Gaseous grinding aids

- Chemicals with high volatility (e.g. ammonia, acetone, methanol)

III. Solid grinding aids

- Dry organic compounds with melting points (slightly) above room temperature
- Colloidal sub-micron particles
- Dry (mainly inorganic) particulate grinding aids with high melting points

Laboratory grinding experiments

I. Liquid / dissolved grinding aids

Liquid and dissolved grinding aids = Most common type

Normally: Commercial grinding aid blends of liquid and dissolved components

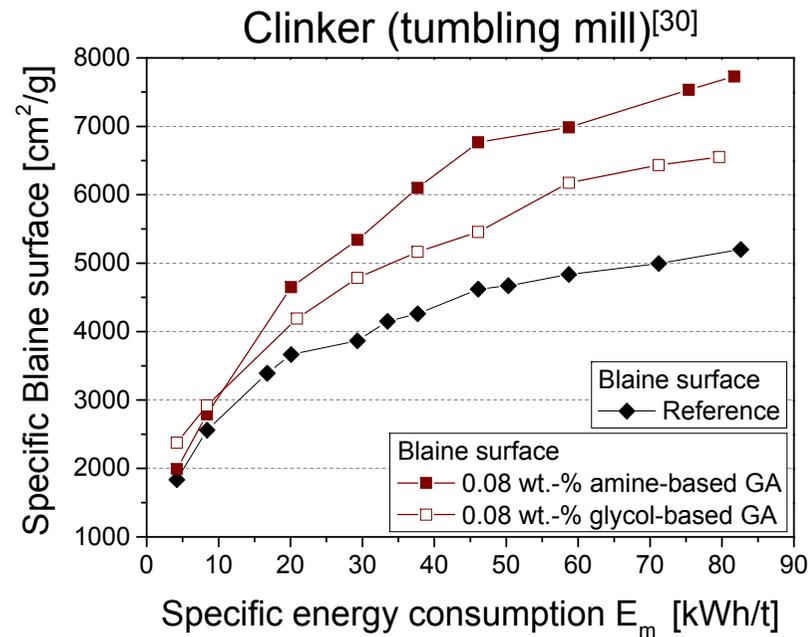
- + Most understood
- + Easy handling
- + Low quantities necessary
- + Miscible
- Possible removal via mill air (up to 13 %^[26])

Originally: Grinding aids in the field of construction materials

- (Pure) cement clinker, Portland cement
- Substitutents (limestone, fly ash, granulated blast furnace slag)
- Blended cements
- Minerals (feldspar, graphite, ...)
- Ceramics (alumina, quartz, pigments)
- Minority: Organic materials

Laboratory grinding experiments

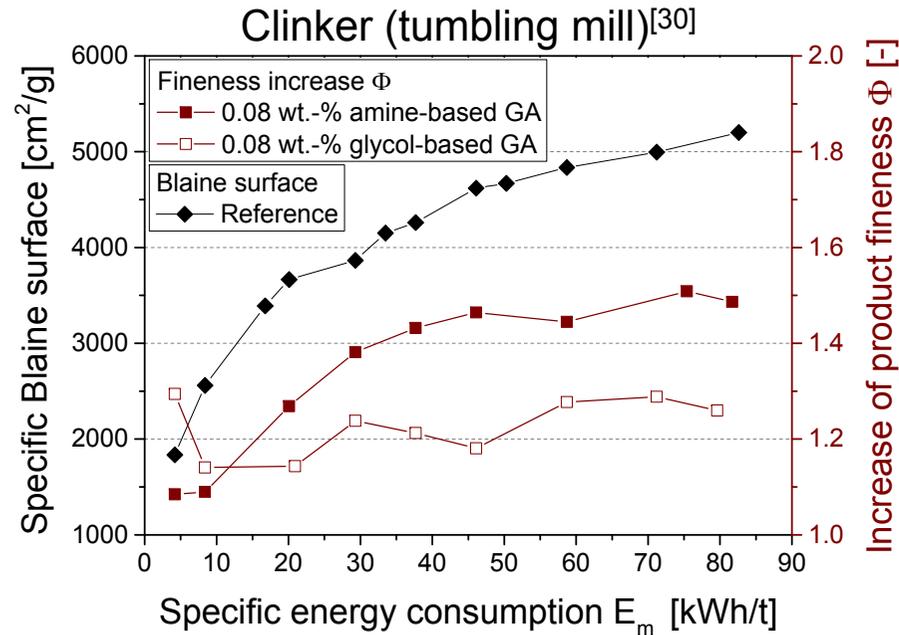
I. Liquid / dissolved grinding aids



- Usually stronger grinding aid effects at higher product fineness
- Grinding aids may act different, also depending on the product fineness

Laboratory grinding experiments

I. Liquid / dissolved grinding aids



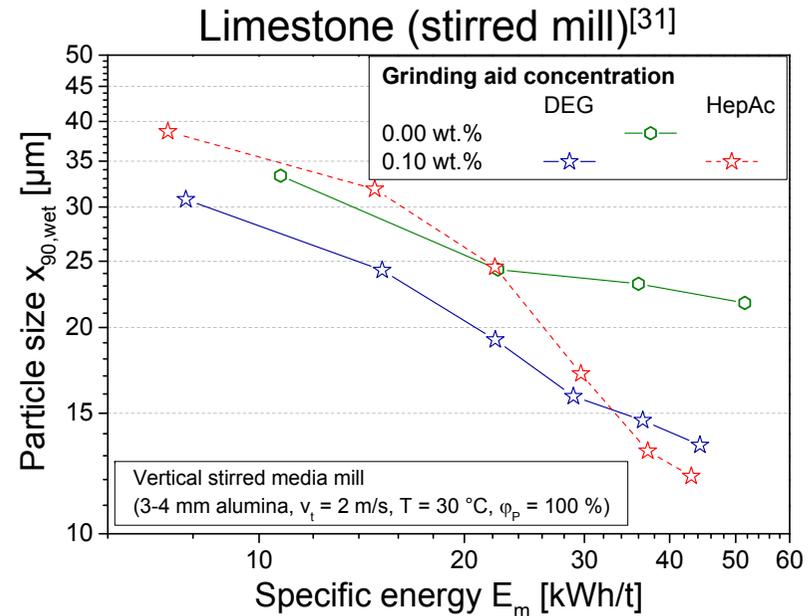
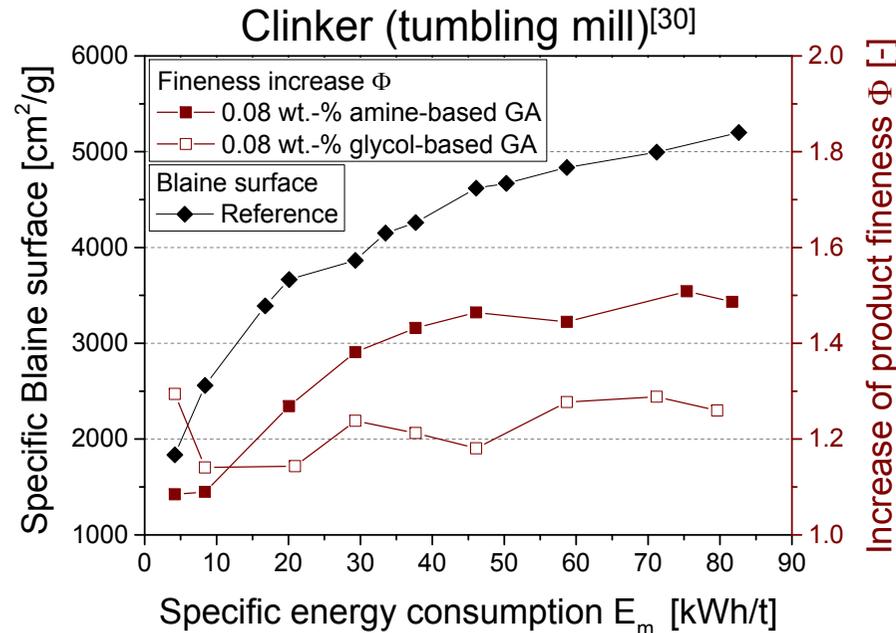
Relative increase of the product fineness

$$\phi_{GA} = \frac{S_{m,with\ GA}}{S_{m,without\ GA}}$$

- Usually stronger grinding aid effects at higher product fineness
- Grinding aids may act different, also depending on the product fineness

Laboratory grinding experiments

I. Liquid / dissolved grinding aids



In the most cases: No information about the actual surface coverage

- Number of added active molecules
- Space requirement of each molecule
- Real specific product surface area

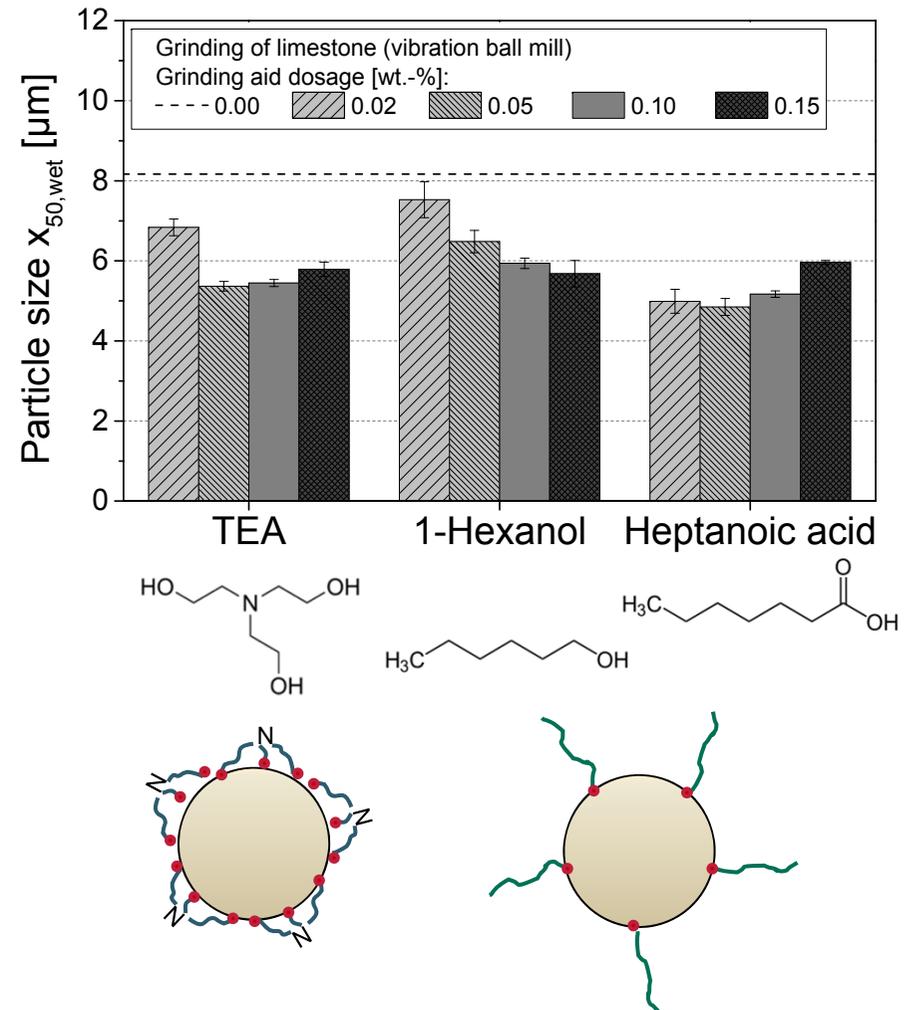
} Optimum concentration?

Laboratory grinding experiments

I. Liquid / dissolved aids - required amount

Example: Grinding of limestone

BET surface [m ² /g]	Optimum conc. [wt.-%]
2.0 – 2.5 [25]	0.05 – 0.15
3.2 [32]	≈ 0.2
> 30 [33]	> 4.0

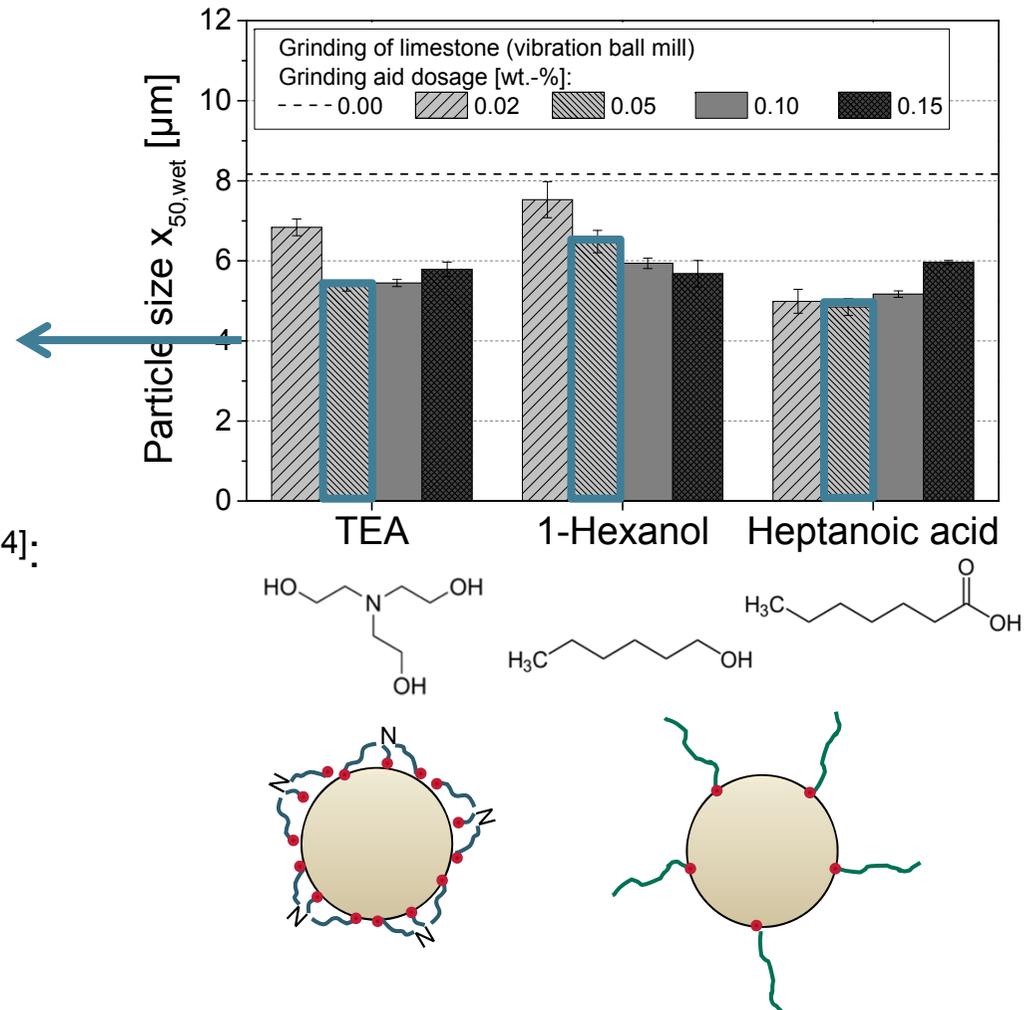


Laboratory grinding experiments

I. Liquid / dissolved aids - required amount

Important: Actual surface coverage

0.05 wt.-% additive	No. Molecules / surface [$10^{18}/\text{m}^2$]
TEA	0.65
Hexanol	1.49
Hep.Ac.	0.82



Adsorption of stearic acid on calcit^[34]:
Monolayer at $3.6 \times 10^{18}/\text{m}^2$

- Actual spec. product surface
- Chemical properties
- Binding geometry

Laboratory grinding experiments

I. Liquid / dissolved aids - Summary

Alcohol amines / poly alcohols

- All-rounder: Efficient for most inorganic materials
- Best grinding aids for cementitious materials [21,35]
 - Cement: $\phi_{GA,max} \approx 1.5$
 - Limestone: $\phi_{GA,max} \approx 1.4$
 - Quartz: $\phi_{GA,max} \approx 1.1$

Relative increase of the product fineness

$$\phi_{GA} = \frac{S_{m,with\ GA}}{S_{m,without\ GA}}$$

Organic acids / salts

- Best grinding aids for limestones [21,25,35] ($\phi_{GA,max} \approx 1.5$)

PCE

- Good performance in closed-circuit plants [36]
- Especially beneficial in combination with conventional aids [36,37]

Waste products

- Grinding performance can be enhanced (e.g. with sulfite waste liquor^[35] or soapstock^[38])
- Inferior to most of the classical chemicals, but cheaper

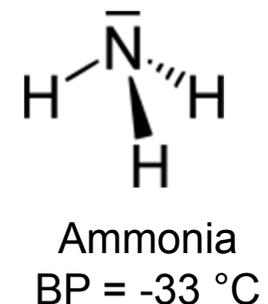
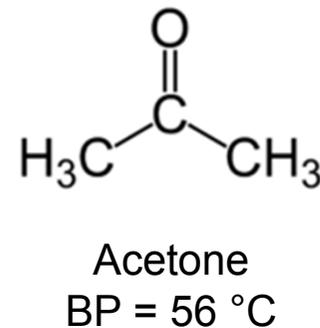
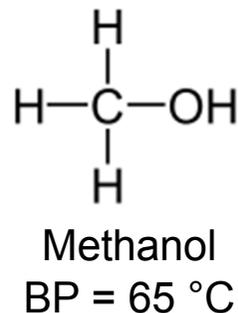
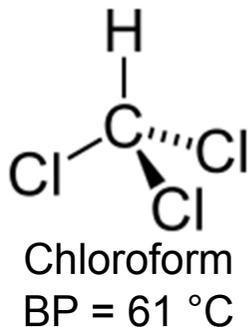
Laboratory grinding experiments

II. Gaseous grinding aids

Gaseous grinding aids = Least applied type

Principally: Similar mode of action as liquid/dissolved chemicals

- + Enhanced distribution via gas phase
- High volatility
- Comparatively low adsorption strength
- Increased removal with mill air
- Only applicable for hermetically sealed mills



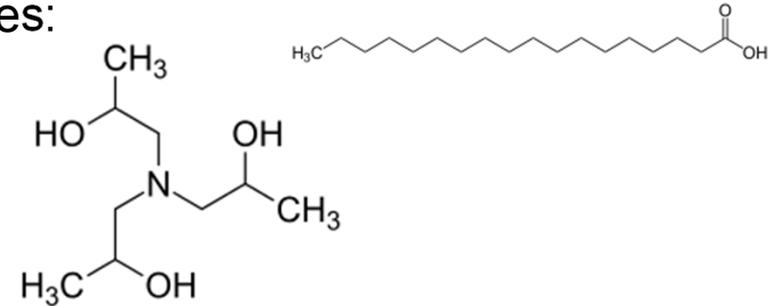
Laboratory grinding experiments

III. Solid grinding aids

Differentiation of different **solid grinding aid** types:

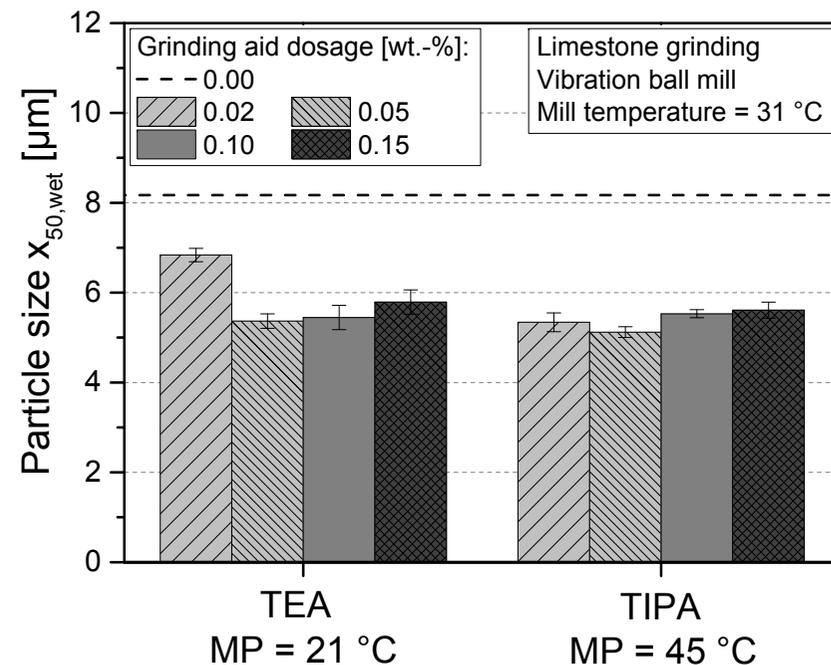
1. Dry organic compounds with melting points (slightly) above room temperature

- Examples: Bigger alcohol amines
Longer carboxylic acids



Mode of action:

- Probably similar to liquid chemicals
- Often applied in dissolved form
- But: Also work as pure (dry) aid



Laboratory grinding experiments

III. Solid grinding aids

Differentiation of different **solid grinding aid** types:

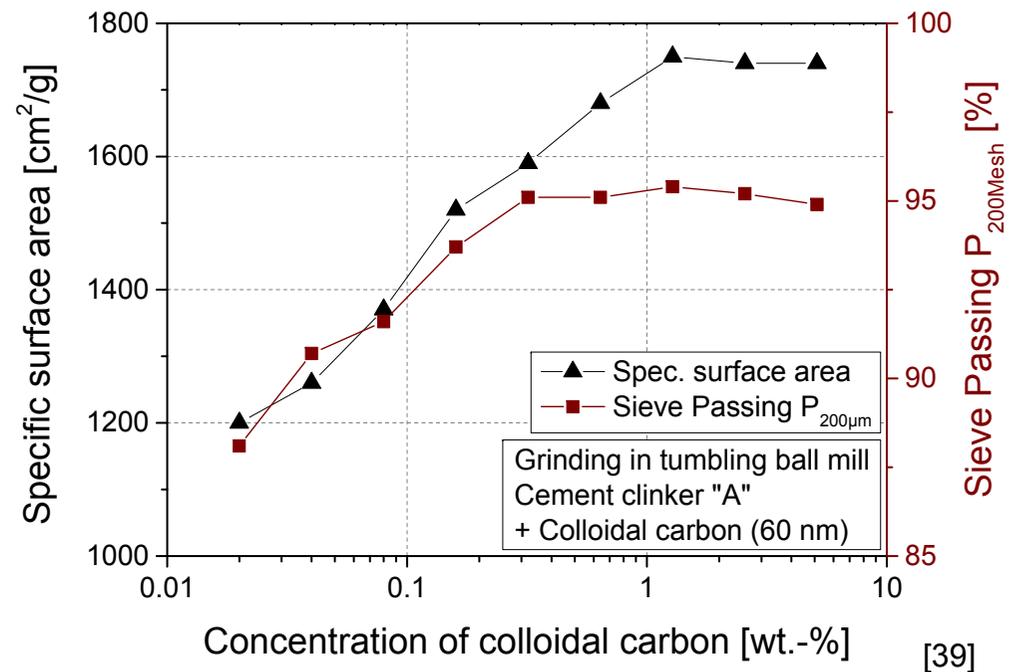
2. Colloidal sub-micron particles

- Examples: Carbon black
Nanoscale silica



Mode of action:

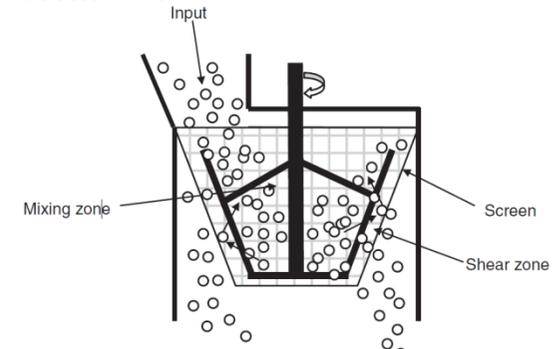
- Similar to flow additives:
 - Particulate additives adhere to host particles
 - Additives act as „spacer“
 - Reduction of adhesive forces



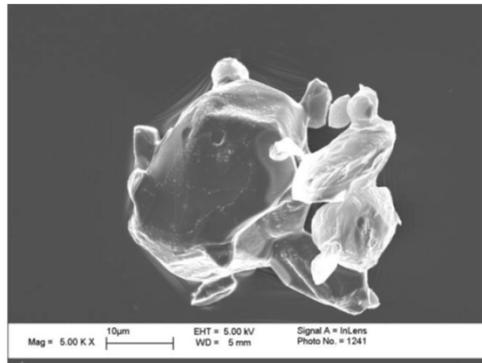
Special case of dry additives: „Co-milling“

- Simultaneous micronization and dry coating
 - Continuous fluid energy milling
 - Comil
 - Jet mill
- Mostly used for cohesive active pharmaceuticals (APIs)
- Rather to improve flow behavior (for subsequent steps) and dissolution rates than grinding process
- Comparatively high concentrations

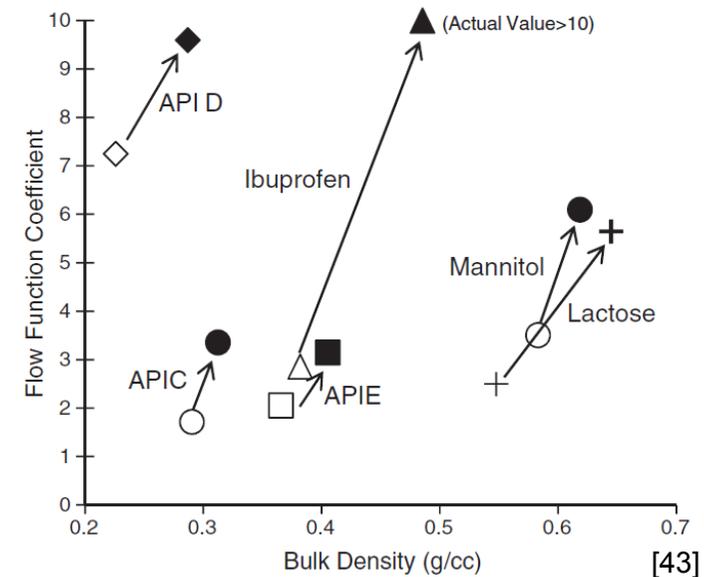
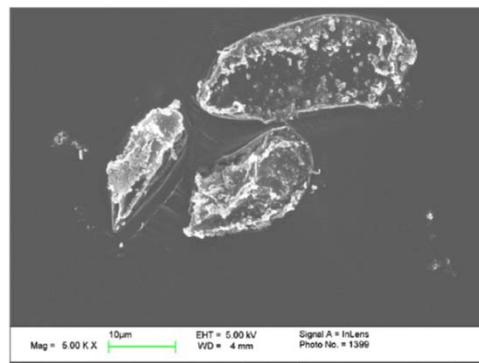
Comil^[43]:



Ibuprofen, uncoated ^[42]



Ibuprofen, nano-silica coating ^[42]



[43]

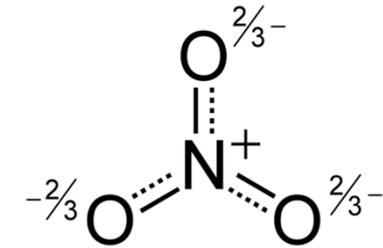
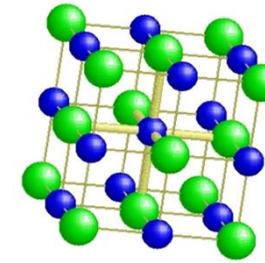
Laboratory grinding experiments

III. Solid grinding aids

Differentiation of different **solid grinding aid** types:

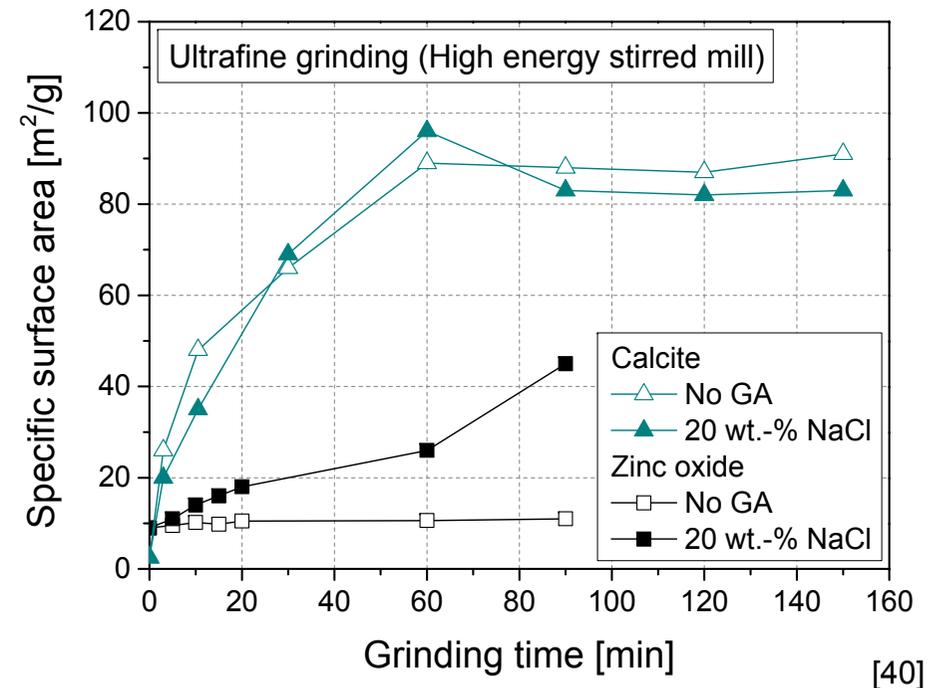
3. Dry (mainly inorganic) particulate grinding aids with high melting points

→ Examples: Inorganic salts
(NaCl, Nitrates, ...)



Mode of action:

- Not clear yet
- Literature: Ion exchange within surface-near areas^[40]
- Also possible: Sub-micronization of salt particles enables similar effects as seen for colloidal stabilizers



[40]

Laboratory grinding experiments

III. Solid grinding aids

Solid grinding aids = „Exotics“

Differentiation of different solid grinding aid types:

1. Dry organic compounds with melting points (slightly) above room temperature
2. Colloidal sub-micron particles
3. Dry (mainly inorganic) particulate grinding aids with high melting points

+ Great effects are possible

→ Especially regarding flow/bulk properties and ultrafine grinding

+ No evaporation

– Comparatively high concentrations needed

– „Contamination“ of the product

– Further impacts on product qualities (e.g. colour or specific surface area)

Agenda

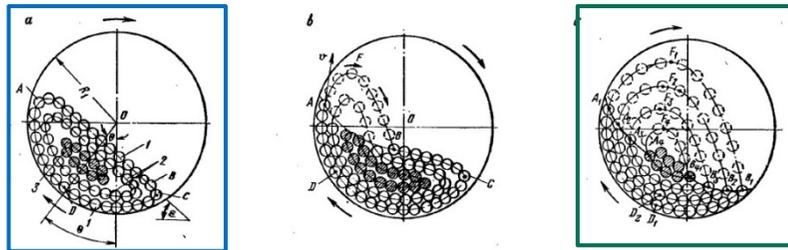
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Impact of the stressing conditions Tumbling ball mills

Inconsistent statements in literature, for instance:

- Dombrowe et al.^[21]: Performance of grinding aids is not affected by milling parameters
- Deckers/Stettner.^[44]: Ball size and ball filling influence grinding aid effects

Moothedath and Ahluwalia^[45]: Operation of ball mill in **attrition mode** and **breakage mode**



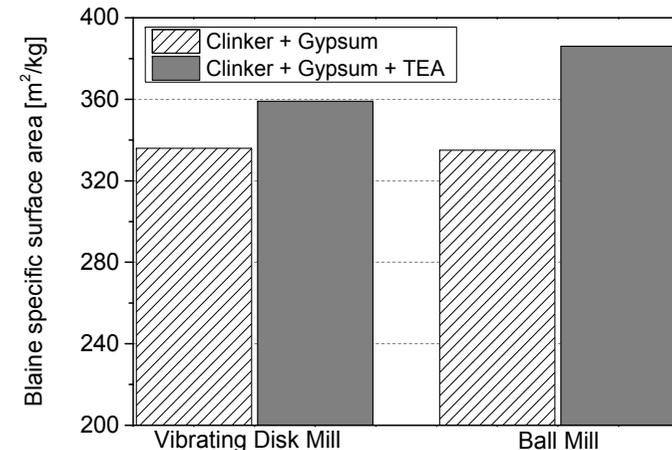
[46]

→ Breakage mode: No differences between different grinding aids

→ But: Different grinding aid effects for attrition

Allahverdi and Babasafari^[47]: Comparison of

- Tumbling ball mill
 - Vibrating disk mill
- Better grinding aid performance in the tumbling mill

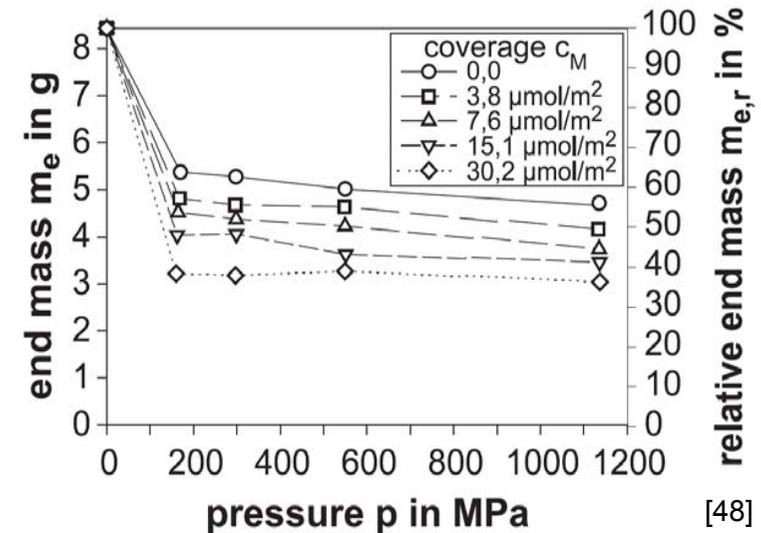
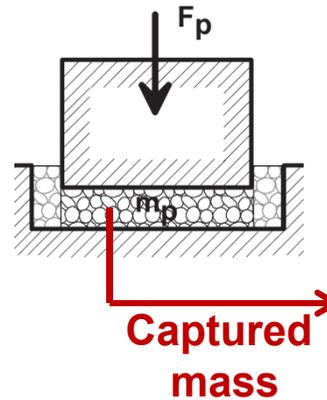


Impact of the stressing conditions

High pressure grinding

Oettel and Huesmann^[48]:

- Specific adjustment of limestone flowability by caproic acid
- High pressure grinding with a force-controlled press
- Strong impact of powder flow on:
 - Powder displacement
 - Energy absorption



[48]

Recchi et al. ^[49]:

- Traditional grinding aids are inefficient in vertical roller mills (VRMs)
- Better results with high-boiling compounds and thickening agents
- Lower evaporation (unlikely? ^[26]) vs. enhanced stressing behavior

Hoffmann and Bernhardt ^[51]:

- Reduced power draw of mill drive with grinding aids



[50]

Impact of the stressing conditions

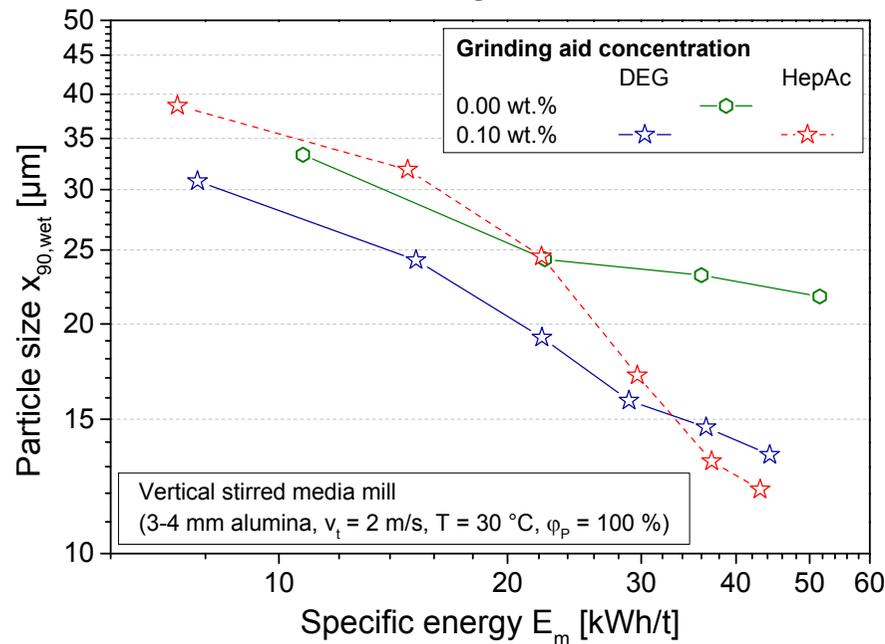
Dry stirred media milling

Prziwara et al.^[31]: Batch-wise dry stirred media milling

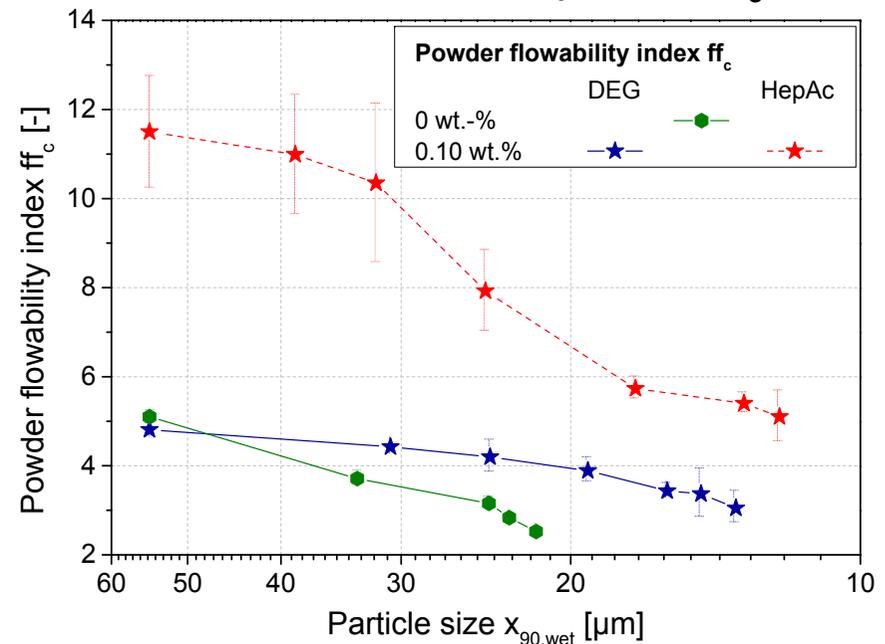
Specific adjustment of limestone flowability by:

Diethelyne glycol (= low flowability) and Heptanoic acid (= high powder flowability)

Grinding result



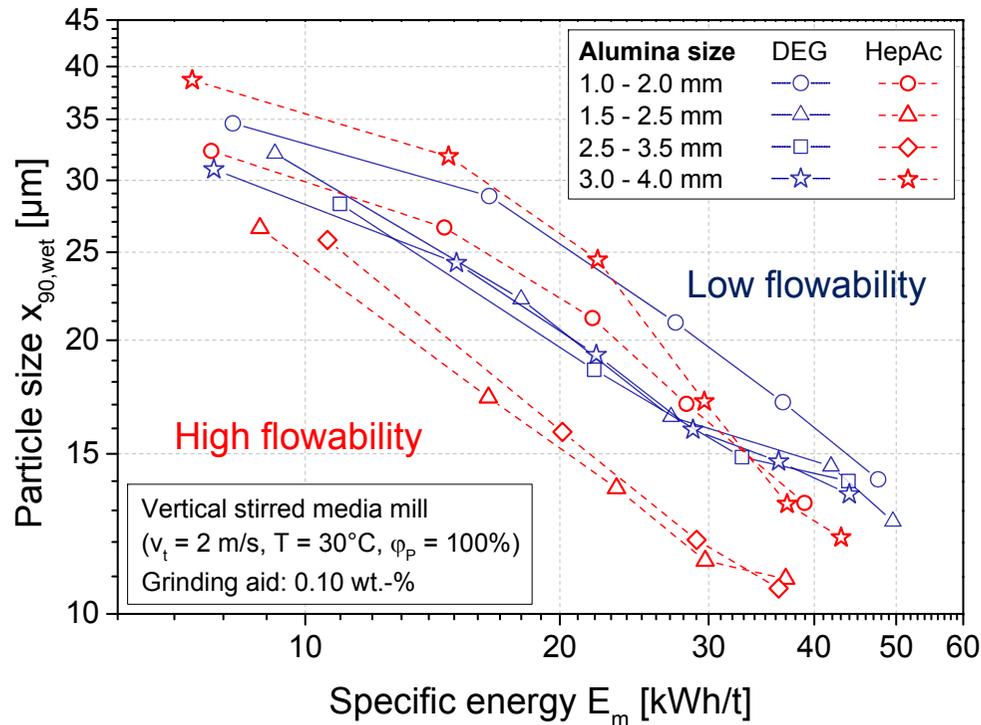
Powder flowability index ff_c



Impact of the stressing conditions

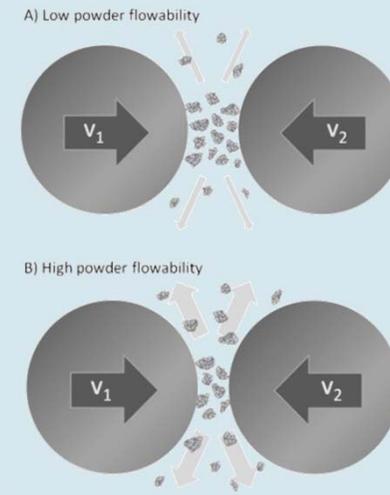
Dry stirred media milling

Prziwara et al.^[31]: Batch-wise dry stirred media milling



Strong dependence of both:

- Powder flowability
- Stressing conditions



- „Powder Flow Optimum“ for each parameter setting
- Tendency: Better results with higher flowability especially at high fineness

Interim conclusion

≈ 100 empirical studies are not sufficient for a comprehensive understanding

Diversity of grinding aids	<ul style="list-style-type: none">▪ Variety of (partly undefined) chemicals▪ Often mixtures / aqueous solution
Diversity of ground products	<ul style="list-style-type: none">▪ Mostly unknown surface properties▪ Partly multi-component systems (e.g. cements)
Grinding conditions	<ul style="list-style-type: none">▪ Use of different mills and stressing principles▪ Varying (unknown) stressing conditions
Test evaluation	<ul style="list-style-type: none">▪ Grinding time vs. specific energy consumption
Measurement equipment	<ul style="list-style-type: none">▪ Specific surface area vs. particle size distribution▪ Dry vs. wet measurement▪ Surface measurement critical with grinding aids
Different fineness ranges	<ul style="list-style-type: none">▪ Semi-coarse vs. fine vs. ultrafine grinding▪ Grinding aid effect depend on fineness range
Grinding aid concentration	<ul style="list-style-type: none">▪ Normally: Gravimetric grinding aid addition▪ Thus, no information on surface coverage available

Agenda

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- 5. Grinding aids in plant operations**
6. Summary and Outlook

Transfer to continuous processes

Most studies focus on batch-wise grinding tests

- Comparabel impacts of grinding aids on product behavior between laboratory tests and industrial applications^[52,54]
- But: Significantly higher benefits of grinding aids in industrial plants compared to laboratory processes
- For instance, different energy savings for cement grinding^[53]
 - Laboratory mill: 7-9 %
 - Industrial grinding plant: 13-18 %



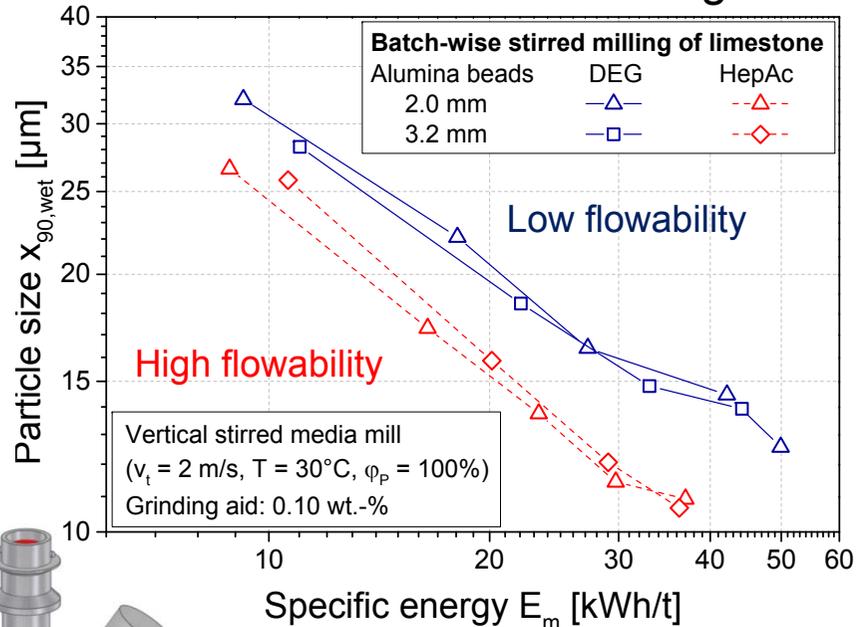
Transfer of results to
industrial processes?



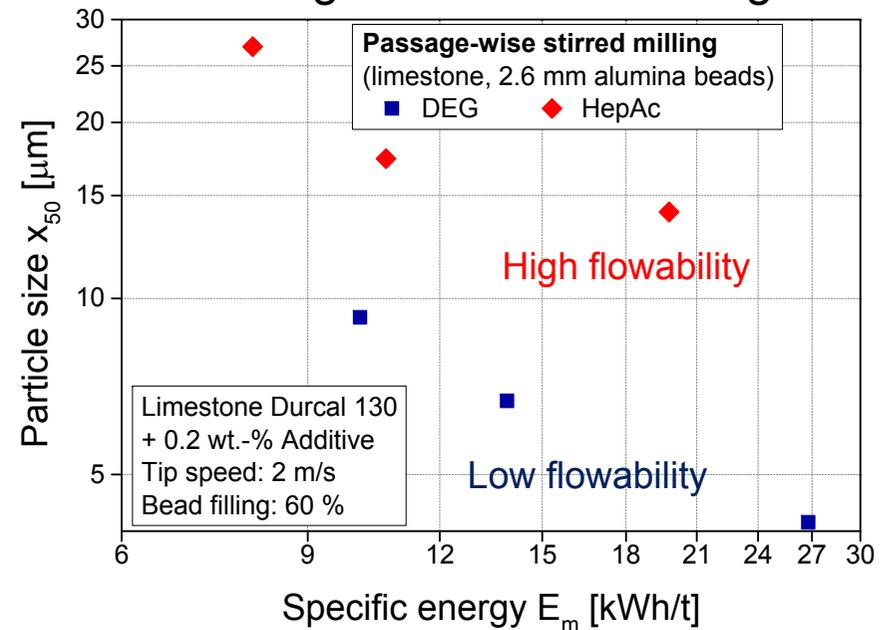
Transfer to continuous processes

Example: Open-circuit stirred mill

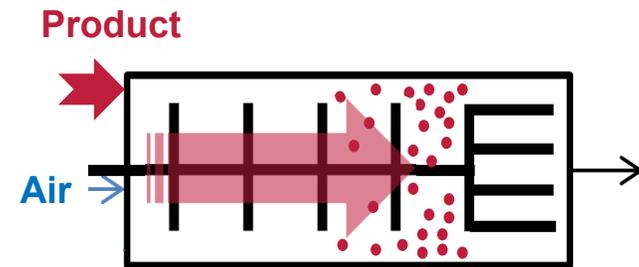
Batch-wise stirred milling



Passage-wise stirred milling

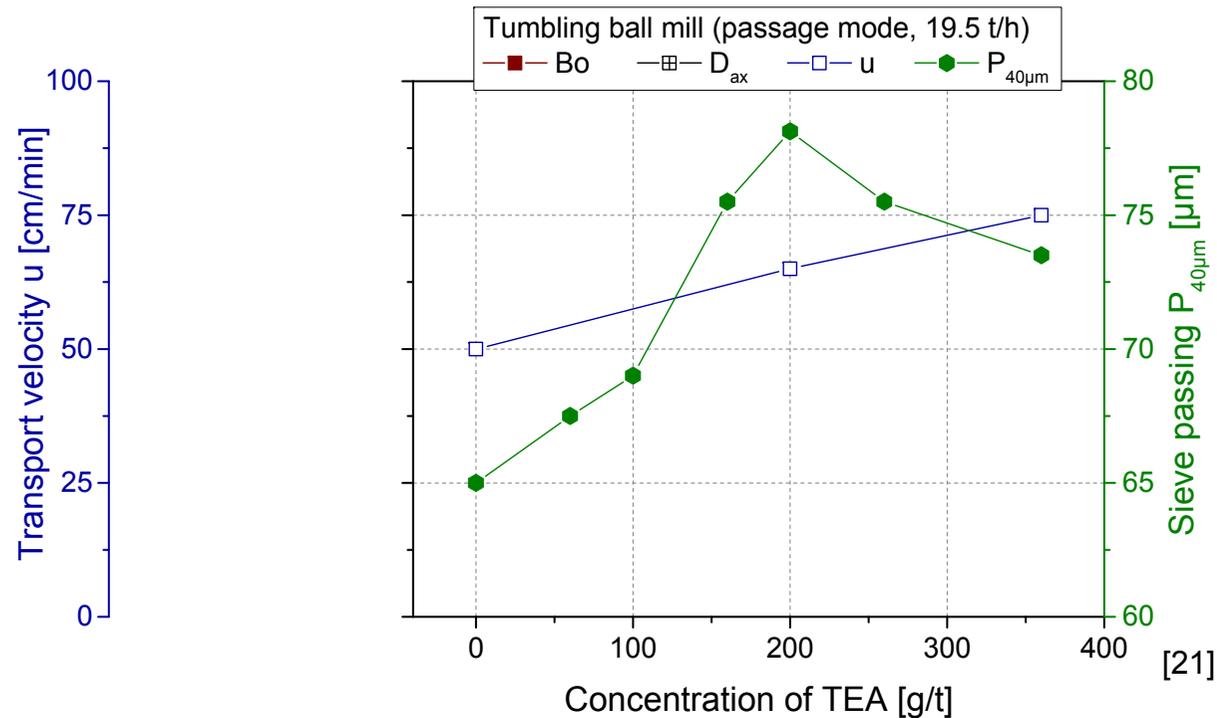


Opposing trends despite comparable stressing conditions
→ Overlapping impact on transport



Impact of grinding aids on material transport

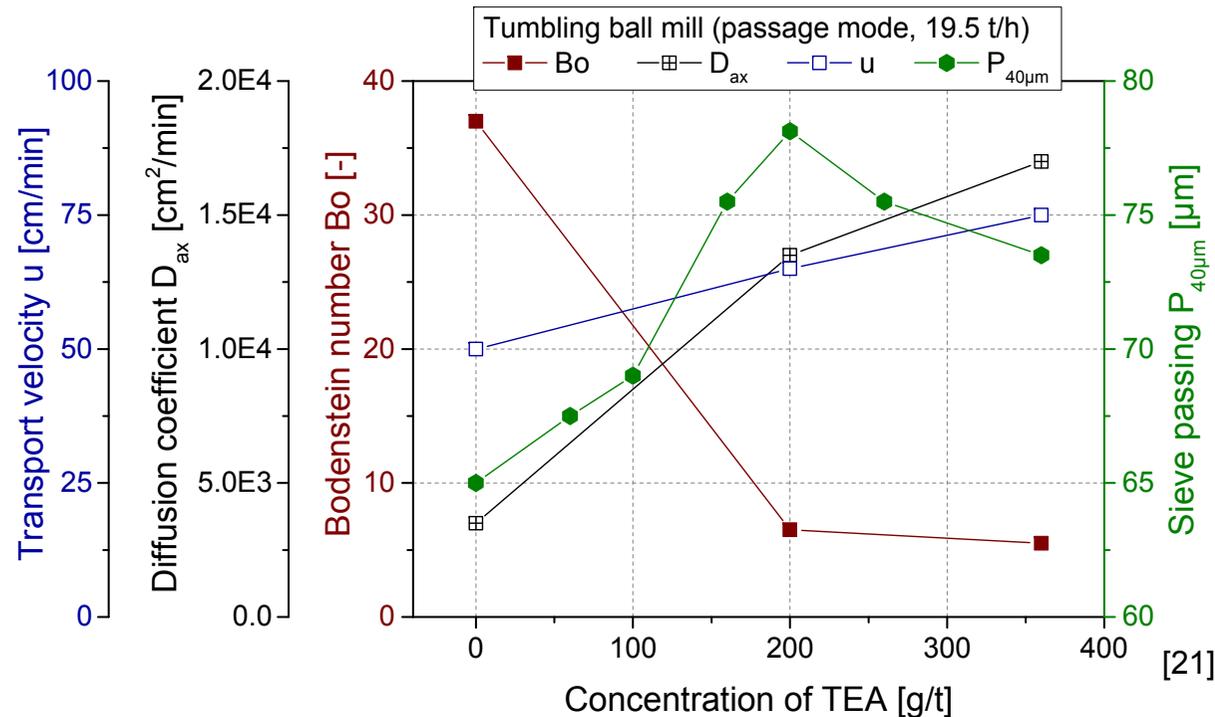
Example: Open-circuit tumbling ball mill



- Higher grinding aid concentrations lead to an increased axial transport velocity
→ This may lead to low residence times

Impact of grinding aids on material transport

Example: Open-circuit tumbling ball mill

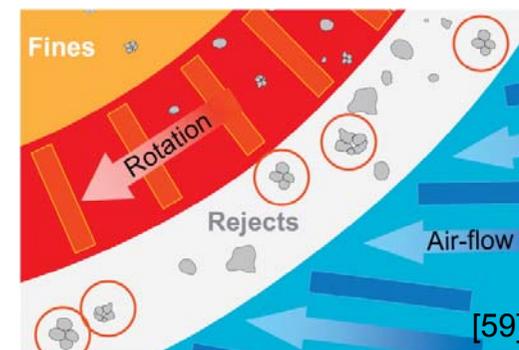
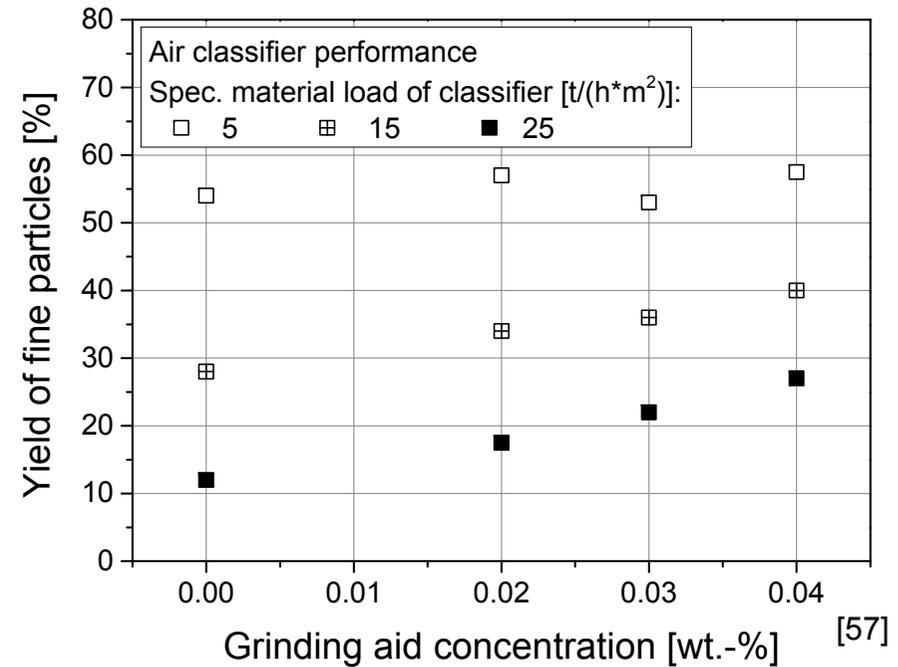
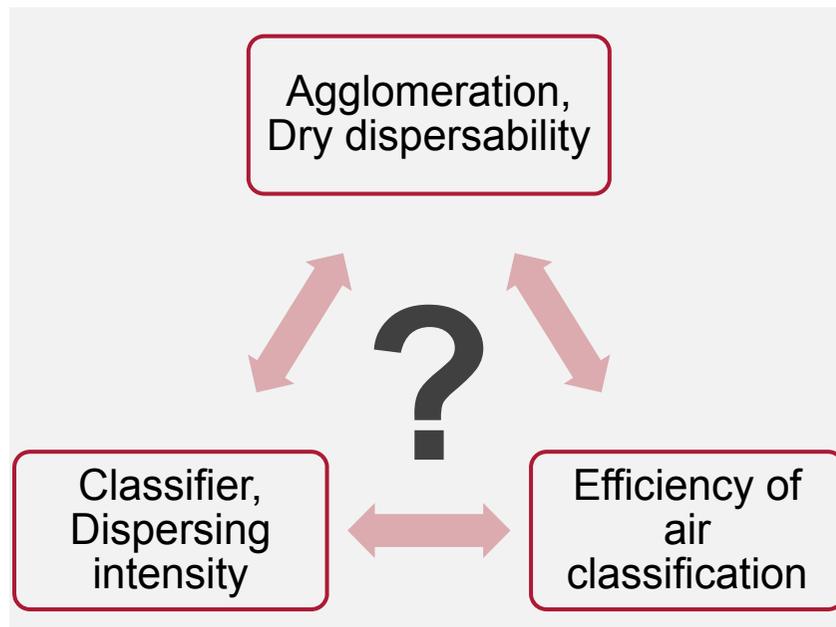


$$Bo = \frac{u \cdot L}{D_{ax}}$$

- Higher grinding aid concentrations lead to an increased axial transport velocity
→ This may lead to low residence times
- But also: Increase of undesired diffusive material transport^[21]
→ It may counteract a high grinding efficiency

Impact of grinding aids on air classification

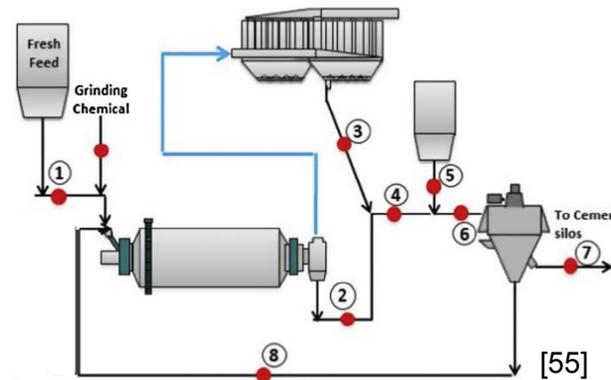
- Decrease of by-pass^[54,55]
- Rather reduction of by-pass than increase of separation sharpness^[56]
- Higher yield of fines^[57,58]



Industrial grinding aid applications

Various studies on closed-circuit grinding processes using **tumbling ball mills**

- Significant increase of production rate (see table)
- Decrease of material recirculation (factor 5 to 2-3)^[21]
- Improvement of classifier performance



Increase of
prod. rate
[%]

10-30 [60]

25-40 [61]

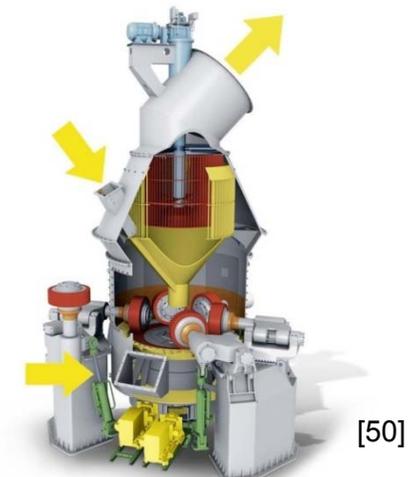
23.5 [62]

24.0 [55]

20.0 [59]

Only a few (contradictory) works on **vertical roller mills**

- Recchi et al.^[49]: Conventional grinding aid do not work
- Pohl et al. ^[63]: 28 % increase of production rate with glycols



[60] L. Sottili, D. Padovani, ZKG International, 53 (2000) 568-575.

[61] L. Sottili, D. Padovani, ZKG International, 54 (2001) 146-151.

[62] F.C. Lai et al., Australian Journal of Basic and Applied Sciences, 7 (2013) 253-259.

[55] N.A. Toprak et al., Construction and Building Materials, 68 (2014) 199-205.

[59] J. Schrabback, Global Cement Magazine (2009)

[21] H. Dombrowe et al., Zement-Kalk-Gips, 11 (1982) 571-580.

[49] P. Recchi et al., ZKG International, 63 (2010) 53-57

[63] M. Pohl et al., Cement International, 10 (2012) 57-69

[50] online: <https://www.gebr-pfeiffer.com> (13th June 18)

Industrial grinding aid applications

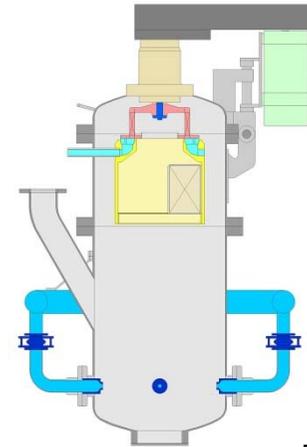
Continuous opposed jet milling

A few studies reveal high potential of grinding aids in jet milling:

- Energy savings^[64]
 - 83 % (ceramic pigment)
 - 62 % (metal oxide)
 - 56 % (hydraulic bonding agent)
- Increase of production rate
 - 88 % (talc)^[65]
 - 460 % (ceramic)^[66]

No information given on:

- Grinding aid type
- Grinding aid conc.



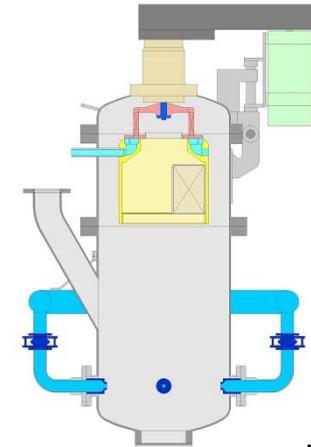
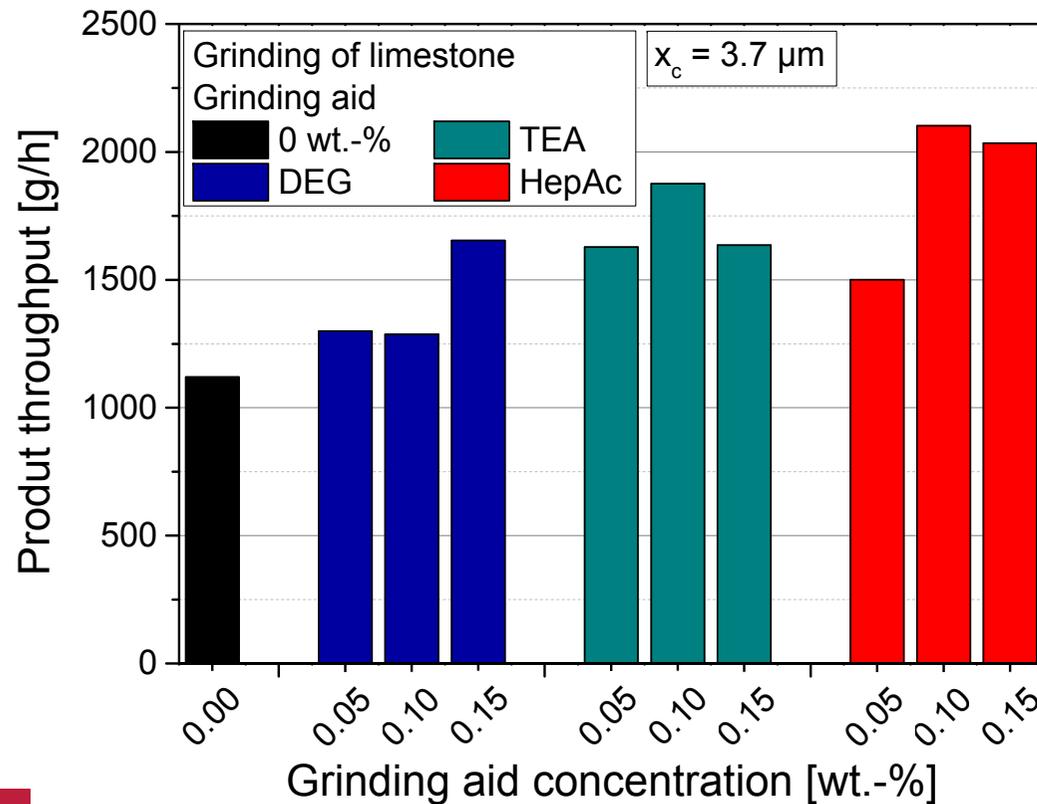
[67]

Industrial grinding aid applications

Continuous opposed jet milling

Internal study:

- Grinding aids are very efficient for both minerals and ceramics
- Lower concentrations are needed compared to media mills



[67]

Agenda

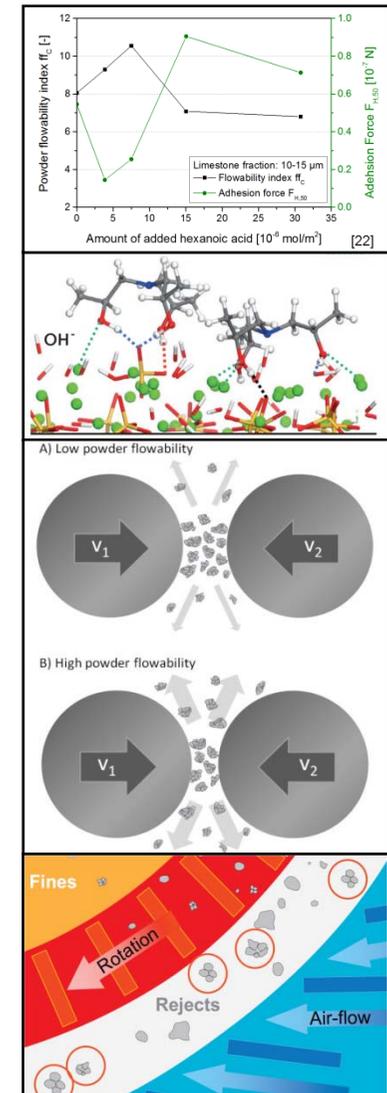
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Conclusion

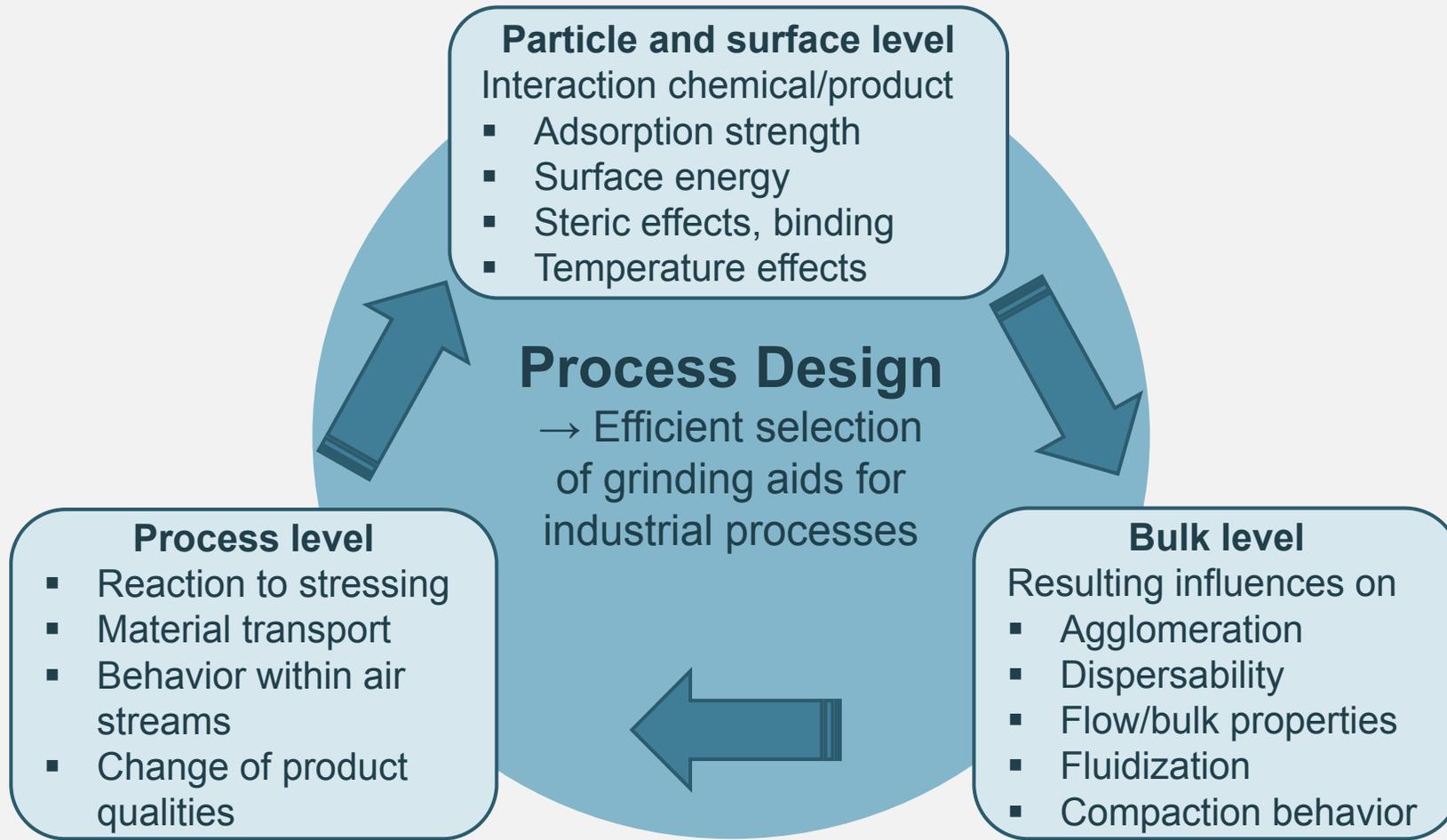
- ✓ Grinding Aids are a powerful tool to improve dry grinding processes (also besides the cement sector)
- ✓ „Reduction of adhesive forces“ is accepted as main mechanism
- ✓ > 100 studies on grinding aids in literature with various promising liquid / dissolved / solid chemicals

But: Still no comprehensive understanding available

- Complex interactions of chemicals and particle surface
- Mostly unknown changes of particle / bulk / flow behavior
- Reactions of the material to stressing and transport conditions are hard to describe
- Many overlapping impacts in industrial plants
- No studies on mechano-chemical effects



Development of a comprehensive, but complex understanding needed



Many thanks for your attention!

9th International Symposium on Fine Grinding and Dispersing

11th and 12th October 2018
Braunschweig/Germany



Grinding and Dispersing with Stirred Media Mills

Seminar and Workshop

08th – 10th October 2018
Braunschweig/Germany

Farben der TU Braunschweig

R 190 G 30 B 60					R 8 G 8 B 8	R 95 G 95 B 95	R 150 G 150 B 150	R 192 G 192 B 192	R 221 G 221 B 221
R 255 G 205 B 0	R 255 G 220 B 77	R 255 G 230 B 127	R 255 G 240 B 178	R 255 G 245 B 204	R 198 G 238 B 0	R 215 G 243 B 77	R 226 G 246 B 127	R 238 G 250 B 178	R 244 G 252 B 204
R 250 G 110 B 0	R 252 G 154 B 77	R 252 G 182 B 127	R 253 G 211 B 178	R 254 G 226 B 204	R 137 G 164 B 0	R 173 G 191 B 77	R 196 G 209 B 127	R 219 G 228 B 178	R 231 G 237 B 204
R 176 G 0 B 70	R 192 G 51 B 107	R 215 G 127 B 162	R 235 G 191 B 209	R 243 G 217 B 227	R 0 G 113 B 86	R 77 G 156 B 137	R 140 G 191 B 179	R 191 G 219 B 213	R 218 G 234 B 231
R 124 G 205 B 230	R 164 G 220 B 238	R 189 G 230 B 242	R 215 G 240 B 247	R 229 G 245 B 250	R 204 G 0 B 153	R 222 G 89 B 189	R 235 G 153 B 214	R 245 G 204 B 235	R 250 G 229 B 245
R 0 G 128 B 180	R 77 G 166 B 203	R 140 G 198 B 221	R 191 G 223 B 236	R 217 G 236 B 244	R 118 G 0 B 118	R 152 G 64 B 152	R 186 G 127 B 186	R 214 G 178 B 214	R 235 G 217 B 235
R 0 G 83 B 116	R 64 G 126 B 151	R 140 G 177 B 192	R 191 G 212 B 220	R 217 G 229 B 234	R 118 G 0 B 84	R 156 G 77 B 136	R 193 G 140 B 178	R 221 G 191 B 212	R 235 G 217 B 230

