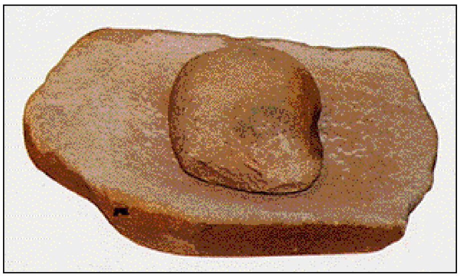
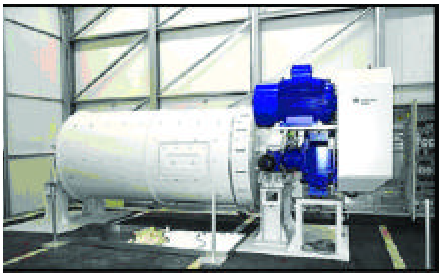
J. Stein, Germany

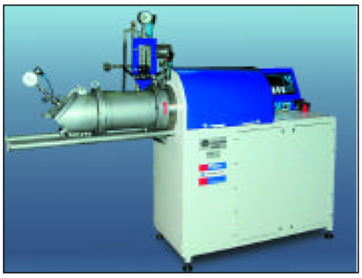
Ultrafine Dry Grinding with Media Mills



Grinding stone



Dry ball mill



Wet media mill

Used since the Stone Age, grinding is the oldest engineering process. Mills have been operated by human muscles and the energy input was created by rubbing, rolling and knocking with pestles and grinding stones. This basic grinding mechanism is still used in modern media and roller mills; today, however, operated with electric engines up to 20.000 Kilowatts. At first, particles sizes in the range of some Millimetres were sufficient; nowadays even particles with a diameter of few Nanometers can be obtained by use of media mills.

1. Grinding Media and Mechanisms

For the production of the finest particles far in the submicron range, without exception grinding with stirred media mills in a liquid phase is successful. Particle sizes from just submicron to some 100 microns can be obtained either by wet or dry milling processes, whereas bigger particles of Millimetre size mainly are made by dry milling. The choice between dry and wet grinding is influenced by several factors. The condition of the raw material and the downstream use as powder or slurry determinate the grinding process in many cases. Other subjects like product fineness, dispersion, hazards or chemical reactivity have to be considered.

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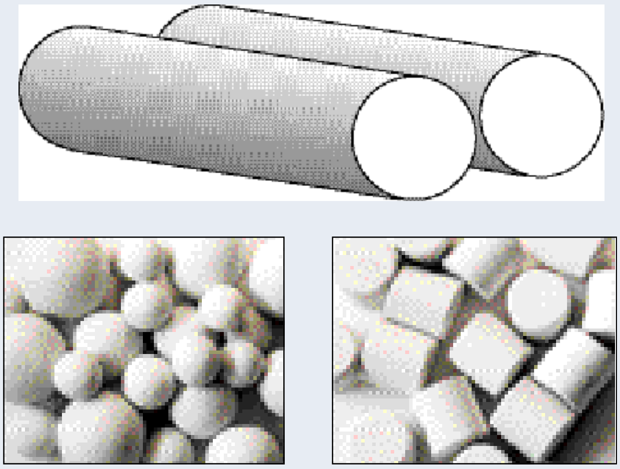
The performance of dry milling processes has been extended to higher finenesses in the past years, particularly by improvement of the classifier technology. However, also the mill technique has a high potential to make its contribution to finer dry particles. A remarkable approach are high energy dry mills, which use very small grinding media analogous to the well known wet media mills.

Grinding media can appear in different shape, size and a big variety of materials. Stones, balls, rods, cylpebs, pearls and irregular grains are the most common shapes. The range of media sizes reaches from some 100 millimetres down to 50 micron. With the increasing power input of the mills, the requirements on the physical properties of the media become important. Hardness, strength, and Young's modulus but also thermal and chemical stability have to be considered. High tech ceramic materials like Zirconia or Silicon Nitride are examples for the development from the traditional Flintstone to high performance media.

Media sizes bigger than 10 mm are for use in gravity driven mills. Smaller grinding media need higher acceleration and can be used in agitated or high speed mills only. The different types of mills all have their characteristic sizes and shapes of grinding media:

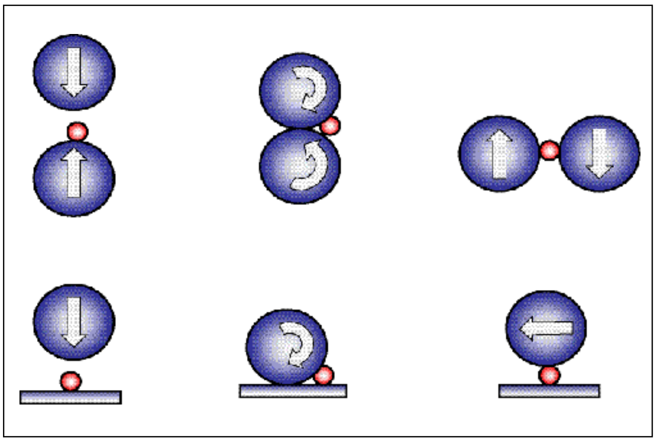
Wet agitated media mills:	balls	0,05 - 3,0 mm
Dry agitated ball mills:	balls	1,0 - 10 mm
Centrifugal mills:	balls	1,0 - 10 mm
Vibration mills:	balls, rods, cylinders	5,0 - 20 mm
Planetary mills:	balls, cylinders	2,0 - 20 mm
Tumbling ball mills	balls, cylinders, rods	10 - 100 mm



Flintstone	> 50 mm
Steatite	5- 100 mm
Steel, Stainless Steel	1 – 80 mm
Glass	0,5 – 3 mm
Aluminium Oxide 85 – 99,9%	0,5 – 80 mm
Zirconium Silicate	0,5 – 3 mm
Zirconium Oxide (Ce-stab.)	0,3 – 3 mm
Zirconium Oxide (Y-stab.)	0,05 – 10 mm
Silicon Nitride	1 – 3 mm
Silicon Carbide	1 - 3 mm
Plastic	2 - 6 mm
Polyurethane, Rubber	5 – 80 mm

Grinding media: materials, sizes, shapes

The stress of the particles in media mills is effected by impact, pressure and shear forces between the grinding media each other and against the mill parts. Depending of the mill type, one of these stress forces can be dominant for the grinding mechanism.



Grinding forces in media mills

Compared to the common wet mills, the dry agitated media mills usually are operated in a vertical arrangement with high media pressure and relatively low speed. Thus the stress on the particles in those mills is mainly created by shearing and pressing forces. Tumbling ball mills can be operated on different speed levels, which has an influence on the share of impact and shear stress. Vibrating mills with their high frequency motion are dominated bay impact grinding, whereas centrifugal mills tend more to shear and pressure stressing. Similar to tumbling ball mills, the planetary mills create different media motion depending on the rotation of drum and centre wheel.

2. Dry Media Mills

For dry milling processes, a large variety of technologies has been developed. Even for the fine particle range below 100 micron, many different mill types can be used. The selection of the right milling equipment depends on properties of the material like hardness and particle size and is influenced by the requirements on the end product, e.g. fineness, particle shape, purity and production capacity.

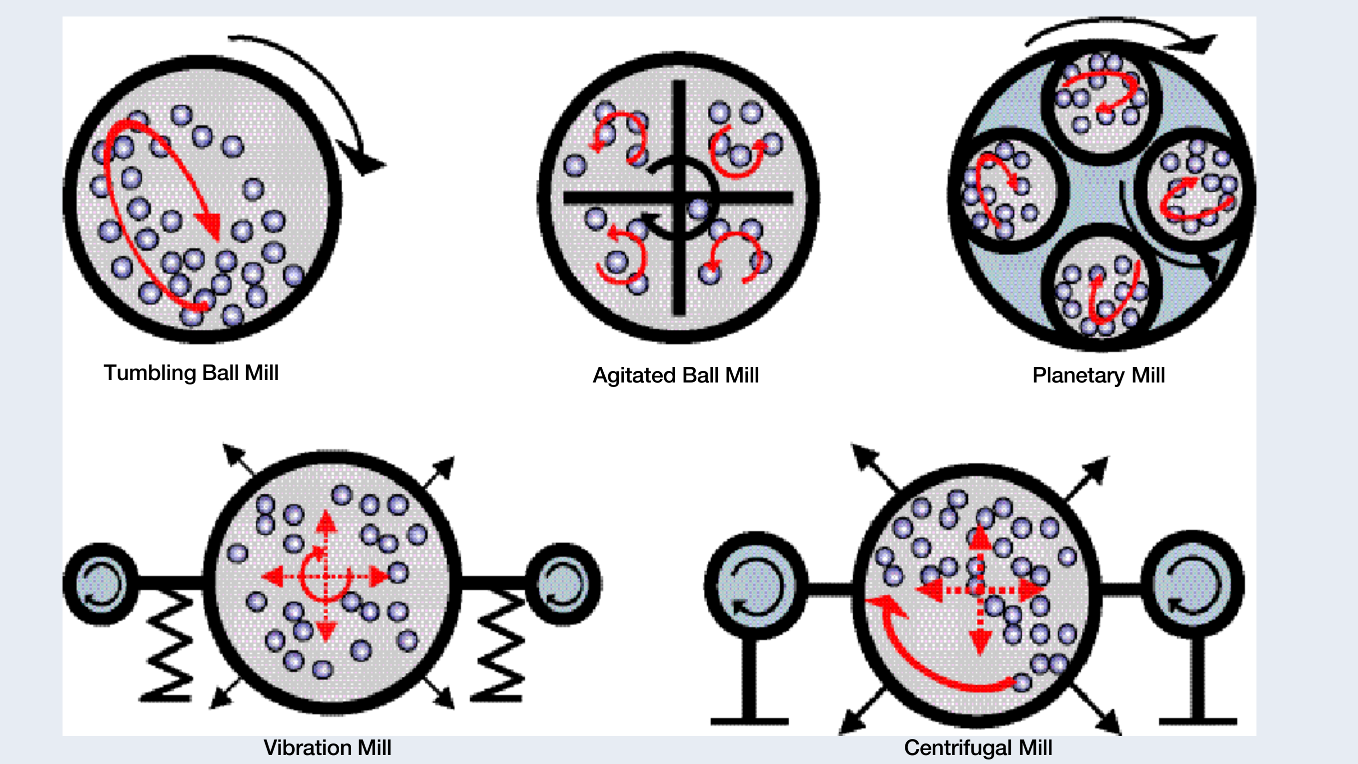
For the fine milling of dry powders, many applications can be covered by high speed rotor impact mills. However, this mill type can not obtain highest finenesses and is limited to low abrasive materials. Jet mills, which create particle to particle impact can grind finer, are not sensitive to abrasion but have a high energy consumption. In the field of dry mineral processing, mainly roller mills and ball mills are applied for high capacities of finest powders.

With increasing fineness, the ratio of ball number and particle number becomes unfavourable. Big grinding media statistically can not create enough impacts to stress the huge number of fine particles. Just as example: a mill volume element of 1 Litre contains about 800 balls of 10 mm size and 350 billions of 10 micron particles! If the ball size is 0.3 mm, the number of balls at least increases to 35 millions, which significantly rises the chance to stress all particles in a reasonable time. Consequently, finest dry milling should be conducted with grinding media as small as possible to increase the stress number in the mill.

However, smaller grinding media have much less weight; the acceleration by gravity in tumbling ball mills creates only low kinetic energy, which is not sufficient anymore to break the fine particles. To keep the stress intensity with small media on a high level, gravity has to be replaced by higher acceleration, which can be realised in mills with rotating agitator or with fast moving mill body.

2.1 Ball Mills

Gravity is the driving force to move the grinding media in ball mills. The mill body usually is a slowly rotating cylindrical or conical drum in horizontal arrangement. Mill dimensions reach up to 25 meters length (tube mills) and 13 meters diameter (SAG mills). The mill drum is wear protected with hard steel or ceramic liners. The same materials are used for the grinding media, which usually have a size of 20 - 100 mm. Some ball mills for very fine mineral products can be operated with relatively small media in the range of 10 - 12 mm. Tests with even

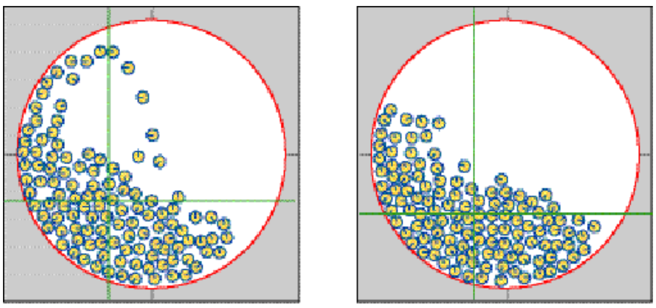


The basic types of media mills (mill and media motion)

smaller balls show, that there is a limit in the stress intensity at 4 - 6 mm media size. Grinding of coarser particles is not possible anymore. And, if the balls are too small, they do not have enough energy to destroy the layers of fine particles sticking at the drum walls and at the media surface.

At the critical speed, the balls are centrifuged to the drum walls and the grinding effect gets lost. Typical rotation speeds are in the range of 60 - 80 % of the critical speed. A high speed level effects a cataract-motion of the balls, which has a high portion of impact stress. The grinding mechanism shifts to a higher portion of shear stress if the mill rotates slower and the motion changes to a cascade-type.

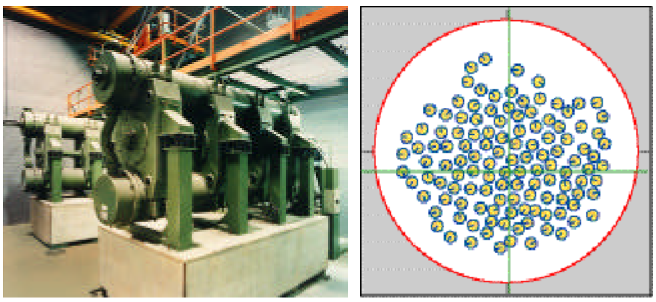
Ball mill – fast and slow rotation



2.2 Vibration Mills

The oldest dry mill type operated with relatively small media is the vibration mill. Typically this machine has one or two cylindrical grinding vessels in horizontal arrangement. The motion of the mill body is effected by unbalance drives and is characterised by a free mill vibration with high frequency and small amplitude. The energy transfer into the media filling is initiated by wall-to-ball contacts and distributed by ball impacts. Depending on frequency, amplitude and media filling, the grinding stress can vary from mainly pure vibration with high impact to a rolling media motion with some portion of shear. Vibration mills can be operated with balls, cylinders or rods (typical size range 5 - 20 mm) for dry and wet milling. The mill

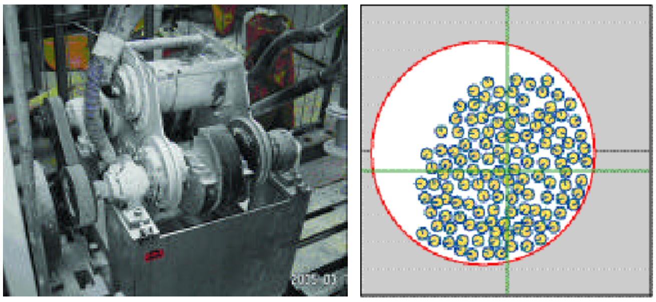
Vibration mill



design is relatively easy and robust, but high stress of the foundation has to be considered. The free motion offers only limited possibilities to adjust the mill for different material and media fillings, because frequency and amplitude can not be changed independently.

2.3 Centrifugal Mills

Different to vibration mills, the centrifugal type mill has a forced motion created by eccentric crank shafts in fixed bearings. The mill vessels mainly are horizontal cylinders too, but also semi-conical shapes with vertical axis are known. Balance weights minimise the forces on the mill foundation.



Centrifugal mill

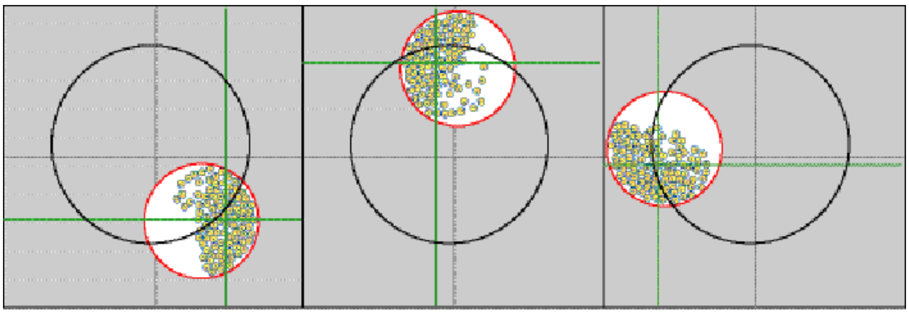
The eccentric motion is characterised by a lower frequency and bigger amplitude compared to vibration mills. The forced eccentricity allows the variation of the mill frequency independently from the vibration amplitude. The dominant grinding mechanism is shear stress, effected by a mainly revolving media filling. High acceleration up to 30 g is possible and opens the possibility to use grinding media (balls) smaller than 5 mm.

2.4 Planetary Mills

Similar to the centrifugal mills, planetary mills have grinding chambers, which are moved with a fixed eccentricity, assembled on a rotating centre wheel. Additionally the single mill body rotates on its centre axis in opposite or same direction as the centre wheel.

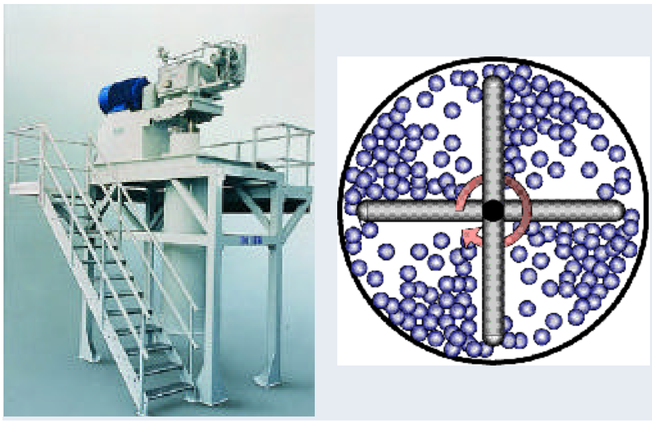
The differential revolution speed creates centrifugal forces, which effect a media motion similar to gravity ball mills, however, with much higher acceleration and the possibility to use small grinding media below 5 mm. By setting the revolutions of centre wheel and mill body, it is possible to create basically three different media motion types: cascade and cataract motion like in gravity ball mills or media rotation similar to centrifugal mills. Accordingly, different stress mechanisms can occur and flexibly being influenced during operation by variation of the two rotations. The machine is well balanced, but the machine design is elaborate. Particularly material feed and cooling water supply are very difficult. Thus, only batch type lab mills with smaller volume are used. Only few approaches to a design of high capacity continuous planetary mills are known, none are in industrial operation.

Planetary Lab Mill



2.5 Agitated Ball Mills

Most of the agitated media mills are used for slurries, only a minority is in industrial use for the fine grinding of dry powders. The grinding energy is transferred into the media by agitation with a rotating stirrer. Also combined agitation by stirrer and rotating body is known. The grinding chamber arrangement



Dry agitated media mill

and shaft direction is vertical and there are three basically different mill types. The so called tower-mill has a screw-type rotor which lifts the grinding media and actually uses the gravity as driving force for media motion. This mill can not be operated with very small media. Second type is an agitated media mill with stationary grinding media filling; material transport is done by gravity or pneumatically. The third type is operated with a circulating media filling; material and powder are flowing through the agitated mill chamber. These two types of dry

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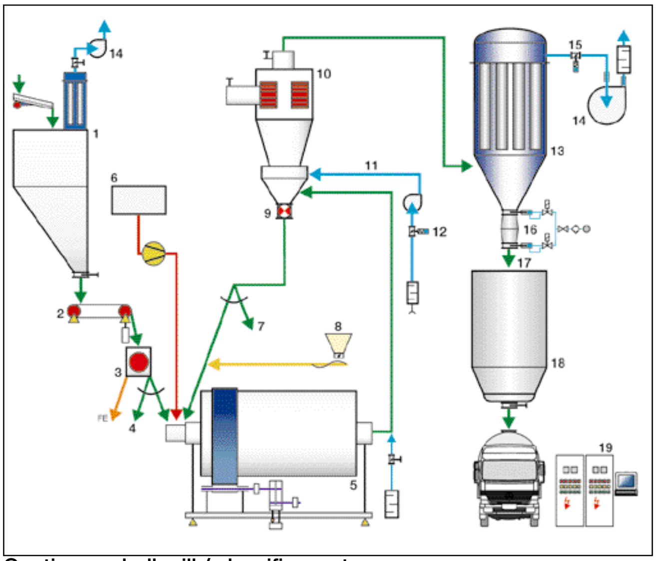
agitated media mills create high kinetic forces on the media and can be used with very small ball sizes.

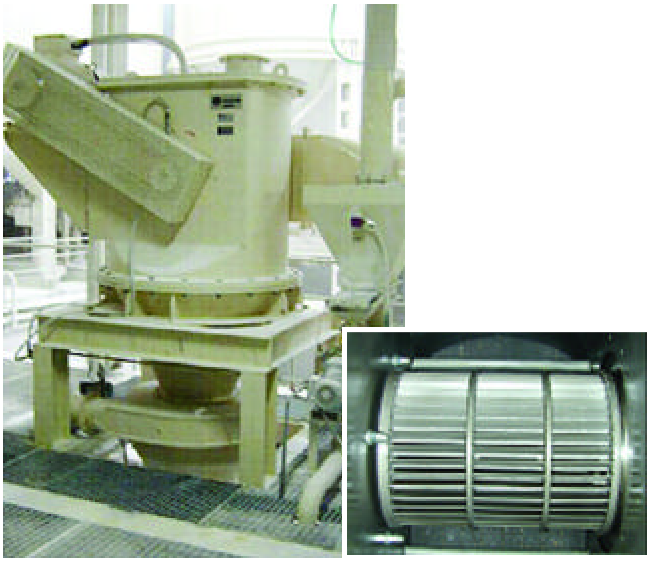
The grinding mechanism can be influenced by variation of the agitator speed and the ratio of media filling. High rotation speed and low media filling level effect a tendency to impact stress, whereas a high filling ratio of beads shifts the mechanism more to shear stress. In contrast to agitated wet mills, dry media mills are typically low speed mills with predominant shear grinding.

2.6 Operation of Dry Media Mills

All described mill types can be operated batch or continuously. In case of a continuous process, analogous to wet media mills, the residence time distribution and the particle size distribution are not steep. Continuous dry mills for very fine powders are always operated in a circuit with an air classifier. The more fine particles the mill creates, the more product can be selected out by the classifier. However, the cut size of classifiers is limited to a certain fineness, thus the classifier is the restricting factor regarding the absolute fineness, which can be produced by a dry media mill. The newest high speed classifiers reach down to cut sizes in the range of 2-3 micron for industrial applications.

The transport of the material through the mill body is from substantial importance. The material conveying can be effected by gravity, bulk pressure or airflow. It has influence on the residence time, the grinding progress and the heat transport. For the mills with high acceleration and high specific energy input, cooling is an important issue. In case of gravity or bulk pressure transport, only the material itself can bring the heat out of the mill. A water cooling jacket at the grinding chamber helps, but is technically difficult for mills with moving body. The most effective cooling can be obtained by use of airflow for the material transport. However, a compromise must be found between cooling efficiency and a sufficient residence time for grinding. A certain advance regarding cooling has the vertical agitated media mill with media circulation, because it is possible to cool the grinding balls outside of the mill during recirculation.

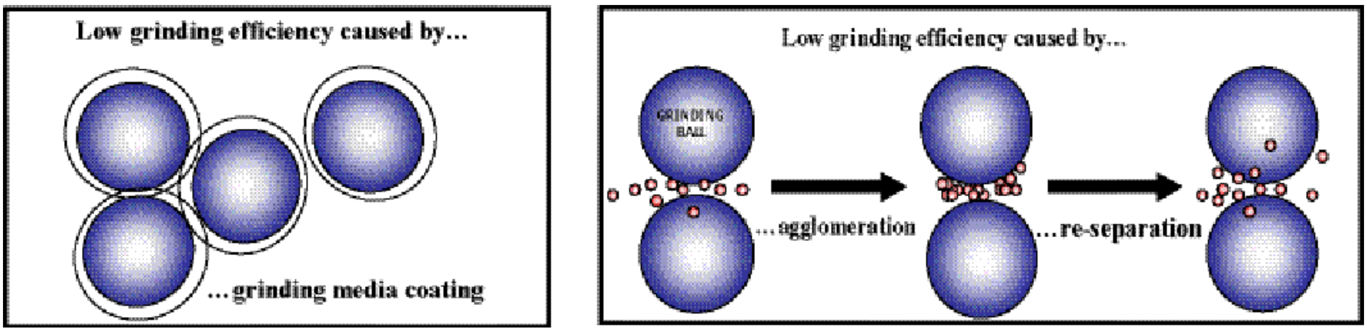

Continuous ball mill / classifier system

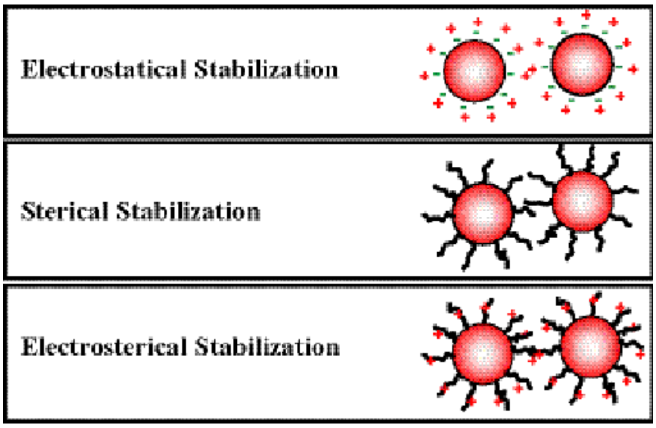

High speed classifier

3. Stabilisation and Additives

The major restricting factor for comminution in the submicron range are the interactive forces of small particles, which are the reason for (re-)agglomeration and sticking. The grinding forces are absorbed by agglomerates, coating of the media or layers on mill parts. This problem is minor in the liquid phase, because the shear forces of the slurries are higher and the transport of additives to the particle surfaces is easier. For several materials, Nano-scaled particles can be obtained by wet grinding with agitated media mills. With a dry milling process it is not yet possible to get a sufficient effectiveness even in the coarser submicron range.

Agglomeration of fine particles in media mills





Different mechanisms of particle stabilisation

Additives help to control the adhesion forces between particles. They can prevent re-agglomeration of just broken particles and reduce the tendency to stick at the media or mill parts. Not only for the grinding process, but also for the classification it is substantially important to avoid agglomeration, because particles can only be separated if the are well dispersed.

The easiest way to stabilise is the control of the electric double layer (Zeta-Potential) by H^+ or OH^- ions (pH-value). This electrostatic stabilisation is mainly applicable in water based slurries. The sterical or electrosterical stabilisation is using long chained molecules, with are applied to the particle surfaces. Those surfactants can also be used for dry particle stabilisation. In comparison to liquid slurries, the quick transport and the homogeneous distribution of the additives to the particle surface is much more difficult.

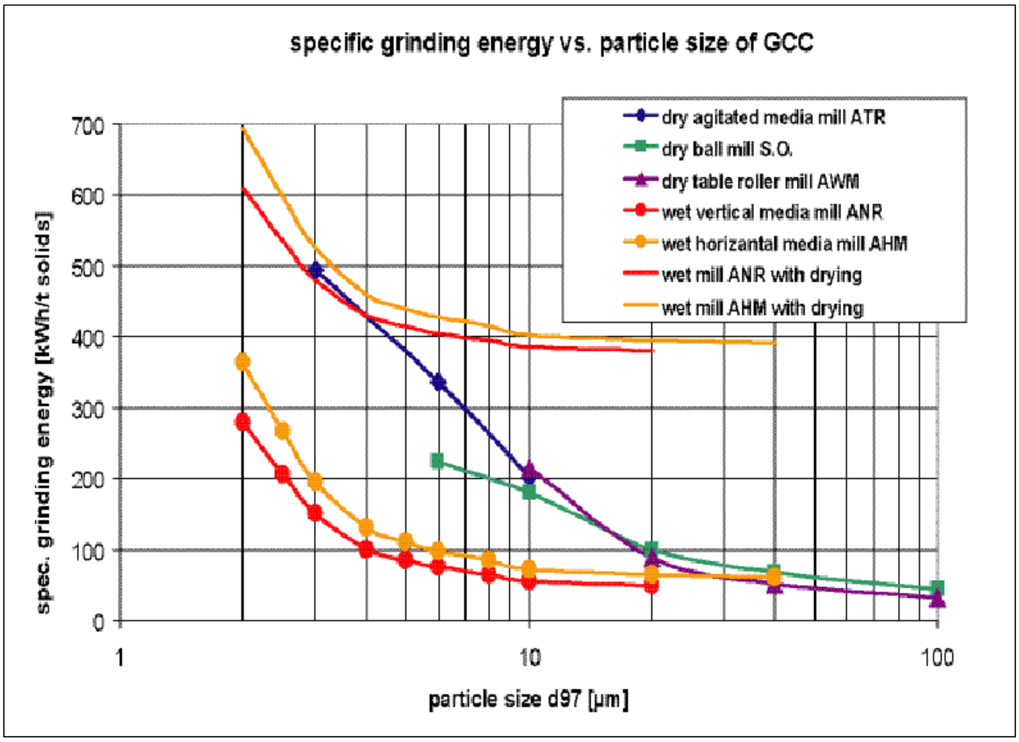
4. Wet or Dry ?

Dry milling and classifying technologies have developed significantly in the past years. Particularly the bead milling technology in combination with high speed classifiers has a certain potential for very high particle finenesses. However, particles in the submicron and Nano range can exclusively produced by wet milling processes with agitated media mills and the use of very small grinding media. Therefore, the decision is easy to use wet grinding for the finest particles below 1 micron.

In case of coarser particles between 1 and 100 micron, there are several other criteria apart from the fineness to be considered regarding the choice of the grinding equipment. The most important may be the energy consumption, which usually has a big impact on the production costs of the material.

The comparison of different dry mills (ball mill, agitated media mill, table roller mill; all with classifier) and wet mills (horizontal and vertical agitated media mills) shows a significantly lower grinding energy requirement in the liquid phase for particles smaller than 10 microns. However, if the final material is used as dry powder, the slurry must be dried after milling and the energy balance shifts in favour of dry grinding. In the range of 3 micron (for the example of GCC) dry and wet grinding are on the same energy level for dry powder as final product. If the end product is used as slurry or if the feed material is already in liquid phase, wet grinding is always the more economic process. And finally, the wet process is the preferred solution if additives are used for particle dispersion and stabilisation, especially for submicron products, as already mentioned above.

Specific energy consumption of different mills for Ground Calcium Carbonate (GCC)



5 Conclusion

Amongst the different types of dry mills, the media mills have the highest potential to perform an economic grinding process for finest powders. The mills must be able to operate small grinding media with high acceleration and energy. Suitable are agitated media mills, planetary mills, vibration mills or centrifugal mills. Fine submicron or Nano particles can currently be produced by wet agitated media mills only. A dry grinding process in the submicron range requires further developments in the classifier technology and particularly investigations about suitable additives and their application for particle stabilisation.