The science of particle making

Mastery of several disciplines is required to make it small in this business.

By Dr. Nancy McGuire
Contributing Editor

“We make big things” smaller; that’s our mission,” says Stanley Goldberg, director of Glen Mills Inc. in Clifton, N.J. His customers use grinding mills in laboratories that support a wide range of industries: food, plastics, mining, fibers, pharmaceuticals, biotechnology, farming, electronics and a host of others. Projects can involve anything from repetitive quality control testing to novel research, so Goldberg and his colleague, sales engineer Ross Kaplan, see a little bit of everything, from tried-and-true applications to “let’s try this and see if it works.”

“There are many [products] in everyday life where you just don’t think about how they get to that form,” says Sara Codrea, who supports grinding media sales for Union Process in Akron, Ohio. Her company’s customers are increasingly aware that the
type of grinding media they use will affect the efficiency of their milling operation, and she notes an increase in customer requests for feasibility testing of new milling options and processes (see Milling: A to Z).

When customers are selecting mills and grinding media, they have to ask, “How does the grinding step fit into your overall process?” says Brett Wilson, Ceramics Fellow at CARBO Ceramics, Inc., in Houston. CARBO manufactures ceramic sphere grinding media for a variety of applications; Wilson helps with the technical direction of the company’s ceramics R&D and supports the technical aspects of ceramic media sales. If milling is a critical or rate-limiting step, he says, then investing in equipment and grinding media to maximize milling efficiency and quality can save time and money in the long run. If milling is a less critical step, then it might be more economical to use more cost-effective grinding media.

**Mill basics**

Comminution, the overall term for particle size reduction, encompasses various forms of grinding, milling, pulverizing and crushing. In this field, the terms milling and grinding are generally used interchangeably. Mills also are used for dispersion processes that include mixing, extraction and de-agglomeration.

Each type of mill produces a different combination of impact, shearing and frictional forces — each suited for working with materials that can be hard, soft, brittle or fibrous.

A fibrous material like grass is handled with a cutting action, brittle materials like rocks are more amenable to impact methods, and oily materials like coffee beans use abrasion.

Ball mills, used for a wide range of applications, are one of the most common mill types. Large-scale industrial operations can process thousands of tons of material weekly using ball mills that are 60 feet long and 20 feet in diameter, containing some 100 tons of grinding balls, says Goldberg. Lab-scale milling equipment for a new product in the development phase can be scaled up later when the product is ready for commercialization.

Jar mills, typically used for laboratory samples or small production runs, use rollers to rotate the sample and grinding balls in a horizontal cylindrical container for a few minutes to several days until the desired final size is attained. Samples are usually dry, but jar mills also do wet grinding. Jar mills have historically been made from steel, but the newer models can be lined with ceramic or polymer materials. Polyurethane or nylon linings protect against high- or low-pH fluids or other corrosive chemicals during wet milling, and they prevent sample contamination by abrasion wear particles from the jar. Often, a polyurethane liner can outlast steel, says Goldberg, because of the polymer’s resiliency.

Goldberg notes that it is difficult to reduce a particle’s size more than a tenth to a fifteenth the starting size in any single step, so particle size reduction is often a multistep process. Hammer mills or jaw crushers, which crumble samples under pressure, can break down rocks or other large chunks of material. Afterward, other types of milling can progressively reduce particle sizes over several hours or days, ending with particles that can be as small as a few tenths of a micron across.

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**Milling: A to Z**

A small sampling of milling applications:

- Agglomeration/deagglomeration of particles
- Biological cell component extraction
- Black powder for ammunition
- Cement manufacturing
- Ceramic and pottery materials
- Chemical microanalysis sample preparation
- Chemical mixing and drying
- Chocolate powder
- Coal waste recovery
- Coffee grinding
- Cosmetics manufacturing
- Electronic device recycling
- Fertilizer manufacturing
- Fiber recycling
- Ink, pigment and glaze manufacturing
- Nanoparticle production
- Ore processing
- Peanut butter
- Pharmaceutical manufacturing and research
- Plant matter for biofuels
- Powder coatings
- Pyrotechnic materials (excluding flash powder)
- Solvent extraction (teas, flavorings, biosciences)
- 3D printing material preparation
- Zinc alloys (mechanochemical synthesis).
Much of CARBO’s grinding media business supports mineral processing operations, which typically use vertical stirred media mills (also called attritors) to break up feed material and facilitate extraction of metals from the surrounding ore. The feed material and grinding media are stirred in a stationary tank equipped with a rotating shaft that turns arms or discs. The result is homogeneous particle dispersion and a narrow product particle size distribution. Attritors, which can be run in batch, continuous or circulation mode, offer low power consumption, efficient milling, a small footprint and low maintenance requirements.

More operations are using horizontal-stirred media mills now that seals have been developed that prevent leaks during processing, Wilson says. Because the depth of the media is less in a horizontal mill than in its vertical counterpart, customers require denser media to provide the same impact forces. Horizontal mills often use smaller ball sizes, which requires an even greater density to provide enough momentum as the balls are stirred through the sample. One advantage to using horizontal mills, Wilson says, is that they are typically more efficient than vertical mills. The product also tends to have a narrower particle size range, he adds.

Union Process has a large manufacturing plant where it makes its signature product, attritor mills, which work using a combination of impact and shear forces (see Figure 1). These mills are continuing to get bigger and bigger, says Codrea. “We even had to put a new door into our manufacturing plant over the past year to be able to take the machines out once we build them,” she adds. For established processes, Union Process provides milling ser-

Grinding mills

- **Attritor (or stirred media) mills** use a stationary tank; arms or discs on a rotating shaft stir the grinding media through feed material, and comminution occurs by particle attrition.
- **Autogenous mills** tumble and collide chunks of feed material. Sand or other materials may be added to assist in the process.
- **Ball mills** use a rotating shaft to turn a horizontal or inclined cylindrical chamber containing spherical grinding media.
- **Bead mills** use a spinning shaft to vigorously agitate small spherical beads.
- **Disc mills** use one or two rapidly rotating discs to abrade small samples.
- **Hammer mills** have a rotating shaft with fixed rigid hammers or flexible hammers on hinges that swing and pound the sample.
- **Knife (or cutting) mills** use blades to cut the feed material.
- **Jar mills** use a grinding chamber atop a set of motor-driven rollers.
- **Jaw crushers** pulverize large chunks of rock or other hard materials using vibrating ridged metal impactors that move up and down in a “chewing” motion.
- **Jet mills** wear sample particles down using compressed air or gas to throw the particles about in the sample chamber.
- **Mixer (or shaker) mills** shake one or several balls back and forth.
- **Pebble mills** are ball mills that use flint or ceramic grinding media.
- **Pin mills** grind feed materials using rapidly rotating plates with cylindrical metal protrusions.
- **Planetary mills** rotate a container with the sample and grinding medium on its axis while it revolves on a platter.

![Photos courtesy of Glen Mills.](https://example.com/figure1.jpg)
Grinding media

Grinding media materials can be metallic (steels or other alloys), polymer (e.g., nylon), glass, ceramic or mineral (flint or sand). Ceramic media may be silicon carbide or silicon nitride, tungsten carbide, zirconium silicate or yttria-stabilized zirconium oxide (see Grinding Media).

One widely used medium consists of aluminum oxide particles in a silica glass binder. Increasing the amount of binder up to a certain point increases the hardness of the media, with 94% alumina balls being a popular choice for minimizing media wear. Some processes use 90% alumina satellites (molded spheres with a thicker band around the equator). These satellites are harder than 94% alumina balls, but the satellite band can wear off, contaminating the milled product and slowing the milling process. Some operations require a softer grinding medium with an alumina content of 99% or more, which increases the cost of the media but can pay off in terms of product quality and purity.

Grinding beads or balls can be composite materials, made from hard ceramic particles (e.g., kaolin, alumina or zirconia), with a silica glass or organic plasticizer binder that, after processing, produces the desired density, hardness, toughness and strength. Forces and stresses produced during bead formation can affect the performance of the final product. Dripping processes produce homogeneous beads, but they may be teardrop-shaped rather than spherical. Granulation processes, in which a seed particle is coated with successive ceramic layers, produce highly spherical beads but may produce internal stresses that cause the beads to delaminate during firing. Even high-quality beads may delaminate, split, crush or spall under imbalanced mill conditions.

Not every shape is available in all materials, says Codrea (see Figure 2). Spherical grinding media are the most common, but other applications require satellites or cylinders. She notes that some customers request grinding media with very exacting specifications, including drawings with specific shapes and dimensions. Complex shapes like satellites are generally made via dry or isostatic pressing. Some spherical media are manufactured using an advanced process where liquid ceramic droplets are passed through a liquid medium to prevent air bubbles and ensure high roundness, she adds.

The biggest changes in technology for ceramic grinding media came about 30 years ago, with the introduction of zirconia and stabilized zirconia ceramics, says Wilson. Recent R&D in this area, he says, is mostly about improving manufacturing processes to be more efficient and make better products. CARBO started out making propellant materials for the oilfield industry, but the company later branched out into foundry and grinding media applications. Today, the company’s grinding media business focuses largely on optimizing manufacturing parameters to improve the media’s wear resistance and extend the service life of their products, as well as extending sizes and densities to serve a wider range of customer needs. Mill manufacturers specify the characteristics of the grinding media that are best suited to their mills, says Wilson, but CARBO occasionally develops ceramics with specific media densities intermediate between the standard densities when a customer’s application requires it.

Grinding media

Balls or beads are the most common grinding media shape. Other common shapes include cylinders, satellites, pebbles and rods. Materials include steels and other alloys, ceramics, rubber, polymers, glass, flint and sand.

Grinding media are available over a range of hardness, density, fracture toughness, mechanical integrity, resistance to cold flow, high-temperature strength and impermeability to liquids and gases. Proper choice of a grinding medium reduces the time and energy needed to attain the desired particle size, minimizes contamination of the product, reduces wear to the mill parts and may give the user some control over product particle morphology.

Grinding media should be denser than the material being ground so that the medium does not float on top of the sample and it impacts the sample with enough force to break down the sample particles. One exception is autogenous grinding, which uses chunks of the feed material itself to impact each other in a rotating drum.

Grinding media particles should be substantially larger than the particles being ground, but small media particles are needed to generate smaller product particles. Thus, several stages of grinding may be required, from coarse materials to successively finer particles.

Media particles should not shatter, abrade, release colored material or otherwise contaminate the product. Steel grinding media can spark during impact and should not be used with flammable materials. Some products can react with grinding media, especially during wet grinding or solvent extraction, causing corrosion to the grinding media and mill components.

**Figure 2.** A visual glossary of media shapes. (Figure courtesy of Union Process.)
Customers must consider how great an effect media residue has on the final product, Wilson says. For most mineral processing, a little bit of worn media in the ore doesn't greatly affect the end product, he says, so mineral operations can use various types and colors of media. On the other hand, even a small amount of wear particles from colored media can affect the final color of pigments or white mineral ores like calcium carbonate. The same holds true for chemical contamination, he adds. Pigment milling processes typically do not use metal balls, since metal wear particles could react with a pigment or discolor it.

"Contamination is the No. 1 concern," says Goldberg, especially in industries under FDA scrutiny (pharmaceuticals, dental and medical devices) and for electronic devices where any ferrous particles could affect the device's electrical properties. For these and other high-end applications where contamination and discoloration can ruin a product, a customer might require jars and matching balls made from specialty materials such as a zirconia-yttria ceramic.

Selecting the operating conditions

When customers are selecting grinding media and milling conditions, says Wilson, they need to consider what they are trying to grind—the material's hardness, how difficult it is to grind and the starting and ending sizes of the feed material particles.

Milling involves any of four basic wear mechanisms, depending on the nature of the sample and the milling conditions. Interfacial adhesive bonds can be formed or broken, abraded, worn, or degraded. Abrasion removes material from the surface, tribochemical reactions alter the chemical species present (including the formation of corrosion or passivation products), and surface fatigue produces cracks that fracture the material. Often, comminution happens as a result of a combination of factors: ball mills use the impact of the balls on the sample and abrasion between sample particles to reduce particle sizes. For wet or soft samples, abrasive media remove material from the surface using a galling action. Abrasion also can remove a small amount of material from a larger piece as a sample for testing. Rotating blades can cut or pinch a sample into smaller pieces.

Milling or grinding product particles with the desired size range and morphology requires optimizing several factors, says Codrea. The shape, size and hardness of the feed material must be taken into account, as well as starting particle properties such as morphology (rounded, sharp or fibrous), friability, stickiness and sensitivity to heat. The desired size of the product particles determines the size and composition of the grinding media, the speed of the mill and the duration of the grinding run. The reactivity of the feed material and the sensitivity to contamination of the final product also influences the choice of grinding media and mill liner materials, and whether the run will be conducted under an inert gas atmosphere or cryogenic conditions.

It is possible to gain limited control of final particle size distribution and shape by adjusting the particular mill's operation, says Goldberg. For ball mills, adjustments can be made to the speed of revolution, the density of the grinding media, amount of sample loaded, the diameter of the grinding media, the amount of grinding media, duration of the run and so on. Casting slurries might require preparation in a blender rather than a ball mill because of density differences between the lubricant phase and the particle phase (magnesium stearate and ceramic particles, for example).

Some customers specify product particle morphologies, including particles with rounded edges or sharp platy fragments, says Goldberg. For example, mold release compounds for ceramic casting or pharmaceuticals might require rounded particles for their lubricating properties. Rolling motion tends to produce rounded shapes, and impact produces platy fragments. There are limits to how much control users have to the final particle shape, he adds.

Smaller grinding media and faster revolution produce smaller particles. Imparting more energy to the system also enhances the comminution: higher rolling speeds, heavier balls, more balls or more hammers produce smaller particles. In all cases, says Goldberg, the better the grinding action, the more the system heats up, and the more the mill's surfaces can be mechanically eroded, which will contaminate the product unless preventive measures are taken.

For any given application, Kaplan explains, grinding media have to be matched to the container. Jars are generally more expensive and less easily replaced than balls. However, it can be worthwhile to invest in high-grade grinding media, which don’t wear out as quickly, and so are less likely to contaminate the sample. Less wear means that you don’t have to change out the media as often (maybe as little as once every year or two rather than every few months), which can help reduce costs in the long run.

The speed of rotation helps determine the final particle sizes and how long it takes to complete the process. Rotating too fast can set up centrifugal forces: the grinding balls cling to the walls of the container rather than falling through the sample. Rotating too slowly causes the balls to stay on the bottom of the container. Running close to the "critical speed" allows the balls to rise and fall to produce the most efficient comminution.

Cryogrinding using a jacketed grinding chamber and liquid nitrogen may be necessary to keep friable or low-melting materials like biopolymers below their glass transition temperature, Kaplan explains. The low temperature not only makes the sample particles more brittle—it also reduces the buildup of frictional heat that could melt or degrade the sample (which can happen over a very small rise in temperature). Cryogrinding is used for pulverizing certain food products like sinew and collagen that can melt at relatively low temperatures. Making a powder requires "an interesting dance"—optimizing the combination of temperature regime and grinding methods, he says.

Testing services

Manufacturers and distributors often have their own lab facilities to assist customers in selecting mills, grinding media...
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and process conditions for specific applications (see Case Study). For example, Union Process performs laboratory wear tests on every type of grinding media the company offers and provides recommendations on how to obtain the best results. The company also does customized testing for client companies and laboratories that are developing new materials and processes. Glen Mills distributes sample preparation equipment, with a focus on mills for processing a few grams to several kilograms of material, and they provide testing services for a wide variety of customer applications.

Customers often send samples of their material for lab testing, but Union Process also encourages customers to visit the company’s facilities and collaborate first hand with the lab technicians to test mills, media and processes for their materials. “Our experts have seen just about everything, and we have a huge database of milling history,” Codrea says, but often, it takes some experimentation to optimize a process involving a new material or new specifications. It helps the lab staff to see the actual material—what it feels like, how it moves in the mill, she says. “You just need to see it to make that determination.”

The Union Process lab facilities are located close to the manufacturing and service milling areas, which facilitates communication among engineers and lab staff. The company custom builds each mill to meet the requirements of individual customers. Customers sometimes request adaptations and improvements of standard grinding media as well, asking for a Cadillac version of a basic grinding ball with better smoothness, wear properties and other features, Codrea says.

Customers may compare various types of grinding media to minimize contamination or reduce wear to the grinding media and mill linings without sacrificing performance. Codrea adds that what customers expect from grinding media is changing: more companies are requesting detailed data sheets with information on media composition and properties and wear test information.

Media wear can contaminate the product, and there are ways to check if a ball charge is wearing away, explains Goldberg. Sifting analysis can help determine if the ball sizes are decreasing due to attrition, and particle analysis can alert the user to contamination problems. An increase in the amount of milling time needed to produce the desired particle size is another sign that the media might be eroding—eroded media particles accelerate too slowly to be effective, and they merely absorb energy during the milling process. Analyzing product particle sizes is standard procedure, he says, but unless users suspect that the balls are eroding, they might not check for contamination as often. Ball breakage, which mixes fragments with the product, is another concern, he adds. Here, installing a catch filter after the milling step is prudent to trap bead debris.

**Milling applications**

“We are both users and producers of media, since we need to grind our raw materials to manufacture the ceramic grinding media,” says Wilson. “We need fine particles to make the media that we use to make fine particles.”

Small particle sizes are important for a wide variety of other applications as well. In his previous work with the Pfaltzgraff Co., Wilson used mills to grind ceramic glazes. “You have to get them fine enough so that they sinter at the right temperature and give you the nice smooth finish you expect from dinnerware,” he explains. One Glen Mills customer uses small-particle tattoo inks to get the best color quality.

For researchers developing new materials, grinding and milling can be a useful way to prepare samples for quality control testing. As lab tests like Nuclear Magnetic Resonance (NMR) Spectroscopy and optical analysis methods become more and more sensitive, sample particle sizes have to go down as well. Fortunately, grinding methods are evolving, says Goldberg, and they can now produce particles in the small sizes these techniques require.

Codrea notes that much of their business supports research and development efforts, which use benchtop mills to process small amounts of material. Cryogenic testing has seen an uptick in recent years, she adds. Union Process also has seen increasing interest in using ultra-fine grinding media to produce even smaller particles. She notes that some pharmaceutical companies request ceramic media such as yttria-stabilized zirconium oxide beads with diameters as small as 0.1 mm. “The beads look like powder,” she says.

In the field of chemical processing, milling can reduce particle size, modify particle morphology or break apart biological cells to activate or liberate chemical components. Mills also can be used for stirring and homogenization, especially for spongy or gelatinous materials. Food processing is another popular area, says Codrea. “We’ve tested chocolate, peanut butter, hazelnut spread and various compound coatings.”

Wet milling can be used to produce ultrafine particles, from a few microns in diameter down to the nanometer.
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range. Dry grinding is used in mechanical alloying processes (cold welding), where metals and additives are reduced to small particles and then beaten together to form agglomerates. The process is repeated to form dispersion-strengthened metals having the desired properties.

Tea and coffee companies and the flavor-and-fragrance industry use mills for solvent extraction operations. As plant material is being ground into fine particles to increase the surface area, solvents mix with the particles and extract the compounds of interest, Goldberg says.

Aside from performing comminution tasks, the tiniest balls (more commonly called beads) also can be used as spacers. Sizing beads, incorporated into a glue used for holding LED lenses in a frame, resist pressure and help maintain the proper distance of the covering lens above the LED display.

Safety first
Milling operations require attention to health, safety and environmental concerns. “We have our own guidelines and standards for environmental waste, and our customers do as well,” says Codrea. Because they deal with such a wide range of materials and processes, Union Process personnel make sure that they know what they are milling and what safety precautions are required. “We keep safety data sheets on everything,” she says. Company personnel also are knowledgeable about the hazards of various combinations of materials, how to mix chemicals in the right order and how ambient conditions factor into safety—sometimes even humidity in the air can create hazardous conditions, she adds.

Goldberg notes that safety precautions are especially necessary during wet milling using organic solvents. Heat produced during milling can generate flammable solvent vapors. These vapors can accumulate, and static electricity on particle surfaces or an electrical spark from plant equipment create a fire or explosion hazard. Cooling equipment and grounded electrical connections reduce this hazard, and small amounts of additives like alcohols may be added to the batch to dissipate static charges. Filling the grinding chamber with an inert gas can reduce the danger of a fire or explosion, as well as retarding oxidation.

The simple failure of the cooling system on a ball mill can lead to disaster when volatile organic liquids are present, says Goldberg. A sealed ball mill will operate nicely when it is continuously cooled, he explains. However, a leaky or plugged fluid line, a failed water pump or lack of sufficient water can restrict or stop the flow of cooling fluid to the jacket surrounding the ball mill. If the ball mill does not have a failsafe shutdown that activates when the mill is getting warm, the liquid’s vapor pressure will rise. This can blow the mill’s door gasket and release a cloud of gas vapors that could flash if an initiation spark is present.

Upcoming applications
Although grinding and milling technology hasn’t changed much, the applications are constantly evolving. “We’re not an industry, we’re a class of activity,” Goldberg says. Recent applications include biopolymers and natural materials. Recycling is another expanding area, he adds. Used cardboard can be recycled into cellulose fibers that can be made into textiles, which is especially beneficial for making low-cost clothing for sale in developing nations. Discarded electronic devices can be pulverized for easier reclamation of precious metals (platinum and gold), copper and rare earth elements and compounds. Milling can be used to rupture E. coli or yeast cells to release compounds that are useful for making artificial meat or drugs.

Better control over particle shapes and sizes is becoming more important with the rise of additive manufacturing (also known as 3D printing). Small hard or brittle particles keep their desired properties when they are incorporated into an extrudable matrix, and the matrix provides the overall shape to the manufactured piece. For example, grafting and implant biomaterials can incorporate protein particles in a nonreactive polymer scaffolding matrix. Circuit boards made using 3D printing can incorporate conductive filaments made from metal particles within a nonreactive polymer matrix.

The sheer variety of applications lends itself to a generalist approach when dealing with customers. “You have to learn the language of each person’s discipline,” says Goldberg, noting that they not only test samples in their own facilities, but they also act as a go-between for their customers and the factories that make equipment and media. “They’re not just one-trick ponies,” Kaplan says, referring to the versatility of mill applications. “We get very excited about this stuff.”

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REFERENCES