

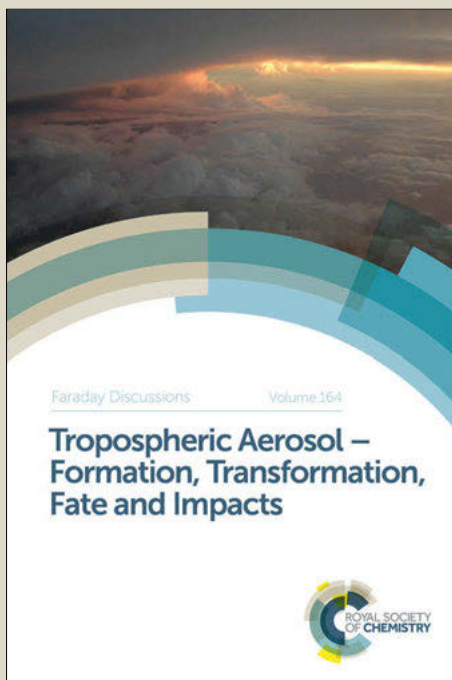
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Scalability in the Mechanochemical Syntheses of Edge Functionalized Graphene Materials and Biomass-derived Chemicals

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5 Jackson^c, Ashlyn Sinclair^c, Alexandra Taraboletti^a, and David T.
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Mechanochemical approaches to chemical synthesis offer the promise of
10 improved yields, new reaction pathways, and greener syntheses. Scaling
these syntheses is a crucial step toward realizing a commercially viable
process. Although much work has been performed on laboratory-scale
investigations little has been done to move these approaches toward
industrially relevant scales.

15 Moving reactions from shaker-type mills and planetary-type mills to
scalable solutions can present a challenge. We have investigated scalability
through discrete element models, thermal monitoring, and reactor design.
We have found that impact forces and macroscopic mixing are important
factors in implementing a truly scalable process. These observations have
20 allowed us to scale reactions from a few grams to several hundred grams
and we have successfully implemented scalable solutions for the
mechanochemical conversion of cellulose to value-added compounds and
the synthesis of edge-functionalized graphene.

Introduction

25 Mechanochemical approaches to chemical syntheses are a growing field. They offer
an attractive solution to industries seeking to improve profitability through
decreased reaction times and reduction of solvent waste. Much of the equipment
and tools developed for mechanochemical reactions has been adopted from the
materials processing community. Attrition technology is focused on the mining and
30 food industries. Mechanical alloying¹⁻³ and more recently the mechanochemical
synthesis of advanced materials⁴⁻⁶ are becoming more and more accepted as cost-
effective tools that also offer the potential for unique products.⁷ Implementation of
chemical reactions in a mill has seen a lot of interest.⁸⁻¹² However, these studies
have had limited scope and do not address routes to industrial implementation.
35 Although quite unique reaction pathways are available mechanochemically, little
work has gone into developing pathways to increase scale.¹³ In contrast, routes from
bench to full scale in traditional syntheses are well established with known solutions
to mixing, heat transfer, and material transport issues. Industrial adopters are often
concerned with the unknowns faced in implementing a mechanochemical process.
40 This leads to the use of existing tools and knowledge to develop assumptions in
assessing a new process. Often, these assumptions lead to incorrect understanding

and failure to implement a profitable process.

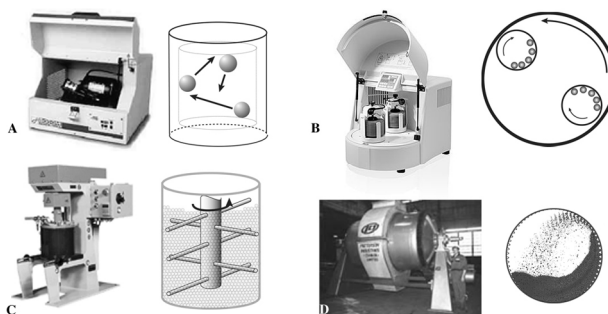


Figure 1. A small set of milling technologies currently available. The motion of the milling media is indicated in schematics next to each mill. These vary from the small scale (A) SPEX mixer mill (65 mL)¹⁴, to the medium scale (B) planetary mill (250 mL)¹⁵, (C) attritor (4 liters)¹⁶, to the production scale (D) rolling ball mill (hundreds of liters).^{17, 18}

There is a large array of milling technologies available. Figure 1 shows some commonly used mills and their attrition modes. The first three mills are often used in academic laboratories for exploratory syntheses. The most popular are the mixer mill (Figure 1A) and the planetary mill (Figure 1B). A mixer/mill is amendable to small exploratory reactions, but does not scale beyond 10 grams. A planetary mill can be used for syntheses up to 100g, but apparatus costs typically limit implementations to the 20-50g range. Attrition mills represent a linearly scalable technology; however laboratory-scale attritors typically require at least 100g for efficient operation. By housing these technologies in a small laboratory a range of reaction scales can be investigated (Figure 2) with an eye toward realizing an industrially relevant solution.

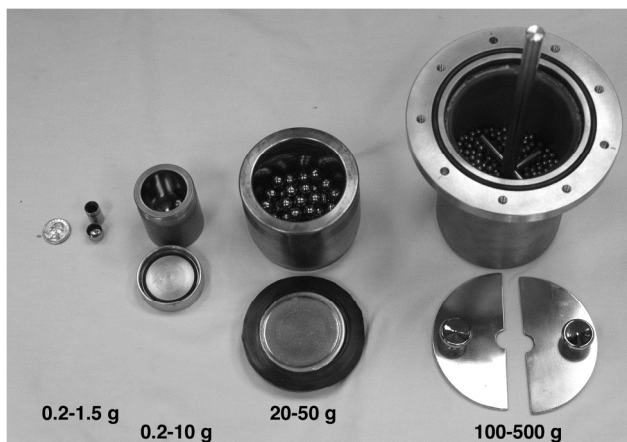


Figure 2. Reaction scales achievable in a small laboratory. From left the right, a microvial for a SPEX 5100 mixer/mill, a vial for a SPEX 8000 mixer/mill, a vial for a Fritsch Pulverisette 6 planetary mill and a tank for a Union Process 01-HDDM attrition mill.

Mixer/mills and planetary mills represent high-energy processing. We have found that reactions for the hydrolysis of cellulose and the oxidation of graphite can be readily moved between the two without the need for excessive process optimization.

However, scaling beyond a 50-gram reaction requires utilization of an attrition mill or other scalable approaches. It is our observation that mechanochemical processes are dominated by two phenomena. Attrition or particle size reduction down to a scale where media impacts can induce meaningful chemical reaction rates. As well as a chemical regime where reactions occur at the point of each impact and are facilitated by the high transient compressive forces generated. Scalability issues were explored through the investigation of two commercially relevant reactions. The solid-catalyzed hydrolysis of cellulose to simple sugars and the oxidation and delamination of flake graphite to produce edge functionalized graphene.

10 Results and Discussion

Scale-up in the Mechanochemical Hydrolysis of Cellulose

Biopolymers such as cellulose and hemicellulose are a potentially rich source of industrially significant compounds for use as chemical feedstock or fuel. However current approaches are not feedstock tolerant, require large capital investments, and produce significant amounts of waste. A first step in realizing value from these materials is hydrolytic depolymerization to simple sugars. Previous work has shown that cellulose can be readily hydrolyzed by solid acids such as kaolinite¹⁹ and through impregnation with minimal quantities of a strong acid²⁰⁻²² combined with mechanical processing. Using basic conditions, lignin can also be mechanocatalytically depolymerized.²³ However this work has been limited to at most 10-gram reactions in mixer/mills and planetary mills. In order to realize an industrially useful process, a route to multi-ton implementation must be understood. Our initial studies with toll milling at Union Process¹⁹ indicated a significant induction period (4 hours, Figure 3) before any appreciable yield was realized. The origin of this induction period was a paradigm difference between the laboratory and the production facility. Typical uses for attrition technology require no chemical change to occur in the ground material. Whereas, mechanocatalytic processes seek to capitalize on the new reaction pathways available under the application of mechanical force. By application of small laboratory attritor we have been able to develop solutions to the induction period issue.

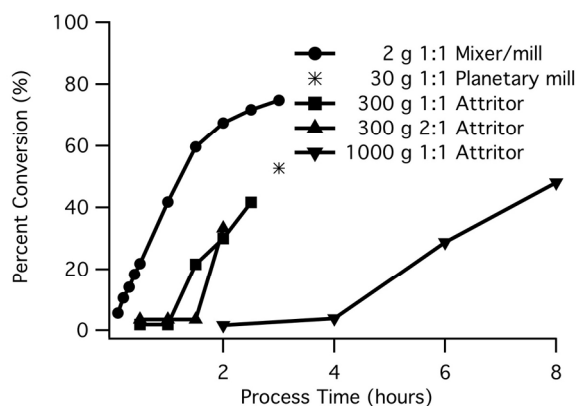


Figure 3. The conversion of microcrystalline cellulose into soluble saccharides at various scales and cellulose:catalyst ratios.

In Figure 3, it can be seen that the mixer/mill induces the fastest conversion of cellulose into sugars. The planetary mill is slightly less efficient and attrition milling has significant induction periods. It should be noted that milling for extended periods of time in an attrition mill results in severe dehydration. This is due to the containment differences between this mill and the others. In mixer/mill and planetary mill implementation the reaction vessel is sealed and any water loss through frictional heating will be minimal. In an attrition mill, there is significant dead space above the media and water can be transferred from the reaction zone to empty, cooler areas. This effectively reduces the water available for hydrolysis and allows dehydration reactions to predominate. Upon examining the results in Figure 3 it becomes apparent that several processes are occurring. First, attrition is reducing the catalyst and cellulose size as well as amorphitizing the cellulose. This process is exemplified by the induction period. Short induction periods indicate effective attrition. Second, acid catalyzed hydrolysis is leading to the production of sugars. Third, frictional heating is producing water loss. Fourth, low water content is leading to dehydration of the sugars produced. In an attrition mill these issues can be addressed individually. The ideal is a process dominated by hydrolysis. Attrition and amorphitization can be accelerated through the introduction of a solid that is harder than cellulose, but softer than the milling media (440C stainless steel, Mohs hardness=5.5). We chose dolomite ($\text{CaMg}(\text{CO}_3)_2$, Mohs hardness=3.5), a commercially available commodity mineral with a cost per ton similar to or less than that for kaolin.

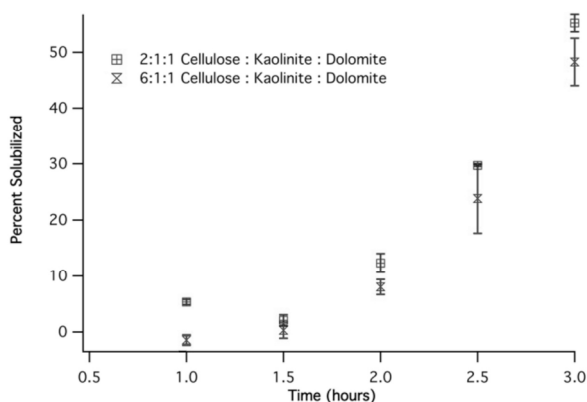


Figure 4. Enhanced conversion of cellulose to saccharides through the addition of a milling aid.

Previous runs had resulted in slower reaction kinetics when the cellulose:catalyst ratio was increased (Figure 3). The introduction of the milling aid, dolomite, allowed an increase of the ratio without a reduction in conversion rates. Dolomite serves two purposes in this reaction, it improves the attrition of cellulose and dilutes the acidic solid, effectively reducing the dehydration rate. Acid catalyzed hydrolysis only occurs during impacts. By increasing the number of impacts, both chemical and mechanical processing rates can be improved. This is typically described as the ball to powder ratio (BPR) in mechanical alloying experiments. In a

mechanochemical process, increasing the BPR produces more collisions. If the media is free to move then this also keeps the force distribution of the impacts similar. However, if severe confinement is produced through the use of large amounts of reactant or media, then compressive forces will be severely reduced. It can be seen in Figure 4 that increasing of the BPR through reduction of the reaction mass resulted in a significant improvement of the reaction kinetics and allowed longer processing without dehydration. The intensity of the collisions can be increased by changing the media size or the milling speed. We explored reactions with 6 mm and 12 mm media at 300 and 700 rpm in the attrition mill. We found that the reaction rate scaled linearly with rotational velocity. Reaction rates also increased with larger media. However, maximum reaction temperatures though frictional heating (48°C for 300 rpm/6 mm, 78°C for 300 rpm/12 mm, 106°C for 700 rpm/6 mm, and 167°C for 700 rpm/12 mm) also increased and dehydration reactions became favored at higher speed/media sizes. Through the application of discrete element modeling (DEM) it is possible to relate the experimental observations to the compressive forces produced in a mill. It was found that the distribution of compressive forces and the fraction of impacts that produce non-zero compressive forces are both critical to the reaction rate. In general, higher rotation speeds and larger media size produce higher collision forces. The complex nature of media motion in a mill is ideal suited to discrete element modelling (see movies in supplemental materials). The exception is a 28 liter attritor where inadequate mixing is evident. In all traditional implementations of the attritor a dead zone forms around the shaft of the tree when the media rises up due to the application of rotation energy. Rotating the tank 90° and using gravity to encourage mixing could eliminate this problem. These examples serve to illustrate the need for whole reactor modelling in scaling mechanochemical reactions. Simple force calculations would not predict inadequate mixing or the formation of dead zones. Favorable conversion kinetics are achieved when the fraction of non-zero force collisions is high (Figure 5). This represents a large scale confirmation of similar phenomena observed in microscale reactions.²⁴

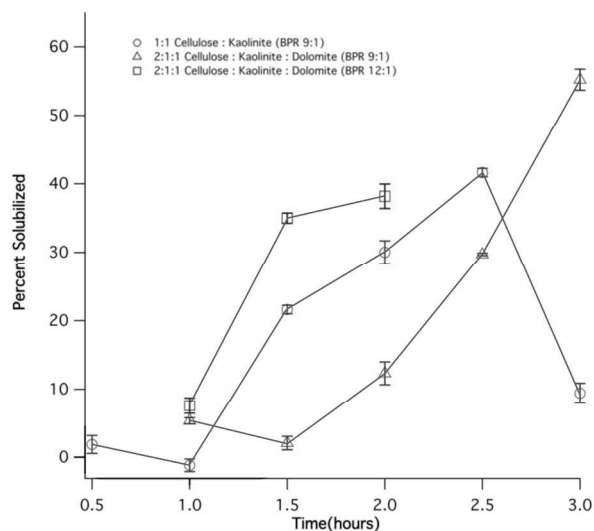


Figure 5. Improved kinetics are realized with a higher media to reactant ratio. The reactions were performed in a Union Process 01-HDDM with 6 mm media. The reduction of solubilization in the 1:1 reaction (circles) is due to severe dehydration of the reaction products.

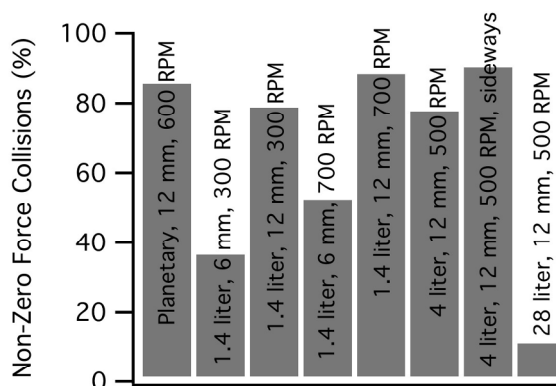


Figure 6 The best hydrolysis rates are achieved when the fraction of non-zero force collisions is high. The four liter and 28 liter values have been modelled, but not yet experimentally confirmed.

Scale-up in the Production of Edge-Functionalized Graphene

Graphene has many useful properties including a low coefficient of friction, good electrical conductivity, and high thermal conductivity. However, current approaches to producing graphene are not scalable or produce large quantities of waste. The most popular route to useful quantities of graphene is through the synthesis and exfoliation of graphite oxide. Graphite oxide contains oxygen attached to the layers as both epoxy bridges and hydroxyl groups²⁵⁻²⁷. Its properties vary from graphene in that it is an electrical insulator, thermally decomposes, and is significantly more hydrophilic, allowing complete exfoliation upon suspension in water^{25, 27-29}. This last property makes graphite oxide a valuable precursor in the mass production of graphene. After exfoliation, the sheets of graphene oxide can be chemically reduced into graphene³⁰. The ability to produce graphene oxide-type materials on a commercially relevant scale is very important because of the utility of graphene, produced from it, for developing number of novel device technologies³¹.

By directly milling graphite powder with a mild oxidizing agent, we can simultaneously oxidize and delaminate graphite producing a product with few layers suitable for a variety of uses. We found that urea hydrogen peroxide adduct (UHPA) and 35% hydrogen peroxide can effectively oxidize graphite in a mechanochemical environment. In this application, moving from a mill that relies on inertia for media motion (Mixer/mill and planetary mill) to one that actively stirs the media resulted in improved reaction kinetics and the ability to use a liquid oxidant. Figure 6 illustrates the problem encountered with UHPA in a planetary mill. The oxidation reaction forms liquid and gaseous products. The liquid products increase the rolling resistance of the media and the gaseous products (Eq. 1 to 5) can

produce explosive failure of the vial's sealing mechanism. In contrast, a stirred media mill can still move the media through quite viscous mixtures and the milling tank can be designed to allow release of reaction products in a controlled manner.



10

The scaled synthesis of edge functionalized few-layer graphene represents a reaction where attrition dominates the rate. This was investigated by pre-grinding crystalline graphite and chemically oxidizing the resultant material. From 8 to 12 hours are needed to produce finely divided, delaminated graphite. But, high levels of oxidation can be achieved in as little as 30 minutes. This phenomena is illustrated by the oxygen content of the product obtained using several grades of graphite representing different flake sizes and crystallinities. Grade TC306 is a delaminated graphite produced by Asbury carbons whereas TC301 is the same graphite with a lower level of delamination. Grade 146 is a highly crystalline, large flake natural graphite that showed little oxidation without pregrinding. By starting with a delaminated graphite or pregrinding graphite (Table 1) it can be seen that preprocessed materials lead to a product with higher levels of oxygen.



25 **Figure 7.** Oxidation of graphite in a planetary mill using UHPA results in the formation of a solid mixture that does not tumble.

Table 1. A representative sample of reactions producing edge-functionalized graphene with mass% oxygen.

Grade	Mass % Oxygen	C _n O	Comment
TC306	8.94	13.5	SPEX mill
TC306	12.03	9.80	SPEX mill Graphite was premilled for 12 hours
TC301	2.70	48.0	SPEX mill
146	20.20	5.27	Planetary mill, 30 g, 12 hours, then 12 hours with UHPA
TC306	13.50	8.54	Attritor [®] , 50 g with hydrogen peroxide

Conclusions

Scaling mechanochemical reaction requires an understanding of the mechanical and chemical processes occurring during the reaction. Through the use of a well-characterized reaction (cellulose hydrolysis) we have developed a measure for the processes in a mill. We have found that reaction rates and yields are governed by two processes - size reduction and the chemical reaction itself. Profitability of mechanochemical syntheses will only be realized with either high value (edge functionalized graphene) materials or low processing times to reduce energy consumption (cellulose hydrolysis). By relating the results of cellulose hydrolysis to discrete element models we have shown that the fraction of non-zero force collisions and distribution of compressive forces realized in a mill are the critical parameters for realizing an increase in reaction scale. Models developed for this study will be applied to a 160 liter attritor and compared to measured hydrolysis rates.

Experimental

Hydrolysis of Cellulose

Small-scale milling experiments were performed in 8000M and 8000D SPEX Certiprep mixer/mills. Milling vials were constructed from 440C stainless steel with an approximate volume of 65 mL. Buna-N quad O-rings were used to maintain a seal during milling. High kinetic energy milling was performed with three 12 mm stainless steel balls weighing approximately 8 grams each. Milling was carried out in 30-minute increments, followed by 30 minutes of cooling to reduce wear on the mill's motor. Hydrolysis was realized by milling cellulose (Microcrystalline, Alfa Aesar, 1.000 g) with kaolin (Kaopaque 10s, Imerys, 1.000 g).

Large Scale milling experiments were performed in a Fritsch Pulverisette 6 planetary ball mill and a Union Process 01-HDDM Attritor[®]. For planetary milling, vials were constructed of X10CrNiS18-9 stainless steel with an approximate volume of 250 mL. A Viton gasket was used to maintain a seal during milling. Milling was performed with 50 12 mm stainless steel balls (440C) weighing 8 grams each. Hydrolysis was realized by milling cellulose (Microcrystalline, Alfa Aesar, 15.000 g) with kaolin (Kaopaque 10s, Imerys, 15.000 g). Milling was carried out in 60-

minute intervals with 30 minutes of cooling between each interval for a total of 3 hours of milling.

Attrition milling was performed in a custom 1.4 liter tank designed to monitor and hold gas overpressure as well as reduce water loss. Typically, 2.72 kg of 6 mm or 12 mm stainless steel balls (440C) weighing 1 gram and 8 grams respectively were utilized as the milling media. Milling was carried out continuously. Cellulose (Microcrystalline, Alfa Aesar, 150 g) was milled with kaolin (Kaopaque 10s, Imerys, 150.000 g) or a mixture of kaolin and dolomite (Dolowhite, Axner Pottery).

Gravimetric Analysis

The extent of hydrolysis was monitored gravimetrically. Conversion of cellulose to water-soluble oligosaccharides was determined by stirring 0.1 g of the reaction mixture in 30 mL of water. Any oligosaccharide with a degree of polymerization <5 will be solvated.³² The production of water-soluble products was measured by filtration through a 47 mm diameter Whatman Nuclepore® track etched polycarbonate membrane filter with a pore size of 0.220 µm. The residue was dried in a 60°C oven for 12 hours and then weighed.

Synthesis of Edge-Functionalized Graphene

All of the graphite used in this study was supplied by Asbury Carbons. Small-scale milling experiments were performed in 8000M and 8000D SPEX Certiprep mixer/mills. Milling vials were constructed from 440C stainless steel with an approximate volume of 65 mL. Buna-N quad O-rings were used to maintain a seal during milling. High kinetic energy milling was performed with three 12 mm stainless steel balls weighing approximately 8 grams each. Milling was carried out in 30-minute increments, followed by 30 minutes of cooling to reduce wear on the mill's motor. This was achieved by milling graphite (1.000 g) with urea hydrogen peroxide adduct (2.902 g). The final product purified by suspension in water, placed in sealed dialysis tubing, and suspended in a 10 liter recirculating deionized water bath to remove any remaining urea, the water was changed daily. After three days the sample was removed and dried by evaporation under forced air flow.

Large Scale milling experiments were performed in a Fritsch Pulverisette 6 planetary ball mill and a Union Process 01-HDDM Attritor®. For planetary milling, vials were constructed of X10CrNiS18-9 stainless steel with an approximate volume of 250 mL. A Viton gasket was used to maintain a seal during milling. Milling was performed with 50 12 mm stainless steel balls (440C) weighing 8 grams each. Milling was carried out in 60-minute intervals with 30 minutes of cooling between each interval for a total of 12 hours of milling. Typically, graphite (TC306, 7.5147g) was milled in one portion with urea hydrogen peroxide adduct (30.0284 g). Once all the milling was complete, the reaction mixture was suspended in water, and placed in a custom flow dialyzer. The dialyzer consisted of a pump circulating a 10 L bath of deionized water and a peristaltic pump moving 800 mL of product/water suspension through a dialysis tube suspended in the water bath. The deionized water was changed once a day. After three days, no urea was present in the product. The product suspension was transferred to a glass tray and dried under the air flow of a fume hood.

Attrition milling was performed in a custom 1.4 liter tank designed to monitor and hold gas overpressure and 2.72 kg of 6 mm stainless steel balls (440C) weighing 1 gram each. Milling was carried out continuously. Typically, graphite (TC306, 50 g)

was milled in one portion dry at 700 rpm for 1 hour. Hydrogen peroxide (108 g) was added and the slurry was milled for another hour at 300 rpm. Once all the milling was complete, the reaction mixture was collected and dried under flowing air.

5 Elemental Analysis

For elemental analysis, dry, urea-free samples were analyzed for C,H,N, and O content by Micro-Analysis, Inc., Wilmington, DE, www.microana.com. Oxygen content was measured using the Unterzaucher method.

10 Discrete Element Modeling

Discrete element models of the milling process were generated using EDEM (DEM Solutions Ltd.).

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- † Electronic Supplementary Information (ESI) available: Movies of DEM model showing the compressive forces generated for the various mills.
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