

Reactive Dry-Milling for Environmental Protection **-encouraging industrial applications for High Kinetic Processing-**

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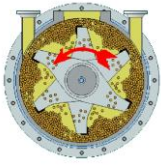

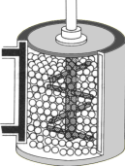
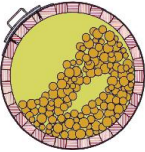
Introduction

The Reactive (dry-) Milling technique [1] is still not widely used, even though mechanical alloying [2-4] has a long tradition and inorganic or more recently organic chemical syntheses are known to proceed to completion without producing wastes [5]. These favorable findings contrast solution reactions that tend to be incomplete and produce side reactions with the necessity of waste producing purifying workup that is in most cases much more expensive than the synthetic step. The alternative by very high temperature syntheses in inorganic solid or melt reactions requires much energy which can be saved if reactive milling succeeds at ordinary temperature. The nanoscopic nature of solid-state chemical reactions has recently been studied in numerous organic solid-state reactions using supermicroscopic techniques like atomic force microscopy (AFM), scanning near-field optical microscopy (SNOM) and nanoindentation/nanoscratching. A consistent mechanistic scheme emerged for the non-tribochemical reactions with far-reaching molecular migrations within the crystal along “easy” paths [5]. While the three-step mechanism of phase rebuilding, phase transformation and crystal disintegration is secured for molecular crystals, organic polymers or infinite inorganic covalent crystals undergo tribochemical reactions by mechanical breakage of covalent bonds. The extremely unsaturated fresh surfaces which occur upon cleavage of the crystals cause local plasmas which allow all kinds of chemical reactions at low temperature [6]. There may be borderline cases between these different mechanisms with salts and metals, but normal non-polymeric organic molecules cannot break covalent bonds upon mechanical interaction by milling unless very high forces are applied with Bridgman anvil type equipment [7]. The latter reactions are without preparative use. We describe here technical applications of reactive milling in the different fields.

Processing (Milling) Techniques

Industrial mills of different types are in practical use for a number of commercial applications. Vibration-mills have to move the mass of the grinding chamber. This limits their size and in particular they are difficult res. impossible to be operated under controlled condition like atmosphere or closed circuit. The same is valid for simple (drum-)ball-mills with a rotating vessel [8]. Jet-mills use large streams of air or inert gas which limits their use in reactive milling. Next to this the non-presence of grinding media does not lead to significant kinetic effects. Bead-mills, horizontally or vertically, do not exhibit a significant kinetic impact as well, since here no high-level relative acceleration of the grinding media occurs which leads to shear- and friction effects but not to collision. Planetary ball-mills and shaker-mills are technically limited to laboratory size [9-10]. The most suitable choice were horizontal rotary ballmills that can be operated in dry processing at high relative velocity of the grinding media (up to 14 m s⁻¹) that cannot be reached by the other types (up to 5 m s⁻¹) under controlled condition like vacuum or inert gas [10] and in closed circuits [11].

Table 1 compares most corresponding devices that are in use for high kinetic processing (HKP) with respect to size and maximal velocity of the milling tools.

device	Simoloyer®	Planetary Ball Mill	Attritor®	Drum(ball)mill
max. diameter [m]	0.9	0.2	1	3
max. total volume [l]	400	8	1000	20000
max. rel. velocity [m/s]	14	5	4.5-5.1	<5
graphic (cross section)				
Simoloyer® is a brand of Zoz GmbH, Germany; Attritor® is a brand of Union Process, USA;				
Table 1: Devices used for HKP				

The Horizontal Rotary Ballmill

Horizontal high energy ball-mills are known from academic as well as industrial applications in mechanical alloying (MA) [2-4, 12-13], high energy milling (HEM) [14] and reactive milling (RM) [1]. They supply the highest relative velocity of grinding media, which leads to a high level of kinetic energy transfer, an intensive grinding effect and short processing times. The contamination of the processed powders by the milling tools is naturally lower since the process is based on the collision of grinding media rather than on shear and friction interaction of the same which usually leads to higher abrasion. Since the grinding media is accelerated by a horizontally arranged rotor inside the grinding vessel, these devices do not have to move unnecessarily any large masses like e.g. the entire chamber/mill in case of vibration-mills.

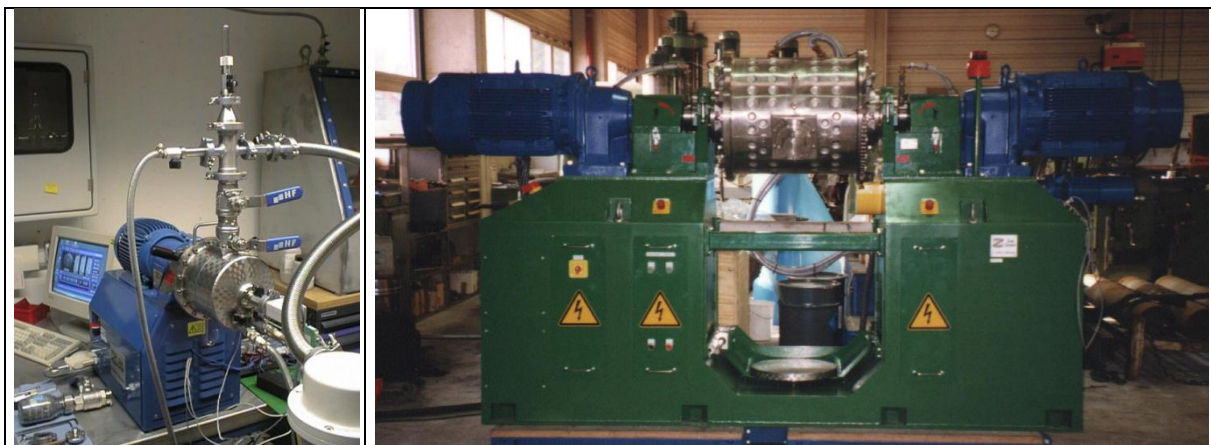


Fig. 1: horizontal rotary ballmill (Simoloyer® CM01-21) with air-lock for loading, operation and unloading under vacuum and/or inert-gas (left); Fig. 2: Simoloyer® CM100-s2, production unit for nano-crystalline metalhydrides

The systems are presently available from 0.5 to 400 liter grinding chamber capacity [15] where larger volumes seem to be possible. Various existing applications for the environment include MA of different metals and/or ceramics [16], room temperature inorganic syntheses, waste-free organic chemical solid-state syntheses with 100% yield [17-18] and decontamination of dangerous residues by using tribochemistry effect of milled sand (SiO₂) [6]. In particular these procedures are economically and ecologically favorable as in most cases they can be operated semi-automatically if they are combined with a continuous or semi-continuous (auto-batch) powder separation system.

We report here on some typical applications of HEM/RM. Figure 1 shows a horizontal rotary ballmill with a 2 liter chamber volume that can be placed on a table next to the process

controlling computer which is operated with water cooling or heating at rotation frequencies up to 1800rpm.

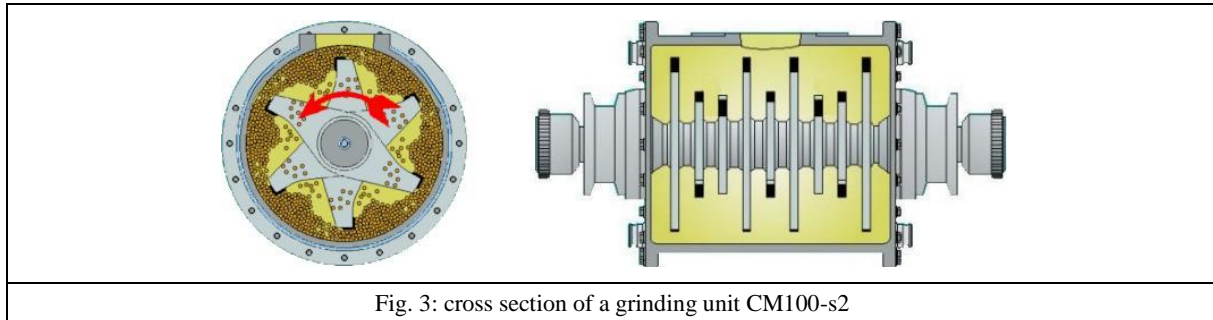


Fig. 3: cross section of a grinding unit CM100-s2

Figure 2 shows a production unit with a 100 liter chamber. The cross sections through the grinding chamber in Figure 3 visualize the working principle where the rotor is the tool to transfer the kinetic energy into the grinding media and the grinding media transfers into the powder material.

Important criteria are safe, continuous and complete collection of the produced powder. There must be no losses and no spoiling of the environment.

To achieve these requirements, the collection in a cyclone within a closed gas circuit is favored and this in particular if continuous or semi-continuous (auto-batch) operation [11, 19] is desired for larger scale productions.

Therefore, an experimental unit VS01a which is originally designed and used for the controlled and continuously production of ductile metal flakes [20] as well as rapid particle size reduction of brittle solids (e.g. enamels and glass-fluxes) [19] seemed to be ideal for the here discussed application, too.

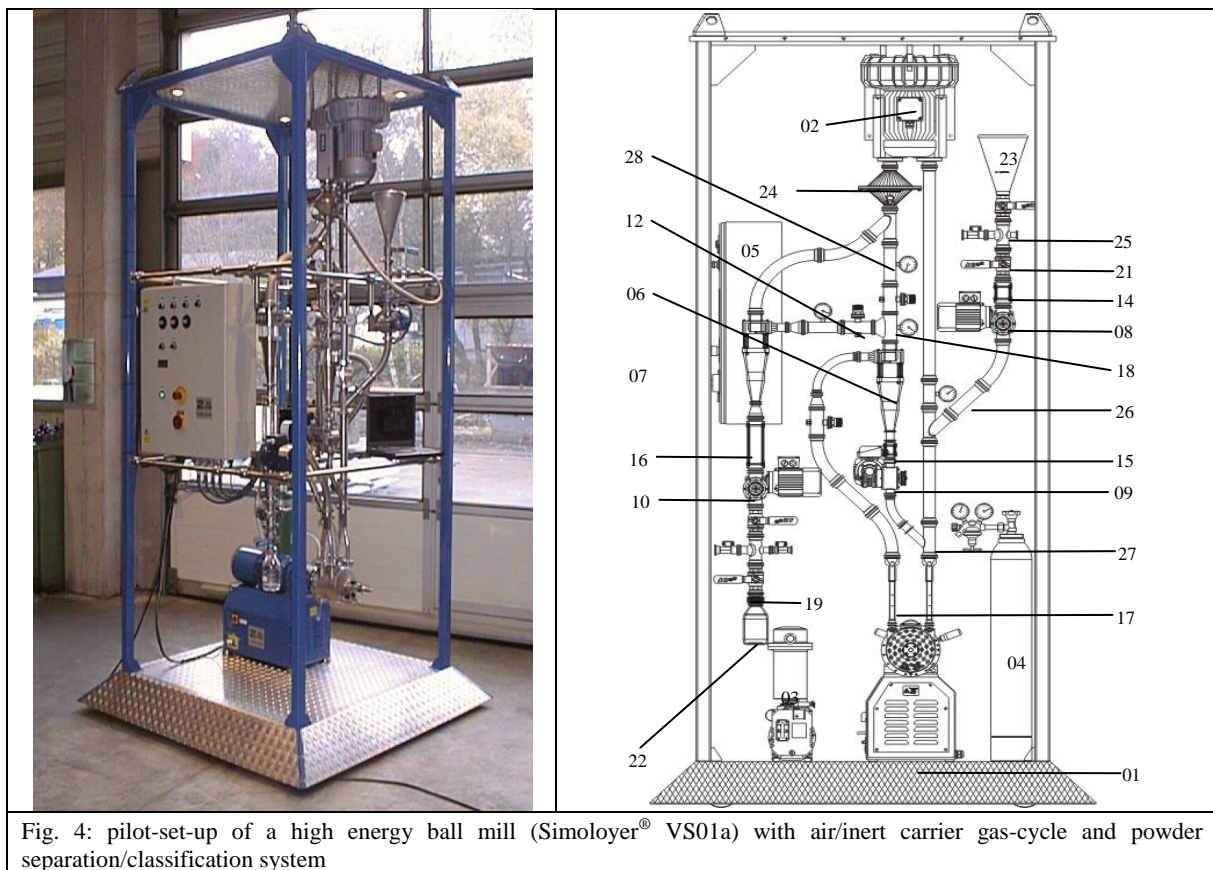


Fig. 4: pilot-set-up of a high energy ball mill (Simoloyer® VS01a) with air/inert carrier gas-cycle and powder separation/classification system

ID	unit	function
01	Simoloyer [®] CM01-s1	High Kinetic Processing
02	side-channel-turbine SKV180a-DN40	carrier gas drive
03	vacuum pump DUO 10	air-lock operation
04	gas-bottle 10 liter	gas supply internal & air-lock
05	electronic cabinet	additional Maltoz [®] -support, control of pump, rotary vane feeders & carrier gas drive
06	laboratory cyclone ZK70-L (a)	separation of to heavy particles in primary circuit
07	laboratory cyclone ZK70-L (b)	separation of all particles in secondary circuit
08	rotary vane feeder ZS40m (a)	pressure compensation supply in injection device
09	rotary vane feeder ZS25m	pressure compensation supply in bypass cyclone (a)
10	rotary vane feeder ZS40m (b)	pressure compensation supply at product port
11	butterfly valve KV-DN40 (a*)	velocity control of multiphase-flow in primary- and secondary circuit
12	butterfly valve KV-DN40 (b*)	velocity control of multiphase-flow in primary- and secondary circuit
13	butterfly valve KV-DN40 (c*)	velocity control of multiphase-flow in primary- and secondary circuit
14	transparent pipe module GR-DN40x100	visual control of injection process of starting powder
15	transparent pipe module GR-DN25x75	visual control of separation process at cyclone (a)
16	transparent pipe module GR-DN40x200	visual control of feed-rate at ZS40m (b) at product port
17	pipe switch RW40-16-A	transfer of multiphase-flow in and out of grinding unit W01-s1
18	KF-space-switch RW40-B	separation in multiphase-flow
19	pipe bends RBA-DN40 & DN25	transfer of multiphase-flow in primary- and secondary circuit
20	adapter KF-A	transfer of multiphase-flow in primary- and secondary circuit
21	valve adapter DN*G*DN*	transfer of multiphase-flow in primary- and secondary circuit
22	KF-glass-container DN40-G1-500 cc	display-container for product after air-lock out
23	KF-valve-container DN40-G1-2l	container for starting powder or granules before air-lock in
24	vacuum screen unit VSK28	protection-filter for carrier gas drive
25	KF-calming pipes	cross-tube for air-lock evacuation and gas-supply
26	KF-tubes, straight	adaptation of measurement sensors and gas-supply
27	KF-junction-tubes	flow switch, bypass and injection
28	pressure-gauge DMD16	record of flow-parameters

This unit (Figure 4) is based on a closed carrier-gas system driven by a side-channel-turbine adapted to a Simoloyer CM01-2ls1 with 2 cyclones for separation/classification, some valves for circuit-control, rotary vane feeders with air-locks, filter, evacuation pump, computer- and electrical control, a special separation and other units. The system has two connected circuits, the primary and the secondary circuit. The secondary circuit is only needed for the processing of ductile metal flakes and therefore closed by means of a valve between the two cyclones. The bypass between the rotary vane feeder and the junction tube can be disconnected and used as the discharging route where the first cyclone is now only used for a solid-separation of the multiphase-flow coming out of the grinding chamber of the HEM-device. If no inert atmosphere is needed, the air-lock parts on the injection-side can be replaced by a simple plastic funnel for charging.

This system is successfully operated in auto-batch mode where the carrier-gas is used to transfer the starting powder into the grinding chamber. The processing is performed batch-wise and the carrier-gas flow is subsequently used again to transfer the as-milled powder out of the vessel after batch-operation. The separation of the powder from the gas flow is then achieved in the cyclone. Since the carrier-gas circuit is a closed system, the gas is fully recycled and used in the next step again for charging of the mill. This procedure resolves the significant disadvantage of relatively long discharging time [21] and thus the high efficiency of the mill can be exploited.

In continuous res. semi-continuous operation, the starting powder is fed continuously and the carrier-gas is continuously transferring the material through the Simoloyer-vessel into the separation system. This principle can up to now only be realized for those processes that require in batch operation a processing time in the range of several minutes e.g. rapid particle size reduction of enamels [11]. Due to the effect, that the fine fraction of particles is continuously which means here also immediately discharged out of the vessel, the dumping

effect of this fraction (like liquid) is terminated and consequently the kinetic of the system increased tremendously. For the today's understanding, this leads then to the found extremely short processing times in the range of several seconds for these materials-systems [11, 19]. For the here given application in the field of mechanochemistry, most important is the complete recovery of the milling product continuously or from various batches in a semi-continuous route without a significant contamination level from the milling tools (due to extremely short processing time) which will be important for synthesis and industrial production. Larger mills work equally well, larger carrier-gas systems are expected to work equally well.

High Energy Milling, Mechanical Alloying and Reactive Milling

Mechanical alloying (MA) has been described as a process where powder particles are treated by repeated deformation, fracture and cold welding by highly energetic collisions of grinding media in a milling process [2-4]. By this technique it is possible to synthesize new materials with new properties that cannot be created by conventional route e.g. due to a not present thermal equilibrium or immiscibility of their components. By structural design, important materials properties can be influenced (e.g. nanocrystalline, amorphous).

High energy milling (HEM) and reactive milling (RM) are performed by the same processing principle where the variation is in general based on the target of the processing, the transformation effect by the kinetic energy and the starting materials.

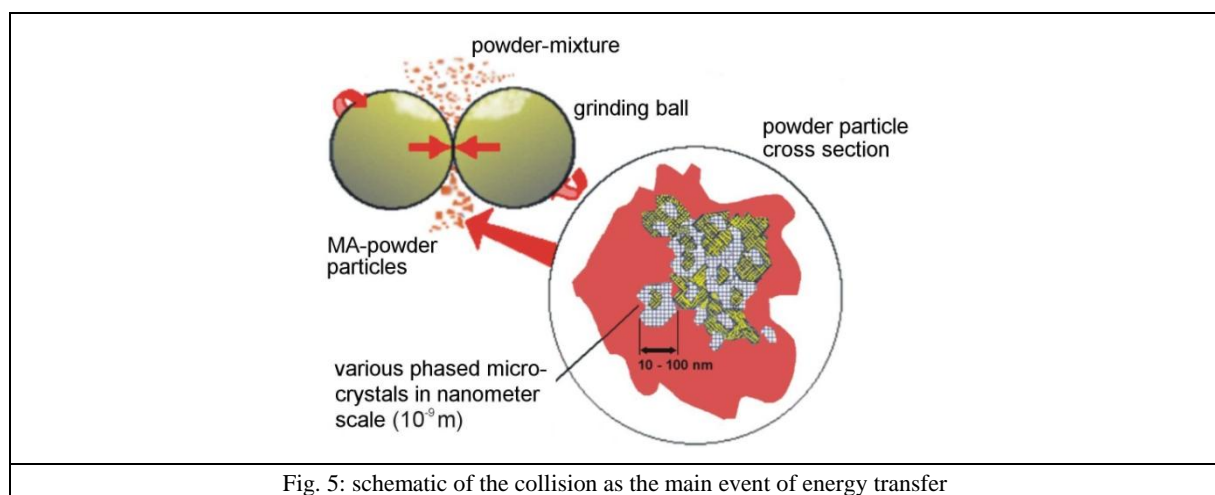


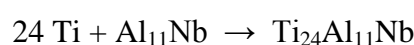
Fig. 5: schematic of the collision as the main event of energy transfer

The different procedures can be described as High Kinetic Processing (HKP) where the collision of the grinding media is the main event of kinetic energy transfer from the milling tools into the powder [2-4, 12]. Fig. 5 shows the schematic of the collision. The basic equation describes the relation between the kinetic energy (E_{kin}) and the mass m and the velocity v of a single ball:

$$E_{kin} = \frac{1}{2} m v^2$$

It is clearly seen that the maximum relative velocity of the grinding media is the most determining factor contributing to the kinetic energy.

A typical example of practical importance that demonstrates the effects that are inherent in Figure 5 has been described in detail [22] in the system:

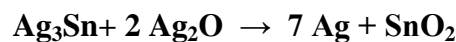


In this work the influence of the milling parameters have been evaluated and basically the processing route of Cycle Operation for CMB-materials [22-23] have been invented. By this technique, the problematic agglomeration and sticking behavior of the in this case Ti-Al-based material in a dry milling process could be significantly reduced which did lead to an

increase of the powder yield from < 4 % to 80 %. Later on similar effects were found in the Ti-Ni-system [24] and in the processing of a number of ductile metal flakes [25]. In 1999, Kim et al. investigated the difference of Cycle Operation and Constant Operation in the Fe-Co-system and found tremendous effects on particle- and in particular crystallite-size reduction [26].

If the here described processing method is applied for particle and /or crystallite size reduction or particle deformation (e.g. flakes) in single systems, this route is described as HEM. The goal can be to receive a special particle geometry e.g. for rapid and large-scale production of ductile metal-flakes in dry process without solvents and less energy e.g. for paint-pigments, conductive pastes and anti-corrosives [10, 14]. On the contrary rapid particle size reduction of brittle solids like Enamels or Glass Fluxes has recently been introduced as a new application field [11].

The definition of RM is suitable if during milling a chemical reaction is wanted and observed. By this route, a dispersion of ultra-fine (nano-scaled) crystals and/or a homogeneous dispersion of transformed phases in a matrix can be achieved [27]. A typical example of practical importance here has been demonstrated in the Ag-Sn-system [1]:



Due to the CMB-behavior of this ductile system, again the processing has to be performed by applying Cycle Operation.

With respect to the starting materials (e.g. Ag₂O instead of Ag), RM in this kind of principle can show economical advantage.

Often these processes are environmentally benign as they avoid wastes e.g. in solid state synthesis where organic solid-solid reactions and others can rapidly proceed without any wastes and in the absence of solvents. A summary of some of the most important applications/products of HKP are given in table 2:

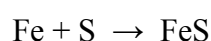
Applications/products of High Kinetic Processing (HKP)		
High Energy Milling	Mechanical Alloying	Reactive Milling
➤ surface, shape, particle size	➤ alloys (pseudo)	➤ chemical reactions
• flakes (particle deformation)	• nanocrystalline materials	• contact materials
• particle coating (LPS, S)	• amorphous materials	• nanocrystalline materials
• nanocrystalline materials	• oxide dispersion strengthened alloys	• mechanochemistry
• highly dispersed materials	• iron and oxide based magnetic materials	• solid state syntheses
• soft magnetic materials	• bearing materials containing solid lubricants	• hydride - dehydride
• particle size reduction (e.g. enamel, ceramics)	• ceramic-metal composites (MMC, CMC, MMC, CCC)	• activation of catalysts

Table 2: important applications/products of HKP

Inorganic Quantitative Syntheses by Reactive Milling

Numerous inorganic syntheses of binary high melting insoluble salts are routinely performed at very high temperatures by glowing or melting of the components or by precipitation from aqueous solutions. Many of these may now be accomplished at room temperature or slightly above by high energy reactive milling of their components. Some examples of this new technique are presented here.

Iron(II) sulphide is a common source for the generation of hydrogen sulphide. It is easily formed if iron powder and sulphur are milled together in stoichiometric quantities:



This waste-free solid-state reaction demonstrates the corrosive power of sulphur towards iron and steel, including steel balls. Therefore, ZrO₂ balls are used in these syntheses, while the stellite housing of the mill and the hard-metal rotor withstand virtually unaffected. The same is valid for the related synthesis of iron(II) sulphide from pyrite and iron powder or turnings by HEM/RM:

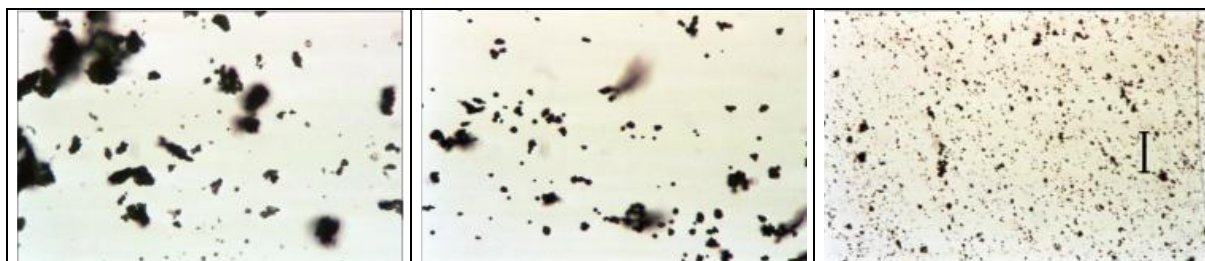
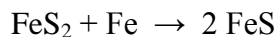


Fig. 5: microscopic images of a) pyrite, b) iron and c) iron (II) sulfide showing the grains of the reaction partners and the product after reactive milling of 200 g batches in the 2 L Simoloyer[®]; the microscopic magnification was 400X; the bar (right) corresponds to 10 µm length

The solid material of FeS arises in sub-micrometer grains as shown in Figure 5. Both the pyrite and the iron started with grains of 1 - 3.5 and 1 - 2 µm diameter. The larger aggregates are composed from the small grains in all three cases.

Similarly, copper powder and sulphur combined to copper(I) sulphide, which is a useful solid for the production of luminophors. This product arises free of water in µm-sized particles:



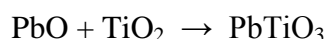
These waste-free low temperature syntheses may be useful and many applications of pyrite and sulphur for the synthesis of metal sulphides might be envisaged.

Furthermore, high melting metal oxides can be combined by HRM to mixed oxides (complex salts) such as chrome yellow (lead chromate, mp 844°C) from lead oxide (mp 888°C) and chromium trioxide (mp 197°C) which can be converted further to chrome red by milling with additional lead oxide:

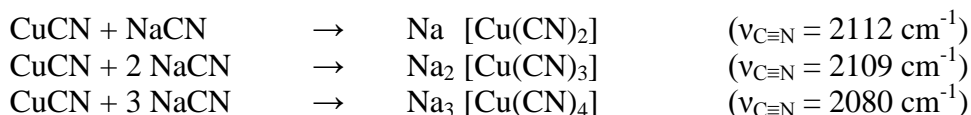


A slurry of the obtained PbCrO₄ in water reacts neutral and does not contain chromic acid. This test proves completion of the reaction more sensibly than the FT-IR spectroscopic analysis. Unlike the precipitation of lead chromate from aqueous solution, these dye pigments can be freely varied to non-stoichiometric composition in order to adjust the desired materials properties. The dry powders arise directly as µm-fine grains.

Further solid mixed oxides are important as ferroelectrics with high dielectricity constants for optoelectronic and piezoelectric applications (PLZT ceramics). For example HRM of stoichiometric mixtures of lead(II) oxide (mp 886°C) and titanium dioxide (mp 1830-1850°C) in the Simoloyer[®] provides lead titanate (mp 450°C) as a fine powder. Clearly, this must be a tribochemical reaction that occurs after mechanical breaking of covalent metal-oxygen bonds.

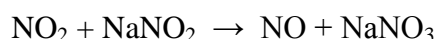


Still further applications of HRM were realized in the formation of complex salts. Examples are the quantitative syntheses of complex cyanides (useful in the galvanotechnique due to their solubility in water) from copper(I) cyanide ($\nu_{\text{C}\equiv\text{N}} = 2164 \text{ cm}^{-1}$) and sodium cyanide ($\nu_{\text{C}\equiv\text{N}} = 2091 \text{ cm}^{-1}$). For example, the stoichiometric ratio with sodium cyanide was varied from 1:1 to 1:3 and the position of the cyano vibration band in the FT-IR spectrum changed monotonously:



All of these reactions were performed with 200 g batches in the Simoloyer[®] CM01-21 at 1300 rpm while excluding hazards from the poisonous cyanides. A wealth of related and further solid-state inorganic reactions by HRM is clearly envisaged.

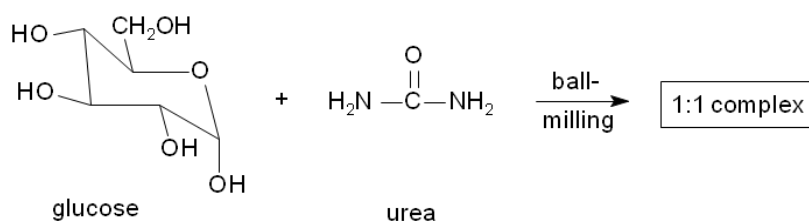
Equally interesting are inorganic reactions between gases and salts. If a passivating cover is formed on the crystals, milling is required in order to constantly create fresh surfaces. An example is the deoxygenation of nitrogen dioxide by sodium nitrite to give nitrogen oxide [28] that was performed with 200 g batches (2.9 mol) and provided the more precious reactive gas in pure form.



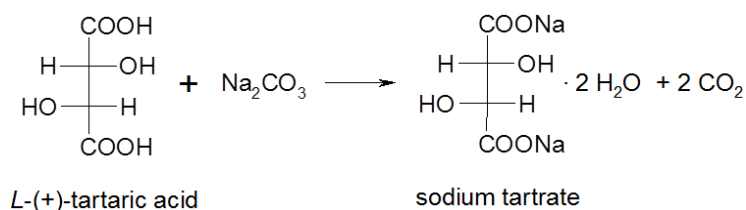
The Simoloyer[®] was evacuated, filled with NO₂ (0.8 bar, 0.07 mol) and operated for 30 min, the colorless gas filled to a pressure container and the reaction continued with further NO₂ until the sodium nitrate was used up, etc.

Organic Solid-State Syntheses without Wastes

More than 1000 stoichiometric organic solid-state reactions proceed with 100% yield and do not require purifying workup, i.e. they are solvent-free and waste-free [5]. Some of these reactions have now been successfully scaled-up with the Simoloyer[®] [6, 17]. Glucose and urea formed the stoichiometric crystalline 1:1-complex within minutes that can hardly be obtained from solution.



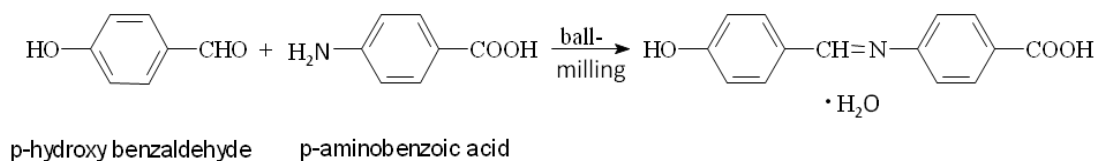
Also the solid-state neutralization of acids may be of technical importance, as many processing steps can be saved if solvents are avoided. For example, 200 g batches of stoichiometric mixtures of *L*-(+)-tartaric acid and sodium carbonate liberated carbon dioxide upon HRM at 1300 rpm in the water cooled Simoloyer[®] and provided cleanly sodium tartrate dihydrate as a powder.



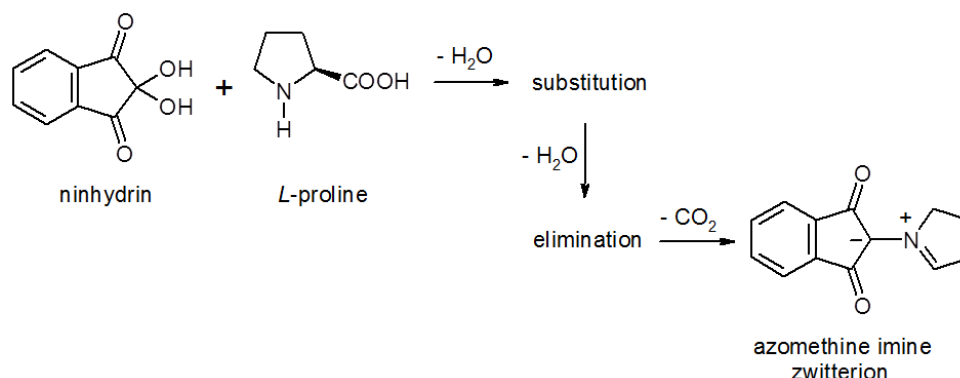
Sodium tartrate is a well known food additive (E 335). Similarly, sodium hydrogentartrate hydrate is prepared by milling stoichiometric mixtures of *L*-(+)-tartaric acid and sodium bicarbonate. These crystals are in use for the preparation of powders or tablets for refreshing drinks. Energy consuming evaporations are avoided that burden the common techniques in water. No excessive heating was observed in this solid-state reaction. The liberated CO₂ was released by a safety-valve.

The formation of covalent bonds is even more important in organic syntheses. Imines (Schiff bases) are versatile building blocks that have been quantitatively synthesized by reactive

milling. The scaling-up of the *p*-hydroxybenzaldehyde condensation with *p*-aminobenzoic acid yielded 200 g batches of the substituted solid imine hydrate that could be dried in a vacuum at elevated temperature if desired [17].



The scale-up is also possible for much more complicated quantitative solid-state cascade reactions [29].



We checked the stoichiometric reaction of the widely used solid reagent ninhydrin with the solid amino acid *L*-proline that gives the versatile solid azomethine imine which is a zwitterion and has interesting properties and uses. Azomethine imines are hard to obtain in pure form.

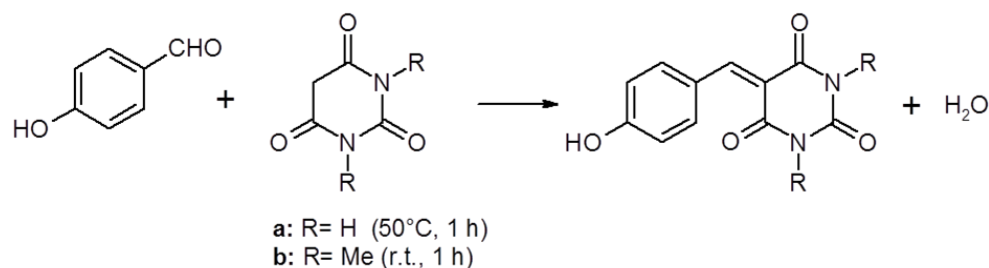
Here we use a solid state reaction cascade of 1.) substitution, 2.) elimination and 3.) decarboxylation at room temperature upon dry-milling and obtain 100% yield: 200 g of a stoichiometric 1 : 1-mixture of ninhydrin and *L*-proline was milled in the Simoloyer[®] CM01-2l charged with 2 kg of steel balls (100Cr6) with 5 mm diameter at 1100 rpm for 40 min when the liberation of carbon dioxide was terminated. The temperature varied from 15°C at the water cooled walls to a maximum of 21°C in the center. The power was 800 W. Quantitative reaction was secured by weight (146 g, 100%) and purity by spectroscopic techniques [29].

The zwitterion and the water of reaction formed a highly dispersed solid which did not form a loose powder but mostly a solid film on the balls and the walls of the mill. In this exceptional case, a different collection technique was applied: the product (its low solubility in water at 22°C is 0.20 g L⁻¹) was not separated in a cyclone (see Fig. 2) but easily milled out with 4 times 250 mL of water each, and the highly dispersed (<1µm) pure azomethine imine product (m.p. 239°C) was obtained after centrifugation and drying in a vacuum.

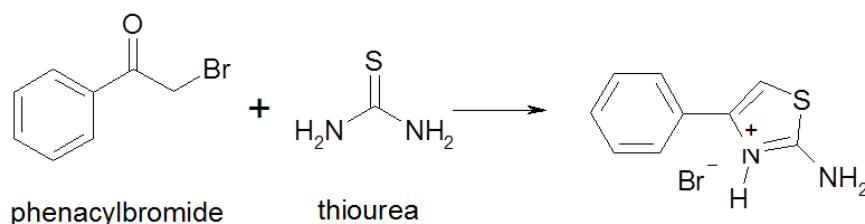
This is an economic, environmentally friendly and essentially waste-free synthesis of a highly interesting reagent, the only ‘by-product’ being 1 L of water containing 0.2 g of the zwitterion, that can, of course, also be isolated by evaporation of the water. The previous syntheses of this zwitterion in solution provided only a 82% yield with much wastes also from the purifying workup [30]. The solid-state technique is by far superior and fully benign.

Further C-C forming reactions of highest synthetic potential are Knoevenagel condensations. These were obtained in solution by catalysis, but more recently also “solvent-free” on solid catalysts or supports with microwave heating, but never quantitatively. Our really solvent-free technique by milling stoichiometric quantities of the reactants in the absence of any

auxiliaries provides the alkene products directly in the pure state and, unlike the previous techniques, no solvent consuming workup is necessary [31]. The scaling-up to 200 g batches was successfully achieved using the Simoloyer CM01-2l with p-hydroxybenzaldehyde and barbituric acid without external cooling (at temperatures up to 50°C) or dimethylbarbituric acid at ca. 20°C (with external water cooling):



An example for the heterocyclic ring formation from phenacylbromide and thiourea [32] was scaled up to 200 g batches in the Simoloyer CM01-2l at room temperature. The 2-aminothiazole hydrobromide salt is quantitatively obtained in a complicated cascade reaction sequence (substitution, cyclization, dehydration, isomerization) and represents a versatile building block for organic syntheses with the acid catalyst already attached to it.

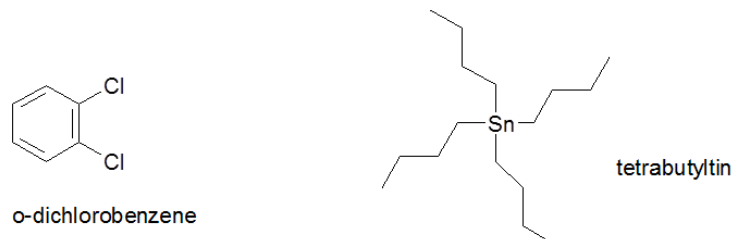


Many further waste-free organic solid-state reactions can be scaled-up in the large-scale horizontal ball mill. The gain in efficiency is enormous and the savings in resources and time are highly rewarding. If the heat production is not excessive as in most organic solid-state reactions there is no reason to stop at 2-liter-size horizontal ball-mills. Scaling-up of the benign technique to the industrially useful scale in 400 liter mills will be possible.

Tribochemistry with Oxides

Ball-milling is very versatile. A further technique with the same equipment is tribochemical milling with mechanochemical breaking of covalent bonds of infinite covalent crystals which are present in many oxides. For example, sand consists of quartz (SiO₂) which forms an infinite covalent crystal lattice. If the crystal is split, all Si-O bonds are broken that existed between the two fragments and the freshly cleaved faces are completely unsaturated with free $\cdot\text{Si}$ and $\cdot\text{O-Si}$ surface radicals and other highly reactive species. They represent a local plasma. This plasma tends to be saturated immediately, a fact that has been used for more than 5000 years to ignite fire by hitting flint in air. Such tribochemistry should be also useful for the mineralization of dangerous environmental poisons such as chlorinated aromatics (PCBs, etc.) or tin alkyls etc., if milling with sand is performed. Such endeavour is much easier and more benign than the reductive removal of halogen from polyhalogenated aromatics by milling sea sand with large excesses of metallic sodium or magnesium (after thermal drying followed by drying with calcium oxide) and ethanol [33] in planetary ball mills (typically 5 h) or eccentric swing-mills (typically 90 min) to form the corresponding (aromatic) hydrocarbons besides hazardous hydrogen that forms explosive mixtures with air.

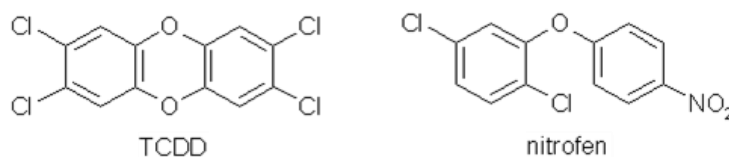
In order to use benign tribochemistry 0.8 g of *o*-dichlorobenzene (a polychlorinated aromatic) and 1 g of tetrabutyltin (a hazardous tinorganic) were milled with 200 g of air-dry quartz sand (Sakret Trockenbaustoffe GmbH & Co KG; 0.1-0.5 mm; washed and dedusted) at 1300 rpm for 1 h in the Simoloyer[®] CM01-21.



Mass spectrometric analysis of the solid powder or ¹H NMR analyses of extracts (dichloromethane, ethyl acetate, or ether) did not exhibit the starting materials any more. At 1 g of *o*-dichlorobenzene and 200 g of sand, there were some traces of the starting material and of chlorobenzene still detectable in the mass spectrum, but benzene was not present if the milling was performed either in the presence of air or under argon atmosphere. This points to mineralization of the hazardous compounds in the plasma of the freshly broken surfaces of the quartz sand. The final diameters of the quartz particles were 1 - 2 μm wide.

These results suggested industrial decontaminations of PCBs, HCHs, DDT, nitrofen, R_(3-n)SnX_(n+1), polychlorinated dibenzodioxines (PCDD) and -dibenzofurans (PCDF), etc.

We therefore studied the system in more detail. XPS measurements showed that the carbon of the halogenated organic compounds was completely graphitized. The chlorine content of the graphite formed was at the detection limit of the XPS technique. The chlorine was transformed to HCl and neutralized by the basic impurities or components of the tribomaterial to form the corresponding metal chlorides. Surprisingly, it was even possible to graphitize methane by high energy tribochemical milling with sand. It is very important, that not only quartz sand but also glass, CaO, MgO, TiO₂, Fe₂O₃, Fe₃O₄, ZrO₂, B₂O₃, FeS, FeS₂, BN, Si₃N₄, B₄C₃, SiC, WC, FeSi₂, TiSi₂, Si, B, granite, quartz porphyr, enamel, ceramics can equally be used for tribochemical decontaminations. For example, we are able to completely mineralize TCDD or nitrofen also in the presence of congeners.



A mixture of TCDD (210 mg) with congeners (295 mg) and KCl (200 mg) or 0.8 g of pure nitrofen was completely detoxified (graphitized) by 30 min milling with 200 g glass (crushed window glass or Duran) at 1300 rpm. No organic materials could be detected any more by mass spectrometry. The μm fine glass powder was melted when the graphite burned to carbon dioxide. After crushing, the glass can be used again for tribochemical detoxification. This is a benign closed cycle low temperature decontamination process for safe and complete removal of the hazards with non-disposable wastes which contain dioxines, or the other poisons mentioned and are mostly stored in barrels at various sites on earth. The up-scaling from the two liter mill to now more than 400 liter horizontal ball-mills is possible and these mills can be operated at the site of such wastes. Thus, even problems with the transportation of such dangerous wastes to other sites are avoided.

Conclusions

High energy milling is an environmentally benign versatile technique that can be performed at the kg scale and can be scaled-up to technical importance. Applications are manifold in mechanical alloying, waste-free inorganic room temperature syntheses, waste-free organic solid-state syntheses and decontamination of dangerous residues by tribochemistry. The size of horizontal high energy mills with carrier-gas operation may be increased to more than 400 liter. Thus, the application to industrial production and decontamination in the various fields that were treated in this survey will be only a matter of time, as environmentally friendly new processes are inevitable for the well-being of our environment.

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References

- [1] H. Zoz, H. Ren, N. Späth, Metall 53, 423-428 (1999)
- [2] J.S. Benjamin, Metall. Trans., Vol. 1, 2943 (1970)
- [3] J.S. Benjamin, T.E. Volin, Metall. Trans. Vol. 5, 1929 (1974)
- [4] C. Suryanarayana, Guo-Hao Chen, F.H. Froes, Scripta Metallurgica et Materialia, 26, 1727 (1992)
- [5] G. Kaupp in Comprehensive Supramolecular Chemistry, Vol. 8, pp. 381-423, Ed. J. E. D. Davies, Elsevier, Oxford, 1996; G. Kaupp, J. Schmeyers, J. Boy, Chemosphere, 43, 55-61 (2001)
- [6] G. Kaupp, M.R. Naimi-Jamal, H. Ren, H. Zoz, Chemie Technik 31, 58-60 (2002)
- [7] V.A. Zhorin, V.Y. Rochev, O.P. Kevdiv, L.B. Kukushkina, V.I. Gol'danskii, N.S. Enikolopyan, Russian J. Phys. Chem. 55, 82-86 (1981)
- [8] H. Zoz, R. Reichardt, J.S. Kim, Keramische Zeitschrift, 53 [5], 384-392 (2001)
- [9] R.M. Davis, B. McDermott, C.C. Koch, Mechanical Alloying of Brittle Materials, Metall. Trans. 19a, 2867 (1988)
- [10] H. Zoz, D. Ernst, R. Reichardt, 3rd Int. Symp. of the school of chemical engineering, University of Mexico City, May 1998
- [11] H. Zoz, H.U. Benz, G. Schäfer, M. Dannehl, J. Krüll, F. Kaup, H. Ren, R. Reichardt, D.J. Viguera: INTERCERAM, Int. Ceramic Review, 50 [5], 388-395 (2001)
- [12] H. Zoz, D. Ernst, H. Weiss, M. Magini, C. Powell, C. Suryanarayana, F.H. Froes, Metall 50, 575-579 (1996)
- [13] H. Zoz, H.U. Benz, K. Hüttebräucker, L. Furken, H. Ren, R. Reichardt, Metall 54, 650-659 (2000)
- [14] H. Zoz, D. Ernst, T. Mizutani, H. Okouchi, Metall 51, 568-572 (1997)
- [15] U.S. Patent No. 5,464,163; Nov. 7 (1995)
- [16] U. Koester, Material Science Forum, 235-238, 377-388 (1997)
- [17] G. Kaupp, J. Schmeyers, M. R. Naimi-Jamal, H. Zoz, H. Ren, Chem. Engin. Sci. 57, 763-765 (2002)
- [18] G. Kaupp, J. Schmeyers, J. Boy, Chemosphere 43, 55-61 (2001)

- [19] H. Zoz, H.U. Benz, G. Schäfer, M. Dannehl, J. Krüll, F. Kaup, H. Ren, R. Reichardt D.J. Viguera: INTERCERAM, Int. Ceramic Review, 50 [6], 470-477 (2001)
- [20] H. Zoz, D. Ernst, R. Reichardt, Metall Vol. 51, 09/98, pp. 521-527, 1998
- [21] H. Zoz, H. U. Benz, T. Suzuki, H. Ikehata and T. Saito, Zoz GmbH (Germany), Toyota Central R&D LABS., INC. (Japan), ESQIE (Mexico): HKP using Carrier-gas Assisted Discharging, abstract submitted to PM2TEC'2003, June 8-12, 2003, Las Vegas, Nevada
- [22] H Zoz, D. Ernst, H. Weiss, M. Magini, C. Powell, C. Suryanarayana, F. H. Froes, Metall Vol. 50, 09/96, pp. 575-579 (1996)
- [23] H. Zoz, D. Ernst, 5th International Conference on Advanced Particulate Materials and Processes, West Palm Beach, Florida 1997, Proceedings
- [24] H. Zoz, D. Ernst, I. S. Ahn, W.H. Kwon, TMS Annual Meeting 1997, eds. C.M. Ward-Close, F.H. Froes, S.S. Cho, D.J. Chellman: Synthesis/Processing of lightweight Metallic Materials, (Proceedings 1997)
- [25] H. Zoz, R. Reichardt, H. Ren, H.U.Benz, PM2Tech'99 Conference MPIF/APMI, June 20 – 24, Vancouver, Proceedings 1999
- [26] J.Y. Chung, J. Kim, Y.D. Kim, Dept. of Metallurgy and Materials Science, Hanyang University, Ansan, Korea, 1999
- [27] B. Wielage, J. Wilden, T. Schnick, A. Wank, J. Beczkowiak, R. Schülein, H. Ren, H. Zoz; ITSC 2002, Conference Proceedings, p, 1047-1052, ASM/DVS March 2002, Essen, Germany
- [28] G. Kaupp, J. Schmeyers, J. Org. Chem. 60, 5494-5503 (1995)
- [29] G. Kaupp, M. R. Naimi-Jamal, J. Schmeyers, Chem. Eur. J., 8, 594-600 (2002)
- [30] W. Johnson, D. J. McCaldin, J. Chem. Soc. 1958, 817-822
- [31] G. Kaupp, M. R. Naimi-Jamal, J. Schmeyers, Tetrahedron, submitted.
- [32] G. Kaupp, J. Schmeyers, J. Boy, J. Prakt. Chem. 342, 269-280 (2000)
- [33] V. Birke, Terra Tech, 5, 52–57 (1998)