APPLIED MECHANOCHEMISTRY OF SOLIDS (A REVIEW)

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Abstract
This review paper deals with the application of broad possibilities of mechanochemistry in mineral processing, extractive metallurgy, chemical engineering, building industry, coal industry, materials engineering, agriculture, pharmacy and waste treatment. In several applications pilot plants units or full commercial units were successfully applied. The environmental aspects of these processes are particularly attractive. The main advantages in comparison with traditional technological procedures are decrease in number of technological stages, exclusion of operations that involve the use of solvents and gases and last but not least the possibility obtaining a product in the metastable state which is difficult to obtain using traditional technological methods. This is a great potential of mechanochemistry in technology and several examples with a possibility for industrial applications will be given.

Keywords: mechanochemistry, application, solid

1. Introduction
Mechanical activation by means of ultrafine milling is an effective procedure where an improvement in technological processes can be attained via a combination of several effects which influence the properties of applied solids. The main advantages in comparison with the traditional technological procedures are decrease in the number of technological stages, excluding the operations that involve the use of solvents and gases and the possibility of obtaining a product in the metastable state which is difficult (or impossible) to obtain using traditional technological methods [1]. Nanoparticles are often formed by this technological approach which add value to the processed solids [2]. The environmental aspects of these processes are particularly attractive [3].

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2. Extractive metallurgy

According to classical view extractive metallurgy is the art and science of extracting metals from their ores by chemical methods [4]. It is actually divided into three sectors: hydrometallurgy, pyrometallurgy and electrometallurgy. Hydrometallurgy is the technology of extracting metals from ores by aqueous methods, pyrometallurgy by dry thermal methods, and electrometallurgy by electrolytic methods.

In general, hydrometallurgy involves two distinct steps (Fig. 1): selective dissolution of the metal values from an ore – process known as leaching and selective recovery of the metal values from the solution, an operation that involves a precipitation method. Sometimes a purification/concentration operation is conducted prior to precipitation. These processes are aimed at obtaining a pure and a concentrated solution from which the metals values can be precipitated effectively. The methods used are: adsorption on activated charcoal, sorption on ion exchange resins, extraction by organic solvents as well as other advanced processes of metals extraction [5]. Selected examples of the applications of mechanical activation in extractive metallurgy will be given in following paragraphs.

2.1 Gold and silver

The technologies hitherto used encounter a problem in processing complex sulphide ores containing gold and silver in an economic way providing sufficient recovery. One of the problems of gold and silver extraction from sulfidic minerals is associated with the form in which the precious metals occur.
Gold and silver are frequently physically-locked within sulphides, may form defects in their structure or can be chemically bonded in the form of solid solutions or compounds [6-8]. Different types of associations of gold with sulphidic minerals are given in Fig. 2.

Fig. 2 Gold associations with sulphide minerals: 1-readily liberatable gold, 2-gold along crystal grain boundaries, 3-gold grain enclosed in pyrite/sulfide (random position), 4-gold occurrence at the boundary between sulfide grains, 5-gold in concretionary pyrite (or other sulfide) along fractures and/or crystal defects, 6-gold as colloidal particles or in solid solution in sulfide [7-8].

Sulphides are also a considerable natural resource of silver. Around 200 minerals bearing silver in major, minor and variable amounts were detected [9]. However, of these, only 10-12 minerals are of practical importance. These are, in order of leachability: elemental silver, silver halides and silver sulfides [10].

The contact of gold and silver (in form of metals or compounds) with leaching reagent plays a fundamental role in the hydrometallurgical extraction of the precious metals. An improvement of the contact can be achieved by pretreatment. The choice of pretreatment method significantly depends on locality and mineralogy of the ore deposit. The oxidizing pretreatment, which can, in principle, proceed in the pyrometallurgical or hydrometallurgical way, belongs among classical methods [7]. Pyrometallurgical pretreatment is the oldest application and consists of an oxidizing roast to convert sulfides to oxides. However, because of environmental demands roasting is becoming more and more suppressed, irrespective of technical innovations [11].

Chemical and biological pretreatments are applied in hydrometallurgical processes, the goal of these processes is to disintegrate the sulphide and thus to facilitate the subsequent extraction of gold and silver. Pressure oxidation can be used for this but has high capital and operating costs. At present, one of the increasingly used processes is biological oxidation, this
is considered acceptable from the view-point of environmental considerations and lower economic demands (see Table 1). However, long reaction times and appropriate design of bioreactors can make difficulties.

Table 1 Relative costs of pretreatment processes [12].

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Costs</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Capital</td>
</tr>
<tr>
<td>Roasting</td>
<td>1.0-1.5</td>
</tr>
<tr>
<td>Pressure oxidation</td>
<td>1.20-1.25</td>
</tr>
<tr>
<td>Biological oxidation</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The process of fine and ultra-fine milling for pretreating gold and silver contents has been used very often in recent years. This process requires finer milling than that attained in the ball mills typically used in comminution for flotation. Particle size of 1-20 µm can be produced in intensive milling where size reduction is accompanied by mechanical activation of mineral components.

The effect of combination of fine milling in ball mill, classification and mechanical activation in attritor on gold and silver recovery from a chalcopyrite concentrate has been studied [13]. The proposed flowsheet is in Fig. 3.

Fig. 3 Flowsheet for the treatment of chalcopyrite concentrate by attrition and acid pressure leaching with catalyst (AgNO₃) including recovery of Ag and Au [13].
The processing of sulfidic concentrate (5-6% CuFeS$_2$, 53-55% FeS$_2$, 8-10% FeAsS) has been studied by the following strategy: two-step cyanidation-mechanical activation-air conditioning-cyanidation [14]. The proposed flowsheet is in Figure 4, condition are given in Table 2.

![Fig. 4 Flowsheet for the treatment of sulfidic concentrate by vibration milling for gold recovery [14].](image)

Table 2 Results of gold extraction from cyanidation of sulfidic concentrate [14].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mechanical activation in NaCl solution (60 g/l)</th>
<th>with MnO$_2$ addition (1%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Revolutions of the planetary mill (min$^{-1}$)</td>
<td>800</td>
<td>800</td>
</tr>
<tr>
<td>Au in solid rest after 1st cyanidation (gt$^{-1}$)</td>
<td>9.8</td>
<td>9.4</td>
</tr>
<tr>
<td>Cyanidation after 1st activation and pulp aeration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCN (g/l$^{-1}$)</td>
<td>0.7</td>
<td>0.4</td>
</tr>
<tr>
<td>Leaching time (h)</td>
<td>19</td>
<td>18</td>
</tr>
<tr>
<td>Au in solid rest (gt$^{-1}$)</td>
<td>4.4-6.0</td>
<td>3.6-5.0</td>
</tr>
<tr>
<td>Cyanidation after 2nd activation and pulp aeration</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCN (g/l$^{-1}$)</td>
<td>0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>Leaching time (h)</td>
<td>22</td>
<td>18</td>
</tr>
<tr>
<td>Au in solid rest (gt$^{-1}$)</td>
<td>3.4-3.8</td>
<td>3.0-4.0</td>
</tr>
<tr>
<td>Au recovery (%)</td>
<td>93.5</td>
<td>93.7</td>
</tr>
</tbody>
</table>
2.2 Chromium

Chromite Fe\textsubscript{2}Cr\textsubscript{2}O\textsubscript{4} is the source mineral for the production of chromium metal, ferrochromium, special alloys and Cr chemicals. The annual worldwide production of chromium chemicals is estimated to be approx. 1 million tons, as sodium dichromate Na\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} [15]. The only relevant process for production of chromates is the oxidative digestion of chromites using Na\textsubscript{2}CO\textsubscript{3} at 1000-1100°C. In order to prevent the melt from stick, a leaning agent such as CaCO\textsubscript{3} is added to the digestion mixture, to give the melt a loose structure and to facilitate the diffusion of the oxygen to the chromite. The process is governed by reactions

\begin{equation}
\text{FeCr}_2\text{O}_4 + 4\text{Na}_2\text{CO}_3 + 4\text{CaO} + 7\text{O}_2 \rightarrow 4\text{Na}_2\text{CrO}_4 + 4\text{CaCrO}_4 + 2\text{Fe}_2\text{O}_3 + 4\text{CO}_2 \tag{1}
\end{equation}

\begin{equation}
2\text{Na}_2\text{CrO}_4 + 4\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{NaHCO}_3 \tag{2}
\end{equation}

Calcium chromate CaCrO\textsubscript{4}, as opposed to sodium chromate Na\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} is poorly soluble, so that the recovery of chromate may be impaired during the leaching of the digestion cake. Na\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} is won as a crystallizate and is the source material for the production of most chromium compounds.

The disadvantage of the above-described process is that it is impossible to achieve a complete digestion of the chromite ores. Mechanical activation as pretreatment step to improve the digestion step has been applied [16].

Two types of mills were used for comparison, a laboratory scale ball mill (BM) and an industrial eccentric vibratory mill (ESM).

![Fig. 5 (left) Relative X-ray intensities I/I\textsubscript{0} and F/F\textsubscript{0} for lattice plane (311) of chromite FeCr\textsubscript{2}O\textsubscript{4} for BM and ESM milling and (right) chromium recovery after digestion of chromite vs. F/F\textsubscript{0} ratio [16].](image)

In Figure 6 the modified flowsheet for the production of sodium dichromate is given. The introduction of mechanical activation step enabled the reduction of the mass flows due to a complete digestion and the improved landfill-suitability of the tailings.
2.3 Aluminium

Investigations were performed in Germany in order to elucidate possibilities to improve processing steps of the hydrometallurgical treatment of bauxite ores by the Bayer process with mechanochemical method [17-19].

Bauxite $\text{Al(OH)}_3$ is usually a composition of three minerals: hydrargillit $\alpha$-$\text{Al(OH)}_3$, böhmít $\gamma$-$\text{AlO(OH)}$ and diaspor $\alpha$-$\text{AlO(OH)}$ with various leachibility. The use of NaOH to leach bauxite was invented by Bayer in 1892 as a process for obtaining pure aluminium hydroxide which can be calcinated to pure $\text{Al}_2\text{O}_3$ suitable for processing to metal [4]. About 2 tons bauxite yield 1 ton $\text{Al}_2\text{O}_3$ from which 0.5 ton aluminium is produced.

The reaction in NaOH leaching are following

$$\text{Al(OH)}_3 + \text{OH}^- \rightarrow [\text{AlO(OH)}_2]^+ + \text{H}_2\text{O} \quad (3)$$

$$\text{AlO(OH)} + \text{OH}^- + \text{H}_2\text{O} \rightarrow [\text{AlO(OH)}_2]^- \quad (4)$$

Tests in an attritor revealed that the pressure leaching extraction of the aluminium hydroxides in the bauxite by sodium hydroxide solutions could already be achieved with high extraction rates at 90°C after relatively short treatment times. Additional favourable results indicate that CaO additions to the bauxite are effective to avoid undersirable sodium silicate formation in the sodium aluminate solution and that the black residual sludge contains up to 70% hematite $\text{Fe}_2\text{O}_3$ and nearly negligible aluminium and sodium amounts which might allow to consider further applications which could avoid disposal problems encountered with the conventional red mud precipitates [18, 19-20]. The comparison of the Bayer process and the mechanochemical processes is given in Table 3.
Table 3 Comparison of the Bayer and mechanochemical processes [18].

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Bayer process</th>
<th>Mechanochemical process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet milling to (-200µm)</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>SiO₂ removal</td>
<td>+</td>
<td>-</td>
</tr>
<tr>
<td>Chemical decomposition</td>
<td>250°C, 100 bar</td>
<td>90°C, 1 bar</td>
</tr>
<tr>
<td>Na₂O content in leaching medium</td>
<td>140 gL⁻¹</td>
<td>250 gL⁻¹</td>
</tr>
<tr>
<td>Maximum content of Al₂O₃ in leaching solution</td>
<td>185 gL⁻¹</td>
<td>300 gL⁻¹</td>
</tr>
<tr>
<td>Residence time</td>
<td>3 min</td>
<td>15 min</td>
</tr>
<tr>
<td>Thickener</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Filtration</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Rest</td>
<td>2 t red mud/t Al₂O₃</td>
<td>0.75 t black mud/t Al₂O₃</td>
</tr>
<tr>
<td>Cooling to 50°C</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Colour of leaching solution</td>
<td>Brown</td>
<td>colourless</td>
</tr>
<tr>
<td>Addition of inoculation substance</td>
<td>300 gL⁻¹</td>
<td>-</td>
</tr>
<tr>
<td>Conditioning</td>
<td>50 h</td>
<td>4 h</td>
</tr>
<tr>
<td>Filtration</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Filtrate to disposal</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

2.4 Copper, nickel and cobalt

During the International Conference Copper Cobre 2003 in Chile the status of copper hydrometallurgy and the most commercially attractive potential applications were reviewed [21]. The main processes applying sulfate leaching are listed in Table 4.

Amongst them, Activox and Nenatech processes apply fine milling. The particle size of concentrate into leaching is usually less than 20 microns. The features of these processes include

- leaching temperature in these process is lower than sulfur melting temperature (119°C)
- element sulfur formed in the processes remains in the leaching residue which leads to the difficulty to recover precious metals from leaching residue
- some sulfate is produced that is precipitated as gypsum
- iron precipitation is as goethite and jarosite

Table 4 New sulfate processes for chalcopyrite concentrate leaching [21].

<table>
<thead>
<tr>
<th>Process</th>
<th>Leach pressure</th>
<th>Sulfur product</th>
<th>Proposed mechanism</th>
<th>Level of development</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activox</td>
<td>Low</td>
<td>$S^0$, $SO_4^{2-}$</td>
<td>Direct</td>
<td>Laboratory</td>
<td>Fine milling</td>
</tr>
<tr>
<td>Nenatech</td>
<td>Atmospheric</td>
<td>$S^0$, $SO_4^{2-}$</td>
<td>Direct</td>
<td>Laboratory</td>
<td>Fine milling</td>
</tr>
<tr>
<td>Dynatec</td>
<td>Pressure (medium)</td>
<td>$S^0$</td>
<td>Direct</td>
<td>Laboratory</td>
<td>With coal</td>
</tr>
<tr>
<td>AAC/UBC</td>
<td>Pressure (medium)</td>
<td>$S^0$</td>
<td>Direct</td>
<td>Pilot plant (planed)</td>
<td>With surfactant</td>
</tr>
<tr>
<td>Placer Dome</td>
<td>Pressure (high)</td>
<td>$SO_4^{2-}$</td>
<td>Direct</td>
<td>Demo plant (started 2003)</td>
<td>High temperature</td>
</tr>
<tr>
<td>Biocop</td>
<td>Atmospheric</td>
<td>$SO_4^{2-}$</td>
<td>Indirect</td>
<td>Commercial (underway)</td>
<td>Bacterial</td>
</tr>
<tr>
<td>Bactech/Mintek</td>
<td>Atmospheric</td>
<td>$S^0$, $SO_4^{2-}$</td>
<td>Indirect</td>
<td>Demo plant</td>
<td>Bacterial</td>
</tr>
<tr>
<td>Geocoat</td>
<td>Atmospheric</td>
<td>$SO_4^{2-}$</td>
<td>Indirect</td>
<td>Pilot plant</td>
<td>Bacterial</td>
</tr>
</tbody>
</table>

The Activox process was developed in Australia as an alternative to the pretreatments of sulfidic concentrates by roasting and bacterial oxidation [22-28]. The process has been applied to the recovery of non-ferrous and precious metals from concentrates and calcines. A principle idea of Activox is shown in Figure 7.
Activox is a hydrometallurgical process combining ultra fine milling to a P_80 of ~10 µm with a low temperature (100°C), low pressure (1000 kPa) oxidative leach to liberate metals from a sulfide matrix. Base metals, (i.e. copper, zinc, nickel and cobalt) are extracted into the leach liquor, while gold and silver remain in the leach residue in a form suitable for further processing. The Activox conditions favour the formation of elemental sulfur over sulfate, thereby using less oxygen (usually less than 1.5 kg of O_2 per kg of S) than required for complete oxidation to sulfate (typically 2.2 kg O_2 per kg S). Other features include rapid oxidation times (1-2 hours), clean pregnant liquors, and the possibility to treat environmentally hazardous species such as arsenopyrite to produce stable ferric arsenate residues [29].

The Activox based flowsheet for the production of Ni, Co and Cu from sulfide concentrates is shown in Figure 8. The flowsheet is based on proven unit operations and only uses readily available commercial reagents. The flowsheet can handle a wide range of feed materials and is not sensitive to short or long term variations in feed grades [30].

As for activation equipments, three different mills including Bradkeen-Metprotech, Netzsch-IsaMill and Metso-Mineral were tested [28, 31]. IsaMill and conditions of its application are given in Fig. 9 and Table 5, respectively.
Fig. 9 The horizontal stirred mill-IsaMill [32].

Table 5 Operating conditions and specific energy consumption for IsaMill [33].

<table>
<thead>
<tr>
<th>Site</th>
<th>Mill pressure (kPa)</th>
<th>% Solid (by weight)</th>
<th>Temperature of exciting pulp (°C)</th>
<th>Size reduction ratio</th>
<th>Specific energy (kWht⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mount Isa</td>
<td>225</td>
<td>40</td>
<td>40-43⁴</td>
<td>1.67</td>
<td>7.6</td>
</tr>
<tr>
<td>McArthurRiver</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-open circuit</td>
<td>300¹</td>
<td>20</td>
<td>40-50⁵</td>
<td>3.75</td>
<td>28</td>
</tr>
<tr>
<td>-close circuit</td>
<td>425</td>
<td>20</td>
<td>40-50⁵</td>
<td>4.30</td>
<td>36</td>
</tr>
</tbody>
</table>

¹Approximate value  
²Depending on ambient temperature  
³Based on net power draw (gross power-no load power)

2.5 Antimony

The Melt process was developed in Slovakia for hydrometallurgical treatment of tetrahedrite sulfidic concentrates in order to obtain antimony in soluble form and copper as copper sulphide [34-36]. The process name is an abbreviation: mechanochemical leaching of tetrahedrites.

Tetrahedrite is one of the most common sulfominerals. The general formula representing the naturally occurring tetrahedrite-tennantite series is (Cu,Ag)₁₀(Cu,Zn,Fe,Cd,Hg,Cu)₂(Sb,Bi,As)₄S₁₃. In most natural tetrahedrites the two Cu²⁺ atoms are replaced by a divalent element such as Zn²⁺ which usually occupies a tetrahedral site in sulfides [37]. Tetrahedrites represent the most important source of copper and antimony and are also of economical interest due to their content of silver and mercury.
The chemistry of the reaction between tetrahedrite (simplified formula Cu$_3$SbS$_3$) and Na$_2$S can be described by equations [38]

\[
2\text{Cu}_3\text{SbS}_3 + \text{Na}_2\text{S} \rightarrow 3\text{Cu}_2\text{S} + 2\text{Na}_{3}\text{SbS}_2
\]  

(5)  

\[
\text{Na}_{3}\text{SbS}_3 + \text{Na}_2\text{S} \rightarrow \text{Na}_3\text{SbS}_3
\]  

(6)  

The soluble Na$_3$SbS$_3$ containing trivalent antimony is oxidized to a product containing pentavalent antimony by the polysulfide ions present in the leaching liquor

\[
(x - 1)\text{Na}_3\text{SbS}_3 + \text{Na}_2\text{S} \rightarrow (x - 1)\text{Na}_3\text{SbS}_3 + \text{Na}_2\text{S}
\]  

(7)  

The behaviour of arsenic leaching from tennantite Cu$_3$AsS$_3$ by Na$_2$S may be described by equation

\[
2\text{Cu}_3\text{AsS}_3 + 3\text{S}^{2-} \rightarrow 3\text{Cu}_2\text{S} + 2\text{AsS}_3^{2-}
\]  

(8)  

The principal flowsheet of operation, in which mechanochemical (I) leaching is followed by chemical (II) leaching, is shown in Figure 10. Alkaline solutions of Na$_2$S have been applied as leaching agent. The results presented in Table 6 show the almost total extraction of Sb can be achieved by alkaline Na$_2$S leaching at 95°C leaving 0.25 % Sb in solid residue.

![Flowsheet of leaching unit](image)

**Fig. 10 Flowsheet of leaching unit: 1-heating, 2-chemical reactor, 3-pump, 4-valve, 5-attritor, 6-cooling. The working regimes: I-mechanochemical leaching, II chemical leaching [39].**

<table>
<thead>
<tr>
<th>Element</th>
<th>Me (%)</th>
<th>As received</th>
<th>Mechanochemically treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>27.36</td>
<td>26.00</td>
<td></td>
</tr>
<tr>
<td>Sb</td>
<td>15.93</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>14.58</td>
<td>16.46</td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>0.33</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>1.02</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>0.74</td>
<td>0.11</td>
<td></td>
</tr>
</tbody>
</table>

Table 6 Chemical composition of tetrahedrite concentrate [40].
3. Crystal engineering

Mechanochemical solid-state reaction of molecular crystals is a rather new but promising direction in application of ultrafine milling. The potential importance of this field relates not solely to the traditional fields of applications of molecular crystals, such as pharmaceutics (see later) but also to the newly discovered possibilities of their utilization as functional materials for molecular electronics, molecular magnets, etc. [2].

Useful contributions into recent literature of organic solid-state reactions, included those activated mechanochemically have been published [41-43]. Various mills were tested for activation, especially those providing the high energy input such as vibratory mills, planetary mills and attritors. It was established that many types of organic reactions can be realized with these devices.

As an example, mechanochemical synthesis of zinc bismethionate, a food additive can be illustrated (Fig. 11). This compound is prepared by solid-state synthesis at ambient conditions without intervening liquid phase and connected operations like heating, washing, distilation, etc.

Fig. 11 Mechanochemical synthesis of zinc bismethionate hydrate: chemistry and milling in an industrial eccentric vibration mill ESM (Siebtechnik, Germany) [44].
4. Materials engineering

Non-equilibrium processing of materials has attracted the attention of a number of scientists and engineers due to the possibility of producing better and improved materials than is possible by conventional methods [45]. One of the processing methods cited in literature under the term mechanical alloying (MA) is very frequently used for the preparation of advanced materials in materials engineering. MA started as an industrial necessity to produce oxide dispersion strengthened (ODS) nickel- and iron-based superalloys for applications in the aerospace industry [46]. The technique of MA was used for industrial applications from the beginning and the basic understanding and mechanism of the process is beginning to be understood only now. One of the greatest advances of MA is in the synthesis of novel alloys, e.g. alloying of normally inmiscible elements, which is not possible by any other technique. The MA products find applications in various industries and these are summarized in Fig. 12.

Fig. 12 Typical current and potential applications of MA products [47].

Mechanical alloying for commercial production is carried out in the mills of up to more than 1000 kg capacity. The ball mills to produce oxide dispersion strengthened nickel- and iron-based alloys, is carried at facilities in the USA and Great Britain (Fig. 13).

Fig. 13 Commercial production-size ball mills used for mechanical alloys [47].
5. Agriculture

Phosphates that occur in volcanic rocks as apatites or in sedimentary rocks as phosphorites are used in agriculture for production of phosphate fertilizers. Natural phosphates have first to be converted to the water-soluble form by their decomposition in acids. Superphosphate is a classical phosphorus fertilizer, produced by decomposition of phosphates in sulphuric acid. A higher grade of superphosphate with 2-3 times higher content of watersoluble phosphatic component can be prepared by decomposition of phosphates in a mixture of sulphuric and phosphoric acids [48]. Traditionally, the following reactions are used:

\[
Ca_3F(PO_4)_3 + 5H_2SO_4 + 2.5H_2O \rightarrow 5(CaSO_4 \cdot 0.5H_2O) + 3HPO_4 + HF
\]  

(6)

\[
Ca_3F(PO_4)_3 + 7H_3PO_4 + 5H_2O \rightarrow 5(Ca(H_2PO_4)_2 \cdot H_2O) + HF
\]  

(7)

Acid soils may fertilized by natural phosphates in the as-milled state. In view of their low immediate effect, they are used as long-term fertilizers. In an attempt to enhance the efficiency extensive research to increase the fertilizing effect was carried out [see references in works 49; 48].

Based on the results of investigation of the structure-reactivity correlation, commercial phosphate fertilizers have been developed. In Figure 14 practical application of mechanically activated Marocco phosphorite for plants treatment is shown. The positive influence of high-energy milling on plant growth is unambigous.

Fig. 14 Influence of mechanical activation of phosphorite (deposit Youssoufia, Morocco) on a plantgrowth. From left to the right: without phosphorite, non-activated phosphorite (-125 µm), phosphorite milled at milling energy 50 kWh/t and 150kWh/t, respectively [50].

Optimal parameters of mechanical activation have been determined for the phosphate ores of different mineral composition [51]. The mills of continuous operation with low energy consumption have been designed, their productive capacity being, at the beginning, 3t/h. Long-term agrochemical tests (for 15 years) of mechanically activated phosphate ores of different composition have been carried out on wide range of soils and with various crops.
These tests demonstrated high fertilizing effect [52-53]. The technology was installed at the Burenkhan deposit of phosphorite ores in Mongolia. It was proved that the mechanochemically pretreated phosphorite fertilizers have prolonged action and are comparable with fertilizer based on superphosphate [54].

The technological advantages of mechanochemical methods over traditional methods are summarized in Table 7.

Table 7 Comparison of traditional and mechanochemical methods for production of phosphate fertilizers [55].

<table>
<thead>
<tr>
<th>Process characteristics</th>
<th>Traditional method</th>
<th>Mechanochemical method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pittman’s probe in % citric acid S</td>
<td>80-85</td>
<td>55-60</td>
</tr>
<tr>
<td>Ammonium citrate</td>
<td>60</td>
<td>40-50</td>
</tr>
<tr>
<td>Increase of harvest related to superphosphate</td>
<td>1.00</td>
<td>0.95</td>
</tr>
<tr>
<td>Duration of production process</td>
<td>20 d (periodical)</td>
<td>20-24 h (continuous)</td>
</tr>
<tr>
<td>Consumption of energy per ton</td>
<td>450 kWh/t</td>
<td>500 kWh/t</td>
</tr>
<tr>
<td>Consumption of reagents per ton</td>
<td>0.7 t H₂SO₄ (60%)</td>
<td>-</td>
</tr>
<tr>
<td>Duration of agrochemical action of the fertilizer</td>
<td>1-2 years</td>
<td>5-7 years</td>
</tr>
<tr>
<td>Release of fluorine into atmosphere</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Increase of acidity of soils</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Possibility to use in small deposits (&lt;1 million tons of phosphorus rocks)</td>
<td>No</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Different machines consume different amounts of power for production of the fertilizers, and the capacity of the mills is also different. It was reported that the vibrocentrifuge mill was the best suited for this purpose and it could also be used continuously. As mentioned above, the first factory to produce the phosphate fertilizer was built in Mongolia. Since then more than 1.5 million tons of the fertilizer has been produced.
6. Pharmacy

Dissolution testing of drug compounds is of fundamental importance in the design and development of pharmaceutical products [56]. Dissolution rate is normally described by Noyes-Whitney equation

\[
\frac{dW}{dt} = \frac{D}{h_D} S_A (C_s - C_t)
\]

where the dissolution rate \(\frac{dW}{dt}\) at time \(t\) is a function of three types of material and experimental parameters, namely specific surface area \(S_A\), concentration gradient \((c_s - c_t)\) and diffusional transport \(D/h_D\) (\(D\)-diffusion coefficient, \(h_D\)-the distance over which diffusion is the dominant transport mechanism).

At present about 40% of the drugs being in the development pipelines are poorly soluble, even up to 60% of compounds coming directly from synthesis are poorly soluble [57]. Poor solubility is in most cases associated with poor bioavailability. Bioavailability is how well a drug will reach an effective therapeutical level in the body, and may be influenced by various factors. A drug may be safe and effective, but never reach the therapeutic level in the body if the bioavailability is poor. Bioavailability essentially depends on three factors: solubility, permeability and dose [58], and the question of the minimum acceptable solubility can only be answered if the other two factors are known. According to biopharmaceutics classification system a drug substance is considered highly soluble when the highest strength dosage is soluble in 250 mL of aqueous media over the range pH=1.0-7.5 [59].

There are two basic approaches to overcome the bioavailability problems of the drugs:

- increase of equilibrium solubility (e.g. by complex formation) and
- increase of dissolution velocity

The first approach was a limited success as clearly demonstrated by the low number of products on the market based on such technologies. A much more straightforward way is increasing the dissolution velocity by increasing the surface area of the drug powder, i.e. micronisation leading to mean particle sizes approximately 3-5 µm. However, many of the new compounds show such a low solubility that micronisation does not lead to a sufficient increase in bioavailability after oral administration. Therefore the next step taken was nanonization. The drug powder is transferred to drug nanocrystals, typically sizes are around 200-600 nm [60].

Drug nanocrystals can be produced by various methods principally the top down and bottom up techniques (Fig. 7).
The bottom up technique is the classical precipitation approach, the drug is dissolved in a solvent which is subsequently added to a nonosolvent to precipitate the crystals. A priori this technique is difficult to handle, the crystal growth needs to be stopped to avoid formation of microcrystals. In addition this technology cannot be applied to the increasing number of drugs being poorly soluble in all media [60]. On the other hand the top down technique (ultrafine milling) is the method of choice for industrial production in pharmacy. In addition to size reduction, milling may alter the crystalline structure and cause chemical changes in some drugs [62-63].

The advantages of mechanochemical approach applying the ultrafine milling can be illustrated for acetylsalicylic acid production.

Acetylsalicylic acid (ASA) is non-steroidal substance often used as an analgesic, antipyretic and as an anti-inflammatory drug. The most popular and used brand name is Aspirin. It has also antiplatelet effect and is used in long-term, low doses to prevent heart attach and cancer. Its solubility in water is 1mg/mL at 20°C. The low solubility of ASA in water decreases its pharmacological efficiency and causes undesirable side effects when the substance is used in drugs. The salts of ASA posses increased solubility. However, with all advantages of ASA salts, these are expensive drugs manufactured on a small scale. During the production, ASA undergoes partial decomposition into salicylic and acetic acid as a result of

Fig. 15 Schematic representation of the top down and bottom up techniques for drug nanocrystals preparation [61].
hydrolysis. The existing requirements to the purity of the product make the production process more complex and the product more expensive [64].

For mechanochemical technology for obtaining soluble materials based on ASA and their subsequent use as drugs the special vibrocentrifugal mills with productivity 10g/h-1t/h have been designed. In order to obtain especially pure products (for pharmaceutical purposes), the inner surface of the drum and the surface of milling bodies can be coated with an inert material. The schematic diagram and a pilot plant unit is given in Fig. 16. The design allows smooth variations of the feeder productivity and mill rate. The technological regulations for production of fast-dissolved substance (brand names Aspinat and later Askopirin) have been developed and coordinated with the Ministry of Health in Russia [64].

![Fig. 16 Schematic diagram (right) and a mechanochemical pilot plant unit (left) for the production of fast-dissolving substances of ASA, 1-turbo mixer, 2,3-accumulating tank with feeding screen, 4-continuous vibrocentrifugal mill, 5-product collector [64-65].](image)

7. Conclusion

The possibilities of ultrafine milling application in extractive metallurgy, materials engineering, agriculture and pharmacy are briefly described in this paper. Mechanochemistry which applies this type of milling, demonstrates the differences in comparison with traditional technological procedures. The main advantage is decrease in the number of technological stages, exclusion the operations that involve the use of solvents and gases and the possibility of obtaining a product in the metastable state which is difficult to obtain using traditional technological procedures. The environmental aspects of these processes are particularly attractive.
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References


