

THE EFFECT OF MILLING ON PARTICLE SIZE AND CRYSTAL STRUCTURE IN MECHANOCHEMICAL PROCESSING OF LEAD-CONTAMINATED SYNTHETIC SOIL

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ABSTRACT

Mechanochemical processing of lead-contaminated synthetic soil involves the use of high-energy milling to reduce particle size and alter the crystal structure, which can immobilize lead and mitigate environmental contamination. Milling as a mechanical treatment plays a critical role in determining the final properties of the processed material. This study investigates the role of particle size and crystal structure in the mechanochemical treatment of lead-contaminated synthetic soil. Two synthetic soil samples were prepared in the laboratory, including lead contamination. Milling of the contaminated soils was carried out in a planetary ball mill. The samples were analysed using a lasersizer and X-Ray Diffraction (XRD) to investigate the change in particle size and identify the crystalline phase after milling. The results showed that milling initially reduced particle size, but further milling resulted in particle agglomeration, which was reflected by partial amorphization in soil samples after milling. Other than the partial amorphization, no phase change was detected in the crystal structure. In conclusion, milling resulted in the change of particle size but did not affect the crystalline phase of the milled sample, despite of partial amorphization.

Keywords: Milling time; Particle size; Crystal structure; Contaminated soil; Mechanochemical processing

INTRODUCTION

Mechanochemical technique has been widely applied in many fields such as mineral processing, mineral engineering, extractive metallurgy, coal industry, materials engineering, chemical engineering, pharmacy, building industry, agriculture, and waste treatment (Baláž, 2008).

Mechanochemical treatment uses mechanical energy to impart solid-state reactions and structural changes to particles, including size reduction. Mechanochemical applications have been increasingly popular due to some practical, economical, and environmental advantages. In the context of lead-contaminated soils, this process can immobilize heavy metals by altering the soil's crystal structure and reducing particle size, thereby reducing the leachability of contaminants (Montinaro et al., 2012)

Mechanochemical activation is related to the increase in the reactivity of solids due to the increasing surface area of particles after size reduction caused by mechanical energy (e.g., grinding). Solid-solid reaction can happen in a dry system if the particles are completely mixed and heated by high-energy milling. The transformation that happens in a solid-solid state reaction can be

correlated with the increase in the surface area of the solids.

As shown in Figure 1, the first stage of solid-solid reaction is related to a progressive increase of surface area due to contact between particles (size reduction). In the second and third stages, the disordered particles start to experience plastic deformation and form new aggregates in which chemical reactions happen. In the third stage, the aggregates crystallize as well as undergo continuous amorphization until they reach a stable state. The extent of changes in solid state reaction explained above is affected by the amount of mechanical energy introduced into the system. Therefore, high-energy milling is required to achieve a complete change where all stages occur in a solid-state reaction.

Milling time plays a crucial role in determining the particle size of the processed soil. Prolonged milling typically leads to a reduction in particle size due to the repeated impact and friction generated between the milling media and the soil particles. Nevertheless, the relationship between milling time and particle size is not always straightforward, as particle agglomeration can occur

after a specific threshold of milling time. (Achimovičová et al., 2011; Zdujic, 2002)

Baláž (2008) stated that milling time is considered the most important milling variable. In a study conducted to reduce the leachability of Pb (II) from bentonitic, sandy, and kaolinitic soil, it was reported that immobilization efficiency increased while the leachable concentration of Pb (II) decreased with longer milling time, although the significance varied for different types of soils (Montinaro et al., 2007)

Longer milling times were also required when the same procedure was applied for treating synthetic soil with a higher amount of contaminant (Montinaro et al., 2007) and real soil and tailing samples (Montinaro et al., 2009, 2012). It was required up to 10 hours to reduce the concentration of Pb in the leachate of treated soil to a level lower

than the USEPA regulatory limit (0.015 mg/l) (Montinaro et al., 2009, 2012).

Particle size plays a crucial role in the mechanochemical processing of lead-contaminated soils. Research suggests that smaller particles have higher surface areas, which can enhance chemical reactivity and improve the efficiency of lead immobilization. For instance, studies have demonstrated that finer soil particles (e.g., <38 μm) tend to immobilize lead more effectively because they have a larger surface area and higher reactivity (Karna et al., 2017; Montinaro et al., 2012)

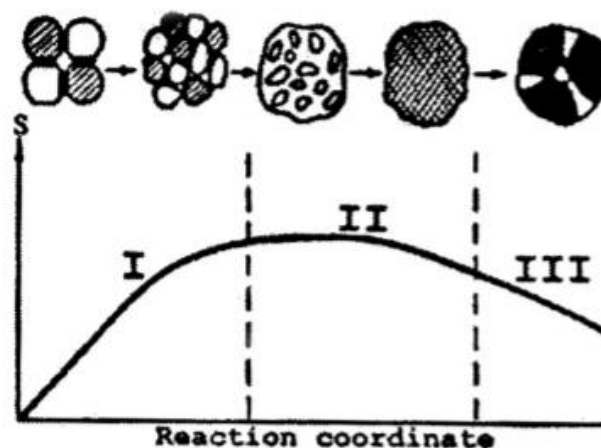


Figure 1. The stages of solid state reaction in relation to increasing surface area (Baláž, 2008)

Mechanochemical processing can cause structural changes, such as amorphization, nanocrystallization, and phase transformations (Achimovičová et al., 2011; Zdujic, 2002). The effect of mechanochemical treatment on particle size distribution and crystal structure was conducted on sandy, bentonitic, and kaolinitic soil (Montinaro et al., 2007). The result of X-ray diffraction analysis on both sandy and bentonitic soil samples showed partial amorphization, while total amorphization occurred on the kaolinitic soil sample.

In the context of lead-contaminated soils, the reduction in particle size and the alteration of the crystal structure contribute to the immobilization of lead (Montinaro et al., 2012). This study aimed to investigate the effect of milling on the occurrence of

agglomerated particles during the mechanochemical treatment and to identify the crystalline phase after milling.

METHODS

Samples used in this study were lead-contaminated synthetic base sandy soil (Soil I) and Fe/Mn oxide-dominated sandy soil (Soil II) prepared in a laboratory. Soil composition was prepared according to Lo & Yang (1999). The soil I sample consisted of 78% quartz, 10% bentonite, 10% kaolinite, 0.5% calcium carbonate, 0.25% manganese dioxide, 0.25% hematite, and 1% humic acid. The quartz used for the soil synthesis was a mixture of three different size range: 90 - 180 μm , 150 - 300 μm , and 0.5 - 2000 μm with a ratio of 1:1:1. Compared to Soil I sample, Soil II sample had

higher amount of quartz (73.5%), manganese dioxide (1.5%), and hematite (1.5%). Both soils were synthesized by preparing the required amount of each soil component and mixing all components by hand shaking in a plastic container.

To simulate Pb contamination, 200 g of synthetic soil was mixed with a lead solution to generate a lead contamination of 1500 mg/kg. The lead solution was prepared by diluting known concentration of PbNO_3 solution with aquadest. The flasks were properly sealed with parafilm and shaken for 24 h in a temperature-controlled incubator shaker (LABWI ZWY-211B, 100 rpm, 22°C). After mixing, the slurries were filtered through a filter paper and the filtered soil was dried in oven at 115°C for 24 h.

Milling of the contaminated soils was carried out in a planetary ball mill (RETSCH PM-100) from

30 minutes to 6 hours at 300 rpm. A 10-minute break time was allocated for the machine to cool down and eliminate the effect of its heating on milling. For optimum milling, a fixed ball-to-powder ratio (BPR) of 10:1 was applied by placing 30 g of the contaminated soil and 300 g of uniform milling balls in the grinding jar. To investigate the effect of silica, experimental setups included the addition of 0%, 1%, 3% and 5% silica while maintaining the soil mass at 30 g. Approximately 1.5 g samples were collected after 0.5, 1, and 3 hours of milling, while all the remaining sample was collected after 6 hours. The samples were analysed using a lasersizer and X-Ray Diffraction (XRD) to investigate the occurrence of agglomerated particles and identify the crystalline phase after milling.

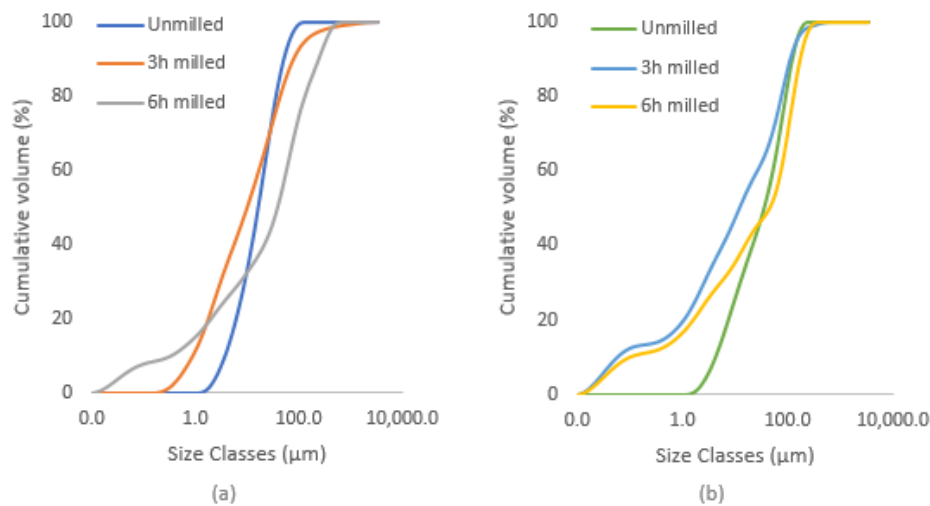


Figure 2. Particle size analysis of unmilled and milled (a) Soil I and (b) Soil II samples with 0% SiO_2 addition

RESULT AND DISCUSSION

Figures 2a and 2b show the particle size analysis of unmilled and milled samples with 0% silica addition for both types of soil. It can be seen that the p_{80} value shifted to the right after milling, meaning that the particle size increased with milling time. This behaviour may play a very important role in soil immobilization efficiency induced by mechanical treatments (Montinaro et al., 2008). This result was similar to that of Montinaro et al. (2007), where increasing particle size confirmed entrapment of Pb (II) and diffusion into new aggregates, and amorphization of kaolinite in kaolinitic soil. This behavior aligns with the kinetics

of crystallite size evolution. Initially, milling time reduces particle size, but eventually, it leads to a steady-state size due to the equilibrium between size reduction and grain growth (Zdujic, 2002). According to study conducted by Achimovičová et al. (2011) on nanocrystalline lead selenide (PbSe), prolonged milling time leads to an agglomeration effect, while the specific surface area increases, reaching a maximum value of 2.4 m^2/g after 12 minutes.

Figure 3 shows the results of XRD analysis of unmilled and 6h milled Soil I without and with the addition of silica. In total, 9 peaks were recognized: 7 peaks belonged to SiO_2 (quartz) while the other 2 belonged to kaolinite and bentonite (Cuevas et al.,

2022; Gruner, 1932; Levien et al., 1980; ZhiLi, 2022). Similar to results of study by Montinaro et al. (2007), the same crystalline phase, specifically quartz, was detected in both the unmilled and milled samples. Ball-milling treatment partially amorphizes soil phases, as confirmed by a small decrease in XRD peak intensity. This accumulation of structural defects, vacancies, and dislocations leads to a loss of crystallinity in soil compounds (Suryanarayana, 1996, 2001). It can be seen from the pattern of the unmilled soil that the peaks of quartz are prominent. Referring to the stages of solid-solid reaction suggested by Baláž (2008), the crystalline phase of quartz is expected to decrease due to the breakage mechanism by milling and eventually form an amorphous phase as a representative of an agglomerate that traps Pb(II). Therefore, milling treatment should reduce the percentage of the crystalline phase of quartz and increase the percentage of the amorphous phase in the milled soil. Decreased crystallite size before

agglomeration, as depicted in Figure 2a and 2b, is advantageous for attaining the desired nanoscale particles. This approach enhances the specific surface area, although agglomeration can potentially compromise the uniformity of the crystal structure (Achimovičová et al., 2011).

To support our explanation, we estimate the crystallinity of all the samples (ZhiLi, 2022) by analyzing the area of each particular peak, as shown in Table 1. Initially, the unmilled sample has a 57% crystallinity, but after 6 hours of milling, the percentage of crystalline in all milled samples decreases as a reflection of amorphization. The sample with 1% addition of silice is more stable since 6 hours of milling only slightly decreased its crystallinity by 3%, indicating minimum partial amorphization.

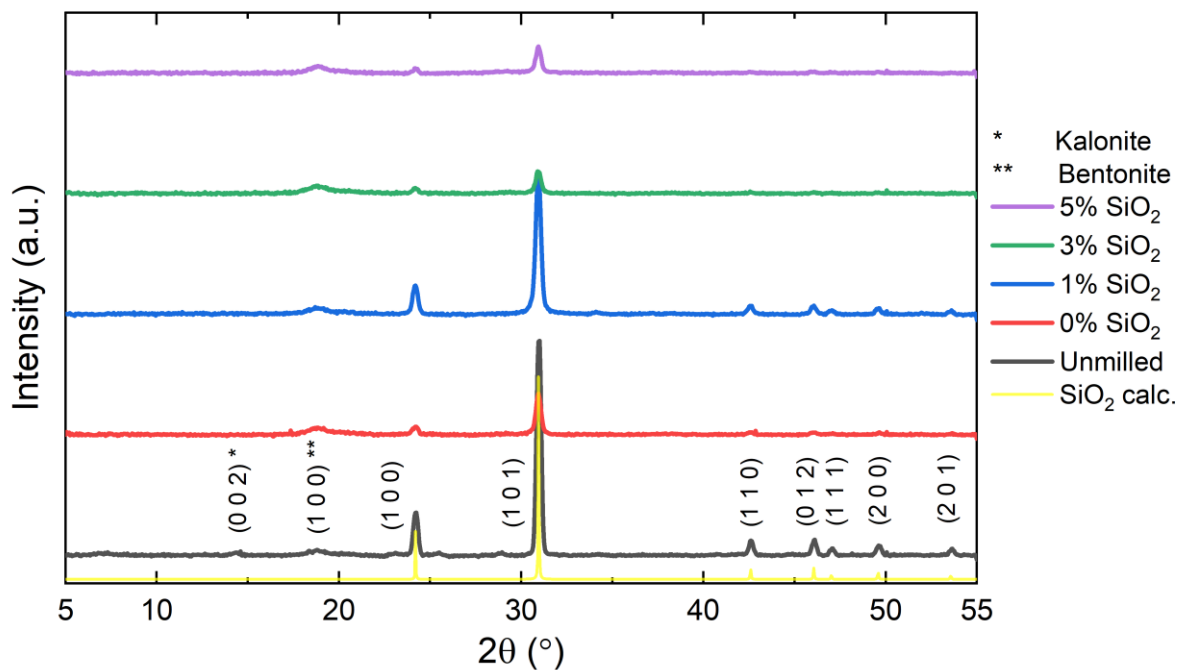


Figure 3. XRD patterns for unmilled and 6 h-milled Soil I without and with the addition of silica

Table 1. Number of peaks and crystallinity

Sample Name	Number of recognized peaks	Crystallinity (%)
Unmilled (0h)	9	57
0% addition of silica (6h)	7	39
1% addition of silica (6h)	9	54
3% addition of silica (6h)	6	31
5% addition of silica (6h)	5	31

Based on the results of the study, it can be concluded that milling as a mechanical treatment decreases particle size, followed by agglomeration, indicated by increased particle size in terms of p80. In terms of crystal structure, there was no detected phase change in the milled samples based on XRD analysis. There were, however, reduced peaks which indicate partial amorphization. This was supported by crystallinity estimation.

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