

# Arsenic Sorption on Mechanically Activated Magnetite and Olivine

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*Arsenic sorption on mechanically activated minerals such as magnetite  $Fe_3O_4$  (Kiruna, Sweden) and olivine  $(Mg,Fe)_2SiO_4$  (Åheim, Norway) has been studied and compared in this work. Experiments were carried out with non-activated and mechanically activated samples. The activation of both minerals was performed in a planetary mill at different milling conditions. The specific surface area and consequent sorption activity were enhanced by mechanical activation. The using of olivine seems to be better than magnetite from the point of view of milling time, which is necessary for achievement of the same sorption effect.*

**Keywords:** Arsenic, Sorption, Magnetite, Olivine, Mechanical activation

## Introduction

Arsenic is a toxic metalloid that contaminates soils, sediments and ground waters. It can originate from different sources. Depending on the redox conditions, arsenic occurs in nature as As(III) and As(V). As(III) is more toxic than As(V) (Cullen, 1989; Goldberg, 2001; Smedley and Kinniburgh, 2002). The contamination of groundwater by arsenic is a global problem, because its concentration levels in many countries exceed the WHO drinking water guideline value of  $10 \mu\text{g}\cdot\text{l}^{-1}$  (WHO 2001). Arsenic in groundwater is often associated with geologic sources, but in many locations with anthropogenic inputs. Large quantities of As are released into the environment through industrial activities, which play an important role in the contamination of soils, waters and air (Juillot et al., 1999; Matschullat, 2000). Arsenic is human carcinogen for which there is an evidence of carcinogenic risk by both inhalation and ingestion. High levels of As are retained for longer periods of time in the bone, skin, hair and nails of exposed humans (Mandal et al. 2003). Inorganic arsenic compounds such as calcium arsenate, lead arsenate, sodium arsenate and many others were used by farmers as insecticides and pesticides. The possible mobilization of As in the soils, and subsequent leaching into ground or surface water or entry into the human food chain, should always be considered as a serious hazard.

Several methods have been proposed for heavy metal removal, e.g. precipitation, membrane filtration, ion exchange and adsorption (Habashi, 1993). Many scientific works present the sorption of arsenic onto different sorbents (Babel and Kurniawan, 2003; Bostick et al., 2003; Deliyanni et al., 2003; Giménez et al., 2007; Jönsson and Sherman, 2008; Su et al., 2008; Mak et al., 2009; Sharma and Sohn, 2009).

Sorption activity can be enhanced by a pretreatment method where solid state properties of minerals could be changed. Mechanochemical pretreatment by high-energy milling belongs to such method. Changes in surface area as a consequence of milling can play important role by intensification of sorption process (Baláž, 2008).

The aim of this work is to study and compare the influence of high-energy milling (mechanical activation) on sorption behaviour of arsenic on magnetite  $Fe_3O_4$  and olivine  $(Mg,Fe)_2SiO_4$ .

## Materials and methods

### Material

The investigation was carried out with the samples of magnetite (Kiruna, Sweden) and olivine (Åheim, Norway). XRD patterns of minerals, which were used in sorption experiments, are shown in Fig. 1. The olivine consists mostly of forsterite and a little percentage of fayalite. Both of the minerals have some minor minerals.

### Mechanical activation

The mechanical activation of magnetite and olivine was performed in a planetary mill Pulverisette 6 (Fritsch, Germany) at the following conditions: 50 balls of 10 mm diameter; material of the milling vial ( $V=250 \text{ ml}$ ) and balls: tungsten carbide, ball charge: 360 g, sample charge: 10 g (magnetite), 18 g (olivine); rotation speed: 500 revs (magnetite), 450 revs (olivine), milling time in range 1-120 min (magnetite), 2-30 min (olivine).

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### Specific surface area

The specific surface area SA was determined by the low-temperature nitrogen adsorption method. The Gemini 2360 sorption apparatus (Micromeritics, USA) was applied.

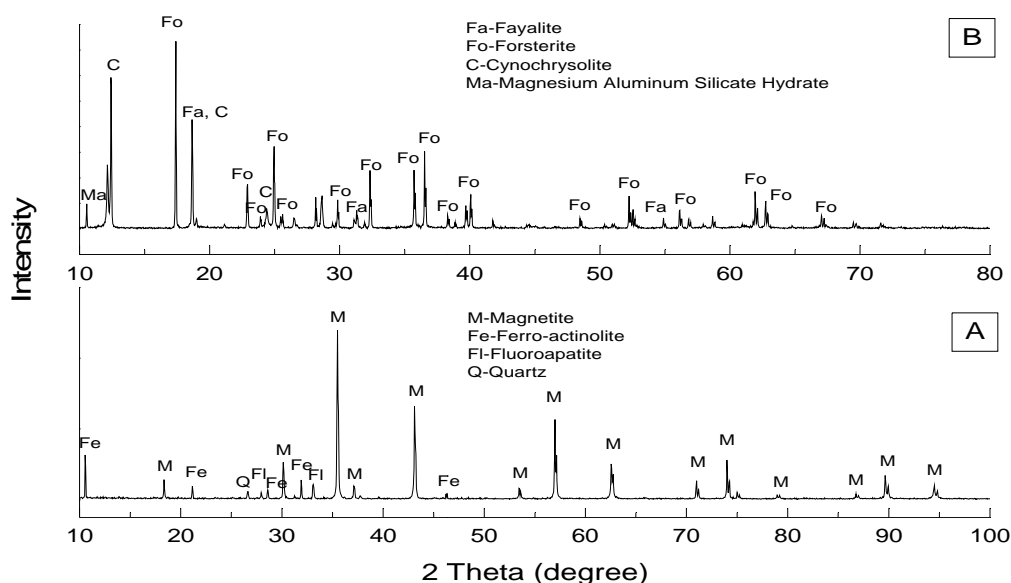


Fig. 1. XRD patterns of (A) magnetite and (B) olivine.

### Sorption tests

The sorption of arsenic was running in Erlenmayer's flasks placed on laboratory shaker constructed at the Institute of Geotechnics, Slovak Academy of Sciences. Initial arsenic concentration prepared from  $\text{NaAsO}_2$  was in range  $1\text{--}100\text{ mg.l}^{-1}$ . Arsenic water solution was freshly prepared before each experiment. During sorption tests the sorbents (magnetite and olivine) concentration were  $8\text{ g.l}^{-1}$  of arsenic water solution. Sorption time was in range 0.25–6 hours. The sorption was performed at 298–300 K. Initial pH for magnetite was 7.9 and for olivine 6.5. Initial and residual concentration of arsenic in solution was determined by the atomic absorption spectroscopy (Spectr AA-30, Varian, Australia).

## Results and discussion

### Mechanical activation

It was detected an increase of surface area of above mentioned minerals with the time of mechanical activation in a planetary mill. The dependence of specific surface area on the time of milling is shown in Fig. 2. As can be seen, specific surface area of mechanically activated magnetite increased from value  $0.1\text{ m}^2.\text{g}^{-1}$  to  $11.9\text{ m}^2.\text{g}^{-1}$  ( $t_M = 90\text{ min}$ ) and olivine from value  $0.3\text{ m}^2.\text{g}^{-1}$  to  $5.2\text{ m}^2.\text{g}^{-1}$  ( $t_M = 30\text{ min}$ ).

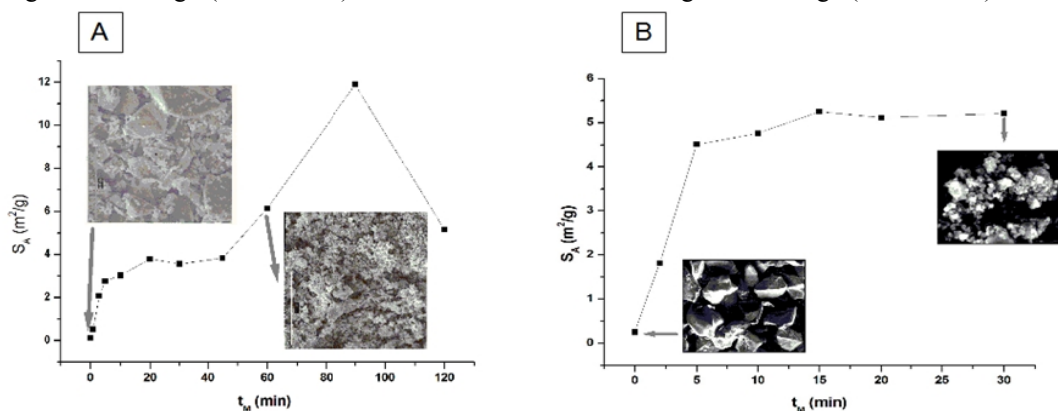


Fig. 2. Specific surface area,  $S_A$  of (A) magnetite and (B) olivine as a function of milling time,  $t_M$  and their SEM photographs.

In both of cases (magnetite and olivine), during the mechanical activation, the small particles are created during the mechanical activation. The consequence of this phenomena is in increase of SA. When

the agglomeration of fine particles is appeared, it is reflected in decrease (magnetite) or stagnation (olivine) of this parameter. The creation of agglomerates is appeared very frequently during the high energy milling (Juhász and Kolláth 1993). In Fig. 2, there are inserted SEM photographs of as-received and milled minerals.

### Sorption of arsenic

Samples of magnetite and olivine were chosen for sorption tests. Initial concentration of As in solutions was  $5 \text{ mg.l}^{-1}$ . The results of arsenic uptake by mechanically activated magnetite particles for 0-120 min are given in Fig. 3A. Milling markedly influences of As sorption; as a consequence the specific surface area increases as well as bulk changes are induced in the mineral.

The increase of As capture was especially enhanced for the milling time 90 min.

This jump is surely in close relation to the specific surface area increase at these milling time as well as bulk disordering. In this case 96 % arsenic uptake was detected after 6 hours of sorption. The sorption of arsenic was not operated at reference (non-activated) sample of magnetite.

In the case of olivine, 99 % arsenic uptake at sample milled 30 min was measured after 6 hours of sorption (Fig. 3B). For comparison, non-activated olivine has no potential for arsenic uptake. Milling time markedly influences arsenic sorption from water solution, which corresponds to an increase of surface area of samples (Fig. 2).

As seen from the Figures the behavior of arsenic removal at these minerals is a little bit different. At magnetite, the equilibrium state of sorption occurs at the beginning of sorption times and then the efficiency of arsenic from water solution increases very slowly. In the case of olivine, this state occurs later and the curve becomes sigmoid.

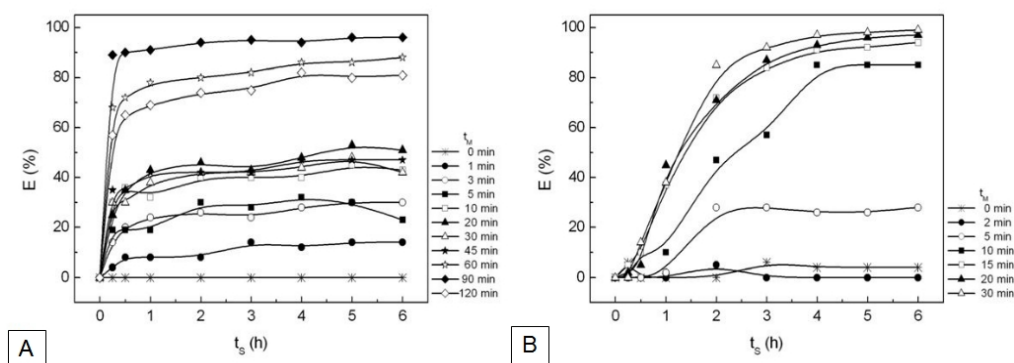


Fig. 3. Arsenic uptake,  $E$ , vs. sorption time,  $t_s$ , for (A) magnetite and (B) olivine,  $t_M$ -milling time.

It follows from Fig. 3, that olivine seems to be more effective than magnetite in arsenic sorption from water solution from the point of view of milling time. Only 30 min milled olivine removes almost 100 % of arsenic from water solution (initial concentration of As was  $5 \text{ mg.l}^{-1}$ ). At magnetite this effect appeared for mineral activated at 90 min. The claim, that the olivine is more effective sorbent than magnetite is confirmed by the values of sorption capacity, which are  $2.75 \text{ mg.g}^{-1}$  for magnetite (120 min) and  $8.5 \text{ mg.g}^{-1}$  for olivine, respectively (Fig. 4). This value for magnetite is not so high as the result in (Štefušová et al., 2010), but in this case the  $\text{Fe}_3\text{O}_4$  was artificially synthesized to achieve high level of  $S_A$  ( $125.7 \text{ m}^2.\text{g}^{-1}$ ). By milling of the natural magnetite in a planetary ball-mill (Simeonidis et al., 2011), the similar sorption capacity ( $2.1 \text{ mg.g}^{-1}$ ) was achieved. The values of sorption capacity for olivine can not be compared with literature, because up to date, the experiments with this mineral were performed only in (Bujňáková et al., 2010).

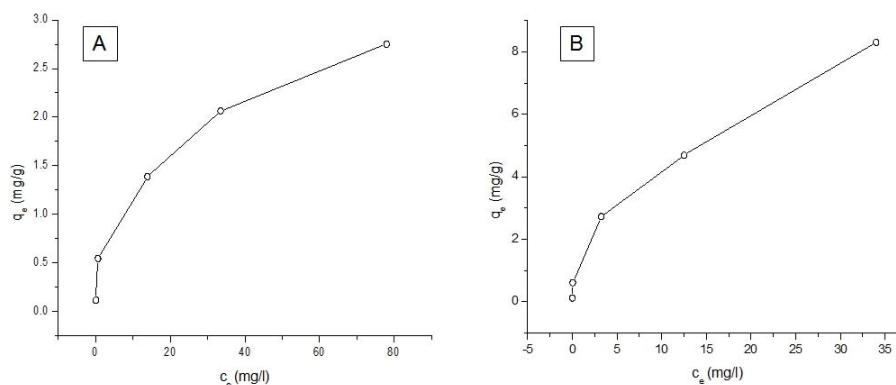


Fig. 4. Amount of arsenic sorbed,  $q_e$ , by (A) – magnetite, (B) – olivine vs. equilibrium concentration,  $c_e$ .

In the following experiments the effect of arsenic concentration on sorption ability of minerals has been observed. All the conditions were the same as before (see part Sorption of arsenic), but the initial arsenic concentrations were different: 1, 5, 25, 50 and 100 mg.l<sup>-1</sup>. Magnetite and olivine were mechanically activated for 5 min (Fig. 5).

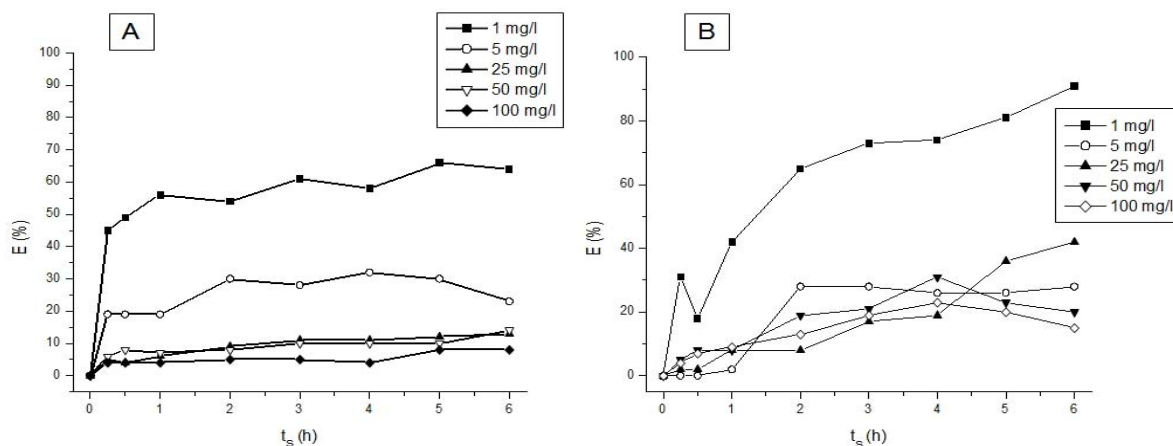


Fig. 5. Effect of arsenic concentration on sorption ability of minerals (A) magnetite (B) olivine;  $t_M = 5$  min.

In this case, olivine has higher sorption ability in comparison with magnetite mostly for the lower arsenic concentration (1 mg.l<sup>-1</sup>). Again, the equilibrium state for magnetite appeared shortly after beginning of the sorption experiments, while for olivine the curves have sigmoid character where the start of sorption is slower. The pH value after arsenic sorption on magnetite was 7.5 and on olivine 8.

### Conclusion

The mechanical activation of magnetite and olivine by planetary mill causes the enhanced of specific surface area values with the time of milling.

The enhanced specific surface area positively influences arsenic removal from water solution.

The use of olivine seems to be better than magnetite from the point of view of milling time, which is necessary for achievement of the same sorption effect.

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