MECHANOSORPTION OF CO₂ BY SILICATES: MECHANISM, KINETICS AND POSSIBLE APPLICATIONS

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Keywords: Silicates, Carbon dioxide, Mechano sorption

Abstract
Mechanically induced CO₂ extensive sorption by silicate minerals (labradorite, diopside, okermanite, ghele nitite, and wollastonite) has been considered. The silicates mechanically activated in CO₂ atmosphere in a planetary mill AGO-2 have been characterized using XRD and IR spectroscopy. Micro- and nanostructure of material resulting from mechanochemical interaction of diopside with CO₂ were investigated using SEM and TEM. The obtained data suggest that CO₂ penetrates the structurally disordered silicate matrix and “dissolves” in the particles volume with formation of homogeneous carbonate-silicate phase. Equations that reasonably good represent kinetics of CO₂ mechanosorption by the silicates have been proposed. These equations enable to calculate mechanosorption coefficients characterizing the diffusivity of CO₂ into disordered silicate matrix under intensive mechanical impact. Correlations between CO₂ content in mechanically activated silicates and CO₂ solubility in the corresponding melts, as well as between mechanosorption coefficients and CO₂ diffusion coefficients in the melts have been revealed. Possible application of the revealed effect in improving of alkali-activated ferrous-magnesium slag binding materials has been discussed.

Introduction
This work is a part of our systematic study of mechanochemical interaction between silicates, complex oxides and CO₂. It started from revealing of unusual reactivity increase of calcium and magnesium containing silicates such as diopside CaMgSi₂O₆, wollastonite CaSiO₃ and others with respect to carbon dioxide during fine grinding in a mortar in air or during mechanical activation (MA) in a planetary mill in CO₂ atmosphere [1,2]. The silicates, which are virtually inert to CO₂ at ambient conditions without mechanical impact, selectively consume carbon dioxide from the environment in the form of carbonate ions in amount comparable with Ca and Mg content in the minerals. In that case, one might expect occurring of reaction yielding corresponding carbonates and silica, e.g.:

\[
\frac{1}{2} \text{CaMgSi}_2\text{O}_6(\text{diopside}) + \text{CO}_2 = \frac{1}{2} \text{CaCO}_3(\text{calcite}) + \frac{1}{2} \text{MgCO}_3(\text{magnesite}) + \text{SiO}_2
\]

However, no reflections of carbonates or other crystalline phases were observed in XRD patterns of MA-silicates. It was shown that extensive mechanically induced carbonization of the silicates does not result in formation of amorphous carbonate and could not be explained by CO₂ chemisorption on the surface of the silicate particles. The obtained data suggest that CO₂ penetrates the structurally disordered silicate matrix and “dissolves” in the particles volume with formation of carbonate-silicate phase as a result of deep mechanosorption [1-4]. According to IR spectroscopic data this phase resembles finely ground glass obtained by quenching of silicate melt wherein CO₂ was dissolved at magma state conditions (T~1800-2000 K, P~1-2 GPa) [1,2]. Remarkable is the fact that the dissolution of carbon dioxide in the melts occurs only under conditions of high temperature and pressure, while in our experiments, silicates consume CO₂ during MA under ambient conditions. Similar to glass, product of mechanochemical interaction between alkaline earth silicates and CO₂ is thermodynamically unstable but kinetically stable substance. It does not change its chemical composition and amorphous state during storage in desiccator at least for several years.

As distinct from Ca and Mg silicates, mechanochemical interaction of Na and K silicates with CO₂ is an ordinary substitution reaction. The products of this reaction are amorphous silica and corresponding alkali metal carbonates or hydrogen carbonates as was substantiated by XRD data [5,6]. This difference in interaction is caused by two main factors. First, for alkaline earth metal silicates, carbonization reaction like reaction (i) is thermodynamically less favorable than corresponding reactions for alkali metal silicates. Second, there are kinetic limitations related to melting temperatures of the silicates and their hygroscopic properties [5,6]. Practical application of the revealed effect deals with purposeful modification of particles outer layers in order to increase their reactivity, e.g. to improve binding or sorption properties. In principle, deep mechanosorption can be used for selective sorption of CO₂ from gas mixtures.

In this paper structural and chemical changes of natural and synthetic silicate minerals (labradorite, diopside, okermanite, ghele nitite, and wollastonite) in the course of MA in CO₂ atmosphere have been studied. Transmission electron microscopy (TEM) data supporting hypothesis of mechanically induced “dissolution” of carbon dioxide in the structurally disordered silicate with formation of homogeneous amorphous carbonate–silicate phase have been obtained. Equations that reasonably good represent kinetics of CO₂ mechanosorption by the silicates have been proposed. Correlations between carbon dioxide mechanosorption by silicates and CO₂ dissolution in silicate melts have been revealed. CO₂ mechanosorption by magnesium-ferrous slag for improving of its binding properties has been considered.

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Ghelenite Ca$_2$Al$_2$SiO$_7$ and wollastonite CaSiO$_3$ were synthesized containing carbonates and micas as admixtures. (Kola Peninsula, Russia) and contained less than 1% of natural minerals as admixtures was subtracted from measured CO$_2$ content of the mineral samples after MA. The specific surface area was measured using FlowSorb II 2300 (Micromeritics) analyzer by the low temperature nitrogen adsorption method. Scanning electron microscopic (SEM) images were obtained on a Supra 50 VP, and TEM images were obtained on a JEOL JEM-2100F instruments. Before measurement the specimens were dispersed in ethanol by agitation for 10 min and then applied to collodion film and dried for 5–12 h.

### Experimental

#### Samples

Natural plagioclase, diopside, okermanite and synthetic ghelenite and wollastonite samples were used for experiments. Chemical composition of the minerals is given in Table 1. Plagioclase sample (fraction -250+125 µm) was from Gorodische deposit (Ukraine). It contained less than 1 mass % of magnetite as admixture. Plagioclases form discontinuous solid solutions from anorthite CaAl$_2$Si$_2$O$_8$ to albite NaAlSi$_3$O$_8$ by substitution of Ca and Al for Na and Si. According to CaO/Na$_2$O percentage (Table 1) the plagioclase sample can be classified as labradorite [7]. Both diopside and okermanite samples (fractions -200+125 µm) were from Kovdor deposit (Kola Peninsula, Russia) and contained less than 1% of carbonates and micas as admixtures.

Ghelenite Ca$_2$Al$_2$SiO$_7$ and wollastonite CaSiO$_3$ were synthesized from reagent grade CaCO$_3$, Al$_2$O$_3$ and amorphous silica. Before synthesis calcium carbonate was heated at 200°C for 24 h. Alumina and amorphous silica were annealed at 1000°C for 12 h. Stoichiometric mixtures of the components in both cases were ground in a Fritsch Pulverisette 2 laboratory mortar grinder for 10 h. After grinding mixtures were annealed at 900°C for 8 h and then at 1300°C for 12 h. Grinding for 10 h and annealing at 1300°C for 12 h were repeated 8 times. According to XRD and optical microscopy analyses the obtained substances were pure ghelenite and wollastonite (in the form of cyclowollastonite).

#### Methods

MA was performed in an AGO-2 planetary ball mill [8] at 40 g centrifugal factor. The initial sample mass was 10 g. The steel ball (5 mm in diameter) load to sample weight ratio was 20. Immediately before grinding, the air in the grinding vial was displaced by CO$_2$ from cylinder using higher density of carbon dioxide, and the vial was sealed hermetically. After 1, 2, 6, 10, and 20 min of MA about 1 g of sample was taken for analysis. After each sampling and every 2 min of MA the vial was repeatedly filled with CO$_2$ at P=10$^7$ Pa. According to chemical analysis of the silicate minerals samples after MA for 30 min in CO$_2$ atmosphere the milling yield was within 1.5–2.0 mass % Fe.

X-ray diffraction (XRD) data were measured using DRON-2 equipment (CuK$_\alpha$ radiation). IR spectra were recorded in potassium bromide pellets with a UR-20 spectrometer. The carbon dioxide amount absorbed by silicates during MA was determined using an AN-7529 gas analyzer. A weighed portion of the sample was calcined at 1200°C and the released CO$_2$ was absorbed by strontium chloride solution resulting in its acidation. The obtained solution was neutralized by electric current and the amount of absorbed CO$_2$ was determined coulometrically. The minor amount of carbonate present in natural minerals due to presence of carbonate minerals as admixtures was subtracted from measured CO$_2$ content of the mineral samples after MA. The specific surface area was measured using FlowSorb II 2300 (Micromeritics) analyzer by the low temperature nitrogen adsorption method. Scanning electron microscopic (SEM) images were obtained on a Supra 50 VP, and TEM images were obtained on a JEOL JEM-2100F instruments. Before measurement the specimens were dispersed in ethanol by agitation for 10 min and then applied to collodion film and dried for 5–12 h.

#### Results and Discussion

XRD and IR measurements

Structural and chemical changes of the silicates in the course of MA in CO$_2$ atmosphere can be briefly reviewed for ghelenite as the example. XRD patterns and IR spectra of initial and MA-samples of ghelenite are shown in Figs. 1 and 2, respectively. As can be clearly seen, during the process of MA, substantial changes in the samples occur. Smoothening of IR bands visible in the 1100-400 cm$^{-1}$ region can be explained by the silicate structure disordering and amorphization, which is supported by XRD measurements.

MA of ghelenite in CO$_2$ atmosphere, in agreement with earlier work [1-3], leads to the appearance of the double band near 1500 cm$^{-1}$ corresponding to $v_3$ antisymmetric stretching vibrations of CO$_3^2-$ group (Fig. 2). The intensity of this band increases in the course of MA due to progressive sorption of carbon dioxide. Carbon dioxide content in MA-ghelenite after 30 min of mechanical treatment in planetary mill in CO$_2$ atmosphere reaches about 12 wt. % CO$_2$ that is equivalent to 27 wt. % CaCO$_3$ content in the mineral. Extensive CO$_2$ mechanosorption occurs alongside with silicate structure disordering and is not accompanied by formation of calcite or other carbonate minerals according to XRD data (Fig. 1).

**Table 1. Chemical composition of labradorite, diopside, okermanite, ghelenite, and wollastonite samples (wt. %)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>CaO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>FeO</th>
<th>Fe$_2$O$_3$</th>
<th>MgO</th>
<th>TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Labradorite</td>
<td>53.7±0.5</td>
<td>26.3±0.2</td>
<td>10.8±0.10</td>
<td>4.65±0.05</td>
<td>0.45±0.03</td>
<td>1.62±0.05</td>
<td>0.61±0.05</td>
<td>1.03±0.05</td>
<td>0.28±0.02</td>
</tr>
<tr>
<td>Diopside</td>
<td>49.7±0.5</td>
<td>1.34±0.05</td>
<td>24.50±0.15</td>
<td>0.43±0.05</td>
<td>0.19±0.02</td>
<td>2.88±0.05</td>
<td>-</td>
<td>16.10±0.10</td>
<td>0.48±0.05</td>
</tr>
<tr>
<td>Okermanite</td>
<td>42.4±0.5</td>
<td>3.60±0.05</td>
<td>34.5±0.2</td>
<td>1.80±0.05</td>
<td>0.10±0.02</td>
<td>2.75±0.05</td>
<td>-</td>
<td>9.40±0.10</td>
<td>-</td>
</tr>
<tr>
<td>Ghelenite</td>
<td>21.92</td>
<td>37.18</td>
<td>40.90</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Wollastonite</td>
<td>51.72</td>
<td>-</td>
<td>48.28</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 1. XRD patterns of ghelenite: 1 – initial sample; 2 and 3 – after 2 and 30 min of MA in CO$_2$ atmosphere, respectively.

Figure 2. IR spectra of ghelenite. Designations are the same as in Fig. 1.

**SEM and TEM Measurements**

To verify the hypothesis of mechanically induced “dissolution” of carbon dioxide in the structurally disordered silicate with formation of homogeneous amorphous carbonate–silicate phase micro- and nanostructure of material resulting from mechanochemical interaction of diopside with CO$_2$ was investigated using SEM (Fig. 3) and TEM (Figs. 4-7).
The diopside sample was ground in a 75T-DRM vibratory mill for 65 h at \( P(\text{CO}_2)=10^5 \text{Pa} \). As a result, according to XRD data (not shown) the mineral was fully amorphized and the \( \text{CO}_2 \) content of the MA-diopside was \( 21.3 \pm 0.8 \text{ wt \%} \). SEM image of MA-diopside (Fig. 3) demonstrates that aggregation of particles took place after such prolonged grinding. The shape of particles and their aggregates were rather smooth. Dispersing the powder in ethanol insured partial disaggregation, as evidenced by TEM images, which showed ultrafine particles one to two orders of magnitude smaller (Fig. 4) than those observed by SEM (Fig. 3). More detailed information about the particle microstructure is provided by high-resolution TEM (HRTEM) image (Fig. 7). Note that no marked inhomogeneities were detected in the bulk of MA-diopside particles. The particles had smooth surfaces, with no sharp edges. The boundary between two overlapping particles was rather easy to discern (Fig. 5). Some of the MA-diopside particles contained inclusions about 10 nm in size - no more than one inclusion in a relatively large particle on the order of 0.5–1 \( \mu \text{m} \) in size. One inclusion is seen in Fig. 6. Presumably, the inclusions are either diopside nanocrystals or iron particles originating from the mill material. On the whole, the diopside activated in \( \text{CO}_2 \) has a homogeneous microstructure as evidenced by HRTEM images (Fig. 7) and selected area diffraction (SAD) patterns, characteristic of amorphous glass-like structure (Fig. 8).

The formation mechanism of this carbonate-silicate glass-like material appears to be related to arising and moving of structural defects and plastic behavior during MA [8-12]. Substantial enhance of transport processes due to plastic deformation in all probability plays here a special part - so called deformational mixing on molecular scale [11]. Besides, intercrystalline boundaries are channels of enhanced diffusion of adsorbed \( \text{CO}_2 \) molecules into the bulk of particles. Density of the intercrystalline boundaries network increases as the size of microcrystallites decreases in the course of MA. Decreasing of microcrystallites size to \( 10^{-6}-10^{-8} \text{ m} \) increases the diffusion rate by several orders of magnitude [11].

**Kinetics of CO\(_2\) Mechanoabsorption by Silicates**

Figure 9 shows carbonization degrees (mass \% \( \text{CO}_2 \)) of the studied silicates depending on MA time in \( \text{CO}_2 \) atmosphere. It follows from Fig. 9 that \( \text{CO}_2 \) content in wollastonite, ghelenite and okermanite samples is similar at the same MA time. Diopside and particularly labradorite exhibit lower mechanically induced carbon dioxide sorption ability. These data are in agreement with previously revealed tendency: the larger the calcium content in the mineral (see Table 1) the higher is its carbonization degree during grinding [1]. According to XRD data in the course of MA, crystal structure disordering of the samples increased. After 30 min of MA ghelenite sample (Fig. 1) and all other studied mineral samples (not shown) were almost completely amorphous.

It follows from the slope of the curves (Fig. 9) that the intensity of carbonization process for all studied minerals gradually slows down with increase of MA time. It should be noted that the rigorous consideration of mehanoabsorption kinetics is a complicated problem due to variety of physical-chemical processes involved in mechanical action upon solid – gas system and their non-equilibrium nature [8-12]. Mechanism and kinetics of mechanically induced absorption of inert gases by metals and chemisorption of hydrogen onto quartz particles surface were...
studied in [9] and [13], respectively. In the former case inert gases physically “dissolved” in the surface layer of metal under mechanical impact. In the latter one hydrogen molecules chemically reacted with free radical centers on the surface of quartz. As was mentioned above in the course of MA of silicates in CO2 atmosphere carbon dioxide molecules both penetrated the structurally disordered mineral particles and chemically reacted with oxygen anions forming CO32− groups [1-3]. Under these circumstances it is reasonable to determine the basic factors that influence mechanosorption and to apply a simplified model.

Two modes of gas sorption were revealed during study of quartz vibro-milling in H2 atmosphere [13]. During initial stage of grinding mechanical energy was mainly spent for fresh surface formation. During this so called cleavage mode hydrogen molecules were chemisorbed on active centers of the newly formed surface. The rate of gas sorption in the cleavage mode was in direct proportion to the rate of active centers growth and consequently to the rate of surface area increase. As the total surface area S raised during grinding, portion of active centers arising due to friction of particles surface increased (so called friction mode). In the friction mode the rate of gas sorption depended on the surface area value instead of on the surface area time derivative as in the cleavage mode. The total rate of gas sorption W can be expressed as [13]:

\[
W = W_{cl} + W_{fr} = a(dS / d\tau) + f_{fr}(S) \tag{1}
\]

where \(W_{cl}\) and \(W_{fr}\) are the rates of gas sorption induced by cleavage and friction, respectively; \(a\) – coefficient that is proportional to the active centers concentration on the fresh surface. Contribution of friction to the total rate \(W_{fr} = f_{fr}(S)\) depends not only on the surface area but also on type of grinding, nature of gas and solid, and other factors. The analytical form of \(f_{fr}(S)\) is unknown. Using this general scheme we can consider carbon dioxide mechanosorption by the silicate minerals. A typical change of mineral specific surface area during MA as a function of MA time and mechanical energy dose is shown in Fig. 10 by the example of ghelenite.

The curve in Fig. 10 can be divided into two parts. During the first 1-2 min of MA the specific surface area \(S_{sp}\) rapidly increased. Then \(S_{sp}\) gradually decreased due to aggregation processes and turned to quasi-steady state. It is reasonable to assume that during the first 2 minutes of MA mechanosorption occurred mainly in the cleavage mode and partially in the friction one. After maximum (more than 2 min of MA) CO2 sorption was virtually totally controlled by friction. During the first 1-2 min of MA in CO2 atmosphere silicate particles with carbonized thin surface layer were formed. At this stage (the cleavage mode) the intensity of CO2 sorption was the highest one (Fig. 9). Then dispersion, i.e. reducing of particles size and growth of surface area, stopped due to the size factor and aggregation processes [8,9] (Fig. 10). Sorption of carbon dioxide by the silicates became slower at this stage because CO2 molecules diffused inside the structurally disordered particles through the outer carbonized layer. It should be noted, that despite the notable decrease of surface area after 2 min of MA (Fig. 10) the rate of CO2 sorption slowed down to only a small extent (Fig. 9). This is evidence that after 2 min of MA sorption mainly occurred in the friction mode. In IR spectra of MA-silicates in 2370-2350 cm−1 region (not shown) there were no bands corresponding to physically adsorbed CO2 or to carbon dioxide dissolved in molecular form [1-3]. Thus under intensive mechanical treatment resulting in accumulation of defects, deformation and break of bonds not only on the surface but also in the bulk of silicate particles, the rate of chemical interaction CO2 + O2− = CO32− was high and the mechanosorption process as a whole was diffusion controlled.

Consider CO2 mechanosorption by a silicate at MA time more than 2 min that is in the friction mode. Equation (1) can be rewritten in the form

\[
W = W_{fr} = f_{fr}(S) \tag{2}
\]

Mechanosorption rate is determined as \(W = dM/d\tau\), where \(M\) – total mass of CO2 absorbed by a silicate, \(S\) – total surface area of a solid. Applying Fick’s laws of diffusion in semi-infinite solid approximation [14] one can derive

\[
W = f_{fr}^{(x)} = dM / d\tau = K_{ms}(S^2 / M) \tag{3}
\]

where \(K_{ms}\) – mechanosorption coefficient (g2m-4min-1). Actually \(K_{ms}\) is a semi-empirical parameter that characterizes mechanosorption ability of silicate with respect to carbon dioxide. Equation (3) can be transformed taking into account changing of \(S\) in the course of MA. \(M\) and \(S\) can be written in the form

\[
M = 0.01C \cdot q / (1 - 0.01C) \tag{4}
\]

\[
S = S_{sp} \cdot q / (1 - 0.01C) \tag{5}
\]

where \(q\) – initial mass of mineral (g), \(C\) – carbonization degree expressed as mass % CO2 in MA-mineral, \(S_{sp}\) - specific surface area of MA-mineral (m2g−1). One should bear in mind that both
C and S_{sp} depend on MA time. After substitution of (4) and (5) in (3) and some rearrangement one can derive

\[-d \ln(1 - 0.01C) = 10^2 K_{ms} \frac{S_{sp}^2}{C} d\tau\]  
(6)

Integration of Eq. (6) from \(\tau = 2\) min to \(\tau = t\) min (the friction mode) leads to

\[F(t) - F(2) = 10^2 K_{ms} \int_{\tau=2}^{\tau=t} \left( \frac{S_{sp}^2}{C} \right) d\tau = 10^2 K_{ms} \Theta(t)\]  
(7)

where

\[F(t) = \ln(1 - 0.01C(t))\]  
(8)

\[\Theta(t) = \int_{\tau=2}^{\tau=t} \left( \frac{S_{sp}^2}{C} \right) d\tau\]  
(9)

For calculation of \(\Theta(t)\) experimental values of \(S_{sp}^2/C\) were fitted by least-squares method using the following expression

\[S_{sp}^2/C = b_0 + b_1 \exp(-b_2 \tau) + b_3 \exp(-b_4 \tau)\]  
(10)

A typical agreement between the experimental values of \(S_{sp}^2/C\) and the calculated ones using Eq. (10) is shown for ghelenite as the example in Fig. 11.

Using Eq. (10) \(\Theta(t)\) can be calculated in the form

\[\Theta(t) = b_0 (t - 2) - \frac{b_1}{b_2} [\exp(-b_2 t) - \exp(-2b_2)]\]

\[- \frac{b_3}{b_4} [\exp(-b_4 t) - \exp(-2b_4)]\]  
(11)

For ghelenite \([F(t)-F(2)]\) values obtained by substitution of experimental \(C(t)\) values to Eq. (8) plotted against \(\Theta(t)\) calculated using Eq. (11) are shown in Fig. 12.

Squares in Fig. 12 from left to right correspond to 2 (point of origin), 6, 10, 20, and 30 min of MA, respectively. Provided that \(K_{ms}\) in Eq. (7) is constant, points in Fig. 12 would display linear dependence with slope being equal to \(10^2 K_{ms}\). However from Fig. 12 it follows that mechanosorption coefficient grew with increase of MA time. It can be explained by the following reason. In the course of MA due to accumulation of defects the silicate mineral structure disordering substantially increased (Fig. 1) thereby facilitating diffusion process.

In order to take into account the growth of mechanosorption coefficient with increase of MA time \(K_{ms}\) can be inserted into Eq. (7) in the form

\[K_{ms}(\tau) = k_0 + k \tau\]  
(12)

where \(k_0\) and \(k\) are empirical parameters, \(\tau\) is MA time, min. Substitution of Eq. (12) in (6) and integration yield

\[F(t) - F(2) = 10^2 (k_0 \Theta(t) + k \Psi(t))\]  
(13)

Where

\[\Psi(t) = \int_{\tau=2}^{\tau=t} \left( \frac{S_{sp}^2}{C} \right) d\tau\]  
(14)

\(\Psi(t)\) can be easily calculated after substitution of Eq. (10) in (14). For evaluating of \(k_0\) and \(k\) it is convenient to introduce \(\Phi(t)\) and \(\Omega(t)\):

\[\Phi(t) = 10^{-2} \frac{F(t) - F(2)}{\Theta(t)}\]  
(15)

\[\Omega(t) = \frac{\Psi(t)}{\Theta(t)}\]  
(16)
$\Phi(t)$ values against $\Omega(t)$ are plotted in Fig. 13. Straight line in Fig. 13 corresponds to linear least-square fit of the points. The slope and intercept of the line are equal to $k_0$ and $k$ in Eq. (13), respectively.

![Figure 13](image)

Figure 13. $\Phi(t)$ values depending on $\Omega(t)$ for MA of gheleinite. From left to right squares corresponded to 6, 10, 20, and 30 min of MA, respectively (see text for details)

For ghelelinite mechansorption coefficient was expressed in the form

$$K_{ma}(\tau) = -(4.3 \pm 0.4) \times 10^{-6} + (2.9 \pm 0.3) \times 10^{-6} \tau \quad (13)$$

(g$^{-1}$m$^{-3}$min$^{-1}$)

Table 2. Calculated $b_i$ coefficients ($i=0,1...4$) in eqs. (10),(11) and $k_0$ and $k$ coefficients in Eq. (12)

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>labradorite</th>
<th>diopside</th>
<th>okermanite</th>
<th>gheleline</th>
<th>wollastonite</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b_0$</td>
<td>11.687</td>
<td>0.9390</td>
<td>-24.281</td>
<td>0.42229</td>
<td>3.3631</td>
</tr>
<tr>
<td>$b_1$</td>
<td>174.703</td>
<td>27.8744</td>
<td>20.4583</td>
<td>11.890</td>
<td>23.2045</td>
</tr>
<tr>
<td>$b_2$</td>
<td>0.12575</td>
<td>0.71481</td>
<td>0.26967</td>
<td>0.23697</td>
<td>0.25916</td>
</tr>
<tr>
<td>$b_3$</td>
<td>-34.199</td>
<td>13.0665</td>
<td>25.2847</td>
<td>7.0824</td>
<td>-4.3228</td>
</tr>
<tr>
<td>$b_4$/$10^7$</td>
<td>3.6342</td>
<td>11.602</td>
<td>0.0323</td>
<td>23.709</td>
<td>1.46</td>
</tr>
<tr>
<td>$k_0$/$10^6$</td>
<td>-0.091</td>
<td>2.5</td>
<td>-0.42</td>
<td>-4.3</td>
<td>-9.1</td>
</tr>
<tr>
<td>$k$/$g^2$</td>
<td>0.009</td>
<td>0.03</td>
<td>0.04</td>
<td>0.04</td>
<td>0.9</td>
</tr>
</tbody>
</table>

Note that extrapolation of Eq. (17) beyond the range of points plotted in Fig. 13, corresponding to time interval from 6 to 30 min of MA may lead to unreasonable results. Calculation of carbonization degrees $C$ in the sampling points (6, 10, 20, and 30 min of MA) from obtained $k_0$ and $k$ values (Table 2) using Eqs. (11)-(14) showed that standard deviation between the experimental (Fig. 9) and the calculated values for all studied minerals was 0.28 mass % CO$_2$. So in spite of the simplified approach, the suggested semi-empirical equations reasonably good described CO$_2$ mechanosorption kinetics. One should bear in mind that generally $K_{ma}$ depends on type of mill, mill load, and MA time. The comparison of $K_{ma}$ values determined for different minerals is valid if only MA is carried out at the same conditions.

Correlations with Dissolution of CO$_2$ in Melts

As was mentioned above mechanically induced absorption of carbon dioxide by silicate minerals in a certain way resembles dissolution of CO$_2$ in silicate melts of similar composition at magma state conditions. It is interesting to compare the carbonization degrees of minerals after MA and solubility of CO$_2$ in silicate melts having the same composition. In geochemical literature interaction of CO$_2$ and other gases (or fluids) with silicate melts is a subject of narrow investigation because even small amount of the dissolved volatile may notably affect physical and chemical properties of magma and as a result its evolution path (see, for example [15,16]). At the same time experimental solubility data for various melt compositions have been determined at different pressures and temperatures and their direct comparison is rather difficult.

In this paper, semi-empirical thermodynamic model advanced by Papale [17] has been used to calculate CO$_2$ solubility at fixed T and P in melts having the same compositions as the studied minerals. The model [17] was formulated assuming mechanical, thermal and chemical equilibrium between liquid magma and gas (fluid) phase. CO$_2$ fugacity in the fluid phase was calculated using Kerrick and Jacobs modified Redlich-Kwong equation of state for gaseous carbon dioxide [18]. Activity coefficients of CO$_2$ dissolved in liquid phase were determined in [17] on basis of strictly regular solution theory for volatile-free magma [19] and assuming P-dependent binary interaction coefficients for carbon dioxide (non-isometric mixing). It should be noted that CO$_2$ is present in MA-silicates only as carbonate group [1-4], while dissolution of carbon dioxide in magmatic melts occurs in two forms: CO$_2$-ion (the major form for the silicate compositions studied here) and molecular CO$_2$ [15]. Model [17] enables to calculate the total CO$_2$ solubility in melts.

For calculation of carbon dioxide solubility in silicate melts $T=1900$K and $P=1.5$ GPa were chosen because at this temperature and pressure all silicates considered here are liquid. In addition, CO$_2$ solubility in the melt at chosen T and P is comparable with mechanically induced carbonization degree of the silicate having the same composition. Calculated CO$_2$ solubility in melts and corresponding CO$_2$ content in the silicates of the same composition after 30 min MA in carbon dioxide atmosphere are shown in Fig. 14. It is seen that there is surprising very good correlation for labradorite, diopside and okermanite (dashed line in Fig. 6) but wollastonite and gheleline fall out this trend. Certainly the number of points is too small for reliable correlation analysis. However one should take into account that errors of calculated CO$_2$ solubility in case of wollastonite and gheleline melts are larger because their composition to a certain extent fall out of the model calibration range due to high calcium content [17] (see Table 1).
In addition to equilibrium solubility data it is interesting to compare CO₂ diffusion in silicate melts with carbon dioxide mechanosorption kinetics. Published experimental data indicate that at constant temperature in the range of carbon dioxide content less than 1 wt. % CO₂ diffusion coefficient D keeps nearly constant with wide changing of melt composition [20-22]. Unfortunately no diffusion data are available for higher CO₂ concentration in melts. However concentration dependence of D can be evaluated using standard relation [14]

\[ D = D_0 \frac{\partial \ln a}{\partial \ln x} = D_0 \frac{\partial \ln (\gamma x)}{\partial \ln x} \]  

(18)

Here a, γ, and x – activity, activity coefficient, and molar fraction of CO₂ in melt, respectively; D₀ – diffusion coefficient assuming γ=1. Derivation in Equation (18) can be easily implemented within thermodynamic model used above for solubility calculation [17]. It is reasonable to assume that D₀ corresponds to the carbon dioxide diffusion coefficient experimentally determined for melts having small CO₂ concentrations. Note that D₀ is not sensitive to melt composition, so it can be used for all silicates at given T,P-conditions. One should mention as well that CO₂ diffusion coefficient is strongly temperature dependent following Arrhenius equation and to much lesser extent is pressure dependent [22]. From carbon dioxide diffusion data presented in [22] it is possible to accept D₀ ≈ 1·10⁻⁹ m²·s⁻¹ at T = 1900 K and P = 1.5 GPa. Figure 15 shows calculated D values (T = 1900 K, P = 1.5 GPa) plotted against K_m. For each mineral mechanosorption coefficients were evaluated according to Equation (12) using k and k₀ derived from carbonization degree data as described above. For comparison purposes D and K_m values were determined at the same carbon dioxide content in melt and in the corresponding MA-silicate (see text for details).

Co₂ Mechanoabsorption by Ferrous-magnesium Slag: Application for Alkali-Activated Slag Binding Materials

In this section the research object was granulated ferrous-magnesium slag from Pechenganickel smelter plant, Murmansk Region, Russia. Chemical composition of the slag (wt. %): SiO₂ - 40.88, Al₂O₃ - 6.90, FeO - 35.40, MgO - 10.71, CaO - 2.65, (Na₂O+K₂O) – 2.1, S - 0.71. Mineral composition of the slag (mass. %): ferrous-magnesium silicate glass – 95-98, olivine – 2-5, Cu-Ni sulfides – 1-3. It is known that ferrous-magnesium slag reacts with sodium hydr oxide solution or liquid glass producing hardened material. The properties of the alkali-activated slag (AAS) binding material depend on interaction between the ground slag surface and alkali containing component. The reactivity of powder surface may change during grinding, particularly due to mechanically induced sorption of gases. Ferrous-magnesium slag is a silicate material containing magnesium, calcium and alkali metal oxides. So, one may expect carbon dioxide sorption by the slag during mechanical treatment in mill in CO₂ atmosphere. We have performed MA of the slag in air and in CO₂ atmosphere in order to investigate the role of carbon dioxide mechanosorption on its binding properties.

Grinding of the slag was performed in an AGO-2 planetary ball mill at 40 g centrifugal factor. The slag mass was 20 g. The steel ball (8 mm in diameter) load to slag weight ratio was 10. The maximum grinding time was 330 sec. From carbon dioxide diffusion data presented in [22] it is possible to accept D₀ ≈ 1·10⁻⁹ m²·s⁻¹ at T = 1900 K and P = 1.5 GPa. Figure 15 shows calculated D values (T = 1900 K, P = 1.5 GPa) plotted against K_m. For each mineral mechanosorption coefficients were evaluated according to Equation (12) using k and k₀ derived from carbonization degree data as described above. For comparison purposes D and K_m values were determined at the same carbon dioxide content in melt and in MA-silicate being equal to half of the silicate carbonization degree in the end of MA experiment. This CO₂ content approximately corresponds to 10 min of MA for each mineral (Fig. 9). As in case of solubility and carbonization degree (Fig. 14) here labradorite, diopside and okeramite points fit linear interpolation very well. Lower precision wollastonite and gheleite data points fall out (Fig. 15). Solid line in Fig. 15 corresponds to linear fit of all plotted data.
Figure 16. Compressive strength of AAS samples. \( S_{sp} \) of ground slag: 1 – 410, 2 - 450, 3 – 750, 4 – 730 m\(^2\)kg\(^{-1}\), respectively. Grinding atmosphere: open symbols and dashed lines – air; solid symbols and solid lines – CO\(_2\).

Figure 17. Compressive strength of AAS samples aged for 28 days as a function of ground slag \( S_{sp} \) and grinding atmosphere.

Conclusions

It has been shown that in accordance with the results obtained earlier, mechanical activation of labradorite, diopside, okeranmite, ghelenite, and wollastonite in CO\(_2\) atmosphere in a laboratory ball planetary mill results in extensive sorption of carbon dioxide molecules by the minerals and their “dissolution” in the structurally disordered silicate matrix in the form of distorted carbonate groups.

The suggested equations can be used for simplified kinetic analysis of mechanically induced CO\(_2\) sorption by silicates. Mechanosorption coefficient \( K_{ms} \) can serve as semi-empirical parameter to characterize ability of silicate to absorb carbon dioxide in the course of MA. In this study, high energy input AGO-2 planetary mill has been used for MA resulting in bulk sorption of CO\(_2\) by the silicates. In order to determine the optimal energy input and type of mechanical treatment for effective carbon dioxide sorption further investigation is needed.

Water present in the mill certainly plays an important role in the CO\(_2\) mechanosorption by silicates. For elucidating the role of water, MA experiments with various amounts of H\(_2\)O added to mineral should be carried out.

The observed correlations support the hypothesis of similarity between carbon dioxide mechanosorption and CO\(_2\) dissolution in melts. It should be emphasized that at first glance the two very dissimilar processes are compared here. Carbon dioxide dissolution in melt occurs at high temperatures and pressures. In addition, CO\(_2\) solubility characterizes true thermodynamic equilibrium between the gas (fluid) and liquid. Silicates consume CO\(_2\) during mechanical treatment as a result of essentially non-equilibrium process occurring at ambient conditions. Nevertheless the observed correlations apparently reflect the resemblance in nature of these processes.

It has been revealed that preliminary grinding of ferrous-magnesium slag in CO\(_2\) promotes hydration processes and leads to higher compressive strength of alkali-activated slag binding materials in comparison to grinding in air. The reason for this is probably an increase in slag reactivity due to mechanosorption of carbon dioxide by the outer layer of the slag particles.

Acknowledgements

The financial support of Russian Foundation for Basic Research (grant № 06-03-32198) is gratefully acknowledged. Author is grateful to Dr. E.V. Kalinkina, Dr. B.I. Gurevich, Dr. V.V. Tyukavkina and Mr. O.A. Zalkind for their help in carrying out the experiments and fruitful discussions.

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