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Activation of Bentonite and Talc by Acetic Acid as a Carbonation Feedstock for Mineral Storage of CO₂

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1. Introduction

The average global temperature has been slightly increasing by 0.76 °C over last 150 years. If the current state will continue, average Earth temperature will increase at the end of this century for about 1.1 – 6.3 °C according to applied emission scenario. Main reason of the observed global warming is the increasing contents of greenhouse gases (GHG), such as carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (NO₂), in the Earth atmosphere. The most important greenhouse gas is CO₂. Carbon dioxide is considered as responsible for about two-third of the enhanced “greenhouse effect”. Its atmospheric concentration has risen from the pre-industrial levels of 280 ppm to 380 ppm in 2005. Human emissions of greenhouse gases are very likely responsible for global warming of the planet surface (IPCC, 2007). The increasing carbon dioxide content in the atmosphere and its long-term effect on the climate has led to increasing interest and research of the possibilities of capture, utilization and long-term storage of carbon dioxide (Yang et al., 2008; Jiang, 2011).

Fossil fuels have been used as the world’s primary source of energy upon over the 20th century and this trend is expected to continue throughout the 21st century (Yang et al., 2008; Maroto-Valer et al., 2005). There is a direct link between emissions of carbon dioxide (C_e), human population (P), economic development that is indicated by gross domestic product (GPD), production of energy (E), amount of carbon-based fuels used for production of energy (C) and CO₂ sinks (S_{CO_2}):

$$C_e = P \frac{GDP}{P} \frac{E}{GDP} \frac{C}{E} - S_{CO_2} \quad (1.1)$$

The emissions of anthropogenic carbon dioxide are increasing with population (P), standard of living (GPD/P); the energy intensity of economy (E/GPD) and the carbon intensity of the energy system (C/E). On the contrary C_e is decreasing with S_{CO_2} . Examination of the Eq.1.1, in principle, proposes that there are five ways to reduce atmospheric emissions of anthropogenic CO₂, of which the first two, i.e. reduction in population and/or decline in economic output are naturally unacceptable. Reducing the carbon intensity of the energy system can be achieved by using hydrogen-rich fuels and renewable energy sources. The

last term indicates that emissions of carbon dioxide can be partially or totally covered by the artificial increase in the capacity and uptake rate of CO₂ sinks (S_{CO2}). Carbon sequestration includes terrestrial or marine photosynthetic fixation of CO₂ by plants and soils, and subsequent long-term storage of CO₂ as carbon-rich biomass or capture and long-term storage of CO₂ emissions at source prior to potential release. These techniques are collectively known as carbon capture and storage (CCS) (Bachu, 2008; Zhang at al., 2007; Piromon at al., 2007; Huesemann, 2006; Hoffert at al., 1998; Kaya, 1995).

The Carbon Capture and Storage technologies have been considered as suitable method for reduction of CO₂ emission, they are relatively abundant, cheap, available and globally distributed, thus enhancing the security and stability of energy systems (Bachu, 2008). CCS can be effectively integrated into various energy systems (Jiang, 2011). The CO₂ capture can be performed following three different technological concepts: post-combustion capture systems, pre-combustion capture systems and oxy-fuel capture systems (Damen at al., 2006; Pires at al., 2011).

The main options for CO₂ storage are:

1. Geological storage – CCGS (Carbon Capture and Geological Storage);
2. Ocean storage – CCOS (Carbon Capture and Ocean Storage);
3. Mineral storage – CCMS (Carbon Capture and Mineral Storage).

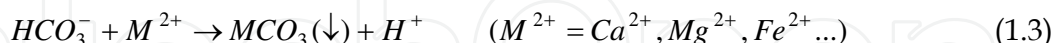
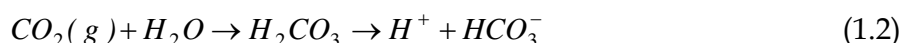
On the other hand there are fears that CCS technologies that offer the extension of the fossil-fuel era by perhaps a few 100 years are a double-edged sword. CCS technology is designed to limit emissions of CO₂ to the atmosphere, but it extends the period during which CO₂ is emitted (Spreng at al., 2007).

Carbon Capture and Geological Storage methods are using the geological media for storage of carbon dioxide at depths of more than one kilometer. Geological media suitable for CO₂ storage requires sufficient capacity, possibilities for CO₂ transport and preventing the CO₂ migration or escaping. Sedimentary basins may possess these requirements, because generally only sandstone and carbonate rock have needed to provide the porosity and then storage capacity and permeability. Confining low-permeability shales and evaporites such as salt beds and anhydrites provide primary physical barrier for CO₂ leakage (Gibbins & Chalmers, 2008; Bachu, 2008; Zhang at al., 2007; Pauwels at al., 2007; Friedmann at al., 2006; Gale, 2004; Soong at al., 2004; Bouchard & Delaytermoz, 2004; Torp & Gale, 2004; Xu at al., 2004).

Carbon dioxide may be stored in geological media by various means with various physical (Physical trapping) and chemical mechanisms (Chemical trapping) as a result of its properties at the pressure and temperature conditions found in Earth's subsurface. Physical trapping of CO₂ occurs when CO₂ is immobilized as a free gas or supercritical fluid. There are two types of physical trapping. Static trapping of mobile CO₂ in stratigraphic and structural traps or in man-made caverns is applied. The second possibility is represented by residual-gas trapping in the pore space at irreducible gas saturation. Chemical trapping occurs when CO₂ is absorbed into organic materials contained in coals and shales (adsorption trapping). Carbon dioxide may react directly or indirectly with mineral resulting to the geologic formation characterized by the precipitation of secondary carbonate minerals - mineral trapping. In direct carbonation process, gaseous CO₂ is in first stage dissolved during indirect (aqueous) process and reacts with solid mineral in following operation (Bachu, 2008; Alexander at al., 2007; Xu at al., 2004).

The dissolution of alkaline aluminosilicate minerals by CO₂ contributes to increasing of concentration of soluble carbonates and bicarbonates in solution, thereby enhancing

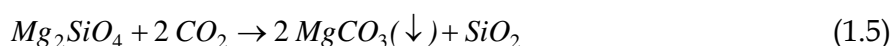
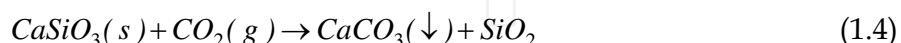
“solubility trapping”. The chemical reactions induced by CO₂ injection are described by Eq.1.1 and 1.2 (Xu et al., 2004). The weathering of alkaline rocks, such as alkaline or alkaline earth silicates is thought to have played a great role in the historical reduction of the atmospheric CO₂ content in atmosphere of Earth (Kojima et al., 1997).



Total estimated storage capacity of geological reservoirs is about 920 Gt CO₂ in depleted oil and gas fields, 400 – 10 000 Gt in deep saline reservoirs and 20 Gt in coal mine coal deposits. The cost for carbon dioxide capture and following storage in geologic formations is estimated about 4 – 48 EUR/t CO₂ (Friedmann et al., 2006; Gale, 2004). The research works concerning in risk assessment of CO₂ geological storage is mentioned in work (Gale, 2004).

Deep-sea storage of anthropogenic CO₂ is an attractive concept that offers large storage capacity comparing to other options. However, storing CO₂ in oceans is limited by its high cost, technology development, potentially high environmental impact, because the storage capacity of the ocean has not been defined. The oceanic processes are controlled long-term processes and large scale storage has been discussed only in general terms. Addition of anthropogenic CO₂ would change the CO₂ chemistry in the ocean by reducing pH at the site. The effects of long-term influence of low pH on planktonic ecosystem and oceanic biological processes are virtually unknown. Addition and CO₂ storage would probably dissolve carbonate deposits on the seafloor and suppress oxidation of organic matter (Wong & Mearns, 1998; Bachu & Adams, 2003).

Mineral storage based on carbonation is a promising CCS method for long-term storage of CO₂ in continental inland utilization. The carbon dioxide is stored through mineral trapping mechanism that requires the participation of cations, including Ca²⁺, Fe²⁺, and Mg²⁺, that can form stable solid carbonate phases (Giammar et al., 2005). This processing accelerates the natural weathering of silicate minerals, where these minerals react with CO₂ and form carbonate minerals and silica. Although the calcium silicate has been successfully carbonated at temperatures and pressures relevant for industrial processes, its natural resources are too small and expensive to be of practical interest. Therefore, current research activities focus mostly on carbonation of magnesium silicates (Teir et al., 2007). Overall course of carbonation process of wollastonite (CaSiO₃), olivine (Mg₂SiO₄) and serpentine (Mg₃Si₂O₅(OH)₄) may be described by Eq.1.4 – 1.6, respectively (Alexander, 2007; Wouter et al., 2007).



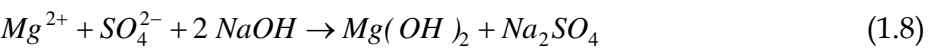
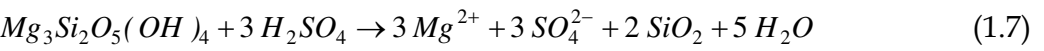
The magnesium bearing minerals typically contain about 40 % of magnesium, whereas the content of calcium is approximately 10 – 15 %. Reactivity of olivine is higher than serpentine, but serpentine reactivity is strongly increasing by physical and chemical activation. Physical activation such as heat pre-treatment (calcination) at approximately

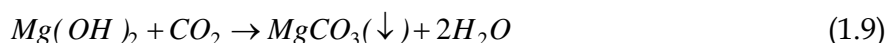
630 °C may remove water (dehydroxylation) from serpentine structure. The conversion to magnesite (MgCO₃) is higher (59.4 %) than the value (7.2 %) found for untreated samples (Alexander at al., 2007). Carbon dioxide sequestration capacity some of major rock forming minerals is listed in Table.1.1.

Mineral	Composition	Storage capacity [kgCO ₂ · m ⁻³]
Plagioclase (anorthite)	CaAl ₂ Si ₂ O ₈	436,4
Olivine (forsterite-fayalite)	Mg ₂ SiO ₄ – Fe ₂ SiO ₄	2014,7 – 1896,3
Pyroxene group - enstatite	(Mg,Fe ²⁺)Si ₂ O ₆	1404,2
Augite	(Ca,Na)(Mg,Fe ²⁺ ,Fe ³⁺ ,Al,Ti)(Si,Al) ₂ O ₆	1306,3
Amphibole group - anthophyllite - cummingtonite	(Mg,Fe ²⁺) ₇ Si ₈ O ₂₂ (OH) ₂	1169,5 – 1041,8
Common hornblende	Ca ₂ (Mg,Fe ²⁺ ,Al) ₅ (Si,Al) ₈ O ₂₂ (OH) ₂	1000,4
Calcium amphiboles - tremolite	Ca ₂ Mg ₅ Si ₈ O ₂₂ (OH) ₂	1119,3
Mica group - galuconite	K _x (Fe ³⁺ ,Al,Mg,Fe ²⁺) ₂ (Si,Al) ₄ O ₁₀ (OH) ₂ ; x < 1	61,97
Mica group-phlogopite	KMg ²⁺ ₃ (Si ₃ Al)O ₁₀ (OH,F) ₂	881,8
Mica group-biotite	K(Mg,Fe ²⁺) ₃ (Si ₃ Al)O ₁₀ (OH,F) ₂	671,0
Serpentine	Mg ₃ Si ₂ O ₅ (OH) ₄	1232,7
Chlorite group	(Mg,Al,Fe ²⁺) ₁₂ (Si,Al) ₈ O ₂₀ (OH) ₁₆	923,4
Clay minerals - illite	(K,H ₃ O ⁺)Al ₂ (Si,Al) ₄ O ₁₀ (OH) ₂	78,42
Clay minerals - smectite	(Ca _{0,5} ,Na) _{0,7} (Al,Mg,Fe) ₄ (Si,Al) ₈ O ₂₀ (OH) ₄ · nH ₂ O	161,2

Table 1.1. Carbon dioxide sequestration potential of some major rock according to work (Xu at al., 2004).

If the rate-limiting step in the aqueous carbonation scheme is leaching of calcium or magnesium, then the production of carbonates may by accelerate via acceleration of dissolution stage. Inorganic (HCl, H₂SO₄, H₃PO₄) as well as organic acids (CH₃COOH), complexing agents and hydroxides (NaOH) were used for chemical activation of minerals. Hydrochloric acid enhances the magnesium ions liberation, however energy intensity production of Mg(OH)₂ has been increasing. Complexing agents were used to polarize and weaken the magnesium bonds within the serpentine structure. The most effective is treatment by H₂SO₄ which increases the surface area from 8 to 330 m²·g⁻¹. Sulphuric acid pre-treatment enables aqueous carbonation of Mg(OH)₂ under milder condition. Temperature and pressure were reduced from 185 on 20 °C and 12.7 to 4.6 MPa. Process may by write as follows (Alexander at al., 2007; M.-Valer at al., 2005):





Industrial by-products, such as iron and steel slags and cement based material, may contain very high percentage of calcium and magnesium oxides and therefore they may be carbonated and exploited for CO₂ mineral storage. Calcium and magnesium can be leached out by acetic acid. Such a process consists of two main steps. The first one, where calcium ions are extracted from natural calcium silicate mineral:



And the second one, where carbon dioxide was introduced into the solution after removing of SiO₂ and calcite has been precipitated from the solution according to Eq.1.11. Acetic acid is recovered in this step and recycled for using of extraction in the first step (Eq.1.10).

Similar reaction proceeds with magnesium silicates:



However, there are also small contents of many other compounds from iron and steel slags (such as heavy metals) which would be released by acetic acid (Teir et al., 2007).

1.1 Kinetics of silicate minerals, rocks, glass and raw materials dissolution

The main reasons for investigation of dissolution and precipitation reactions of silicate minerals and raw materials is in importance to understand the extent and environmental significance of the chemical weathering in nature (Cama et al., 1999;), study of its potential to utilization as the source of the divalent cations that is necessary for the sequestering of carbon dioxide into carbonates (Saldi et al., 2007), in order to improve their catalytic activity (Komadel & Madejová, 2006; Pushpalettha et al., 2005), study the puzzolanic activity in mortars and cements (Massazza, 1993) drug delivery (Viseras et al., 2010), synthesis of geopolymers (Buchwald et al., 2009), zeolites (Baccouche et al., 1998) and organic-clay composites (Yehia et al., 2012).

The kinetics of mineral dissolution is an area in geochemistry that has received considerable attention over the past several years (Knauss et al., 2003). Hence, numerous works dedicated to investigation of clay mineral dissolution kinetics can be found in the current literature (Table 1.2).

A basic concept in chemical kinetics is that reactions consist of a series of different physical and chemical processes that can be broken down into different "steps". For dissolution, these steps generally include at a minimum (Morse & Arvidson, 2002; Dorozhkin, 2002):

1. Diffusion of reactants through solution to the solid surface;
2. Adsorption of the reactants on the solid surface;
3. Migration of the reactants on the surface to an "active" site (e.g., a dislocation);
4. The chemical reaction between the adsorbed reactant and solid which may involve several intermediate steps where bonds are broken and formed, and hydration of ions occurs;

- 5. Migration of products away from the reaction site;
- 6. Desorption of the products to the solution;
- 7. Diffusion of products away from the surface to the “bulk” solution.

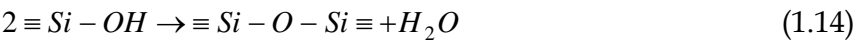
Mineral	Solution properties	E _A [kJ·mol ⁻¹]	Rate limiting step of process	Reference
Wollastonite	pH 3 – 8	79.2	Diffusion ^(a)	Rimstidt & Dove, 1986
	Diluted acetic acid, pH 2 – 3.5	47.1	Two-dimension diffusion	Ptáček at al., 2011
Enstatite	pH 1 – 11; 28 – 168 °C	48.5	Reaction ^(b)	Oelkers & Schott, 2001
Forsterite	pH 2; 25 – 65 °C	63.8	Reaction ^(b)	Oelkers, 2001
Olivine	pH 2 – 5; 65 °C	125.6	Reaction	Chen & Brantley, 2000
Serpentine	3 M H ₂ SO ₄ ; 60 – 90 °C	66.5	Reaction	Jonckbloedt, 1998
	2 M H ₂ SO ₄ ; 30 – 70 °C	68	Diffusion	Teir at al., 2007
	2 M HCl; 30 – 70 °C	70		
	2 M HNO ₃ ; 30 – 70 °C	74		
Talc	pH 1 – 10.6; 25 – 150 °C	45.0		Saldi at al., 1995
Anorthite	pH 2.4 – 3.2; 45 – 95 °C	18.4 ^(c)		Oelkers & Schott, 1995
Diopside	pH 2 – 12; 25 – 70 °C	40.6	Surface reaction	Knauss at al., 1993
Basaltic glass	pH 7.8 – 8.3; 90 °C	9.8	Diffusion	Daux at al., 1997

^(a) Under low pH values. ^(b) Forming of rate-controlling precursor complex. ^(c) Under pH = 2.6.

Table 1.2. Dissolution kinetics of silicates. Table is extracted from the work (Ptáček at al., 2011).

A central concept in dissolution kinetics supposes that one of these steps is the slowest than other. The reaction cannot proceed faster than the rate limiting step. Above mentioned steps 1 and 7 involve the diffusive transport of reactants and products through the solution to and from the surface. When this process is rate-limiting, the reaction is said to be diffusion controlled. Steps 2– 6 occur on the surface of the solid and when one of them is rate controlling the reaction is said to be surface controlled (Morse & Arvidson, 2002; Dorozhkin, 2002).

The dissolution of solids in liquids (or melts) consists of a surface chemical reaction and transport of the reaction components to the reaction boundary (Šesták, 1984). Many multicomponent silicate minerals under acidic condition are dissolved incongruently. The Ca²⁺ ions were replaced by H₃O⁺ ions and leached layer of silica was formed. This layer wasn't homogeneous and its structure was changing with time as a consequence of polymerization of silanol groups (Weissbart & Rimstidt, 2000):



Monosilic acid may be liberated from silicates which contain SiO₄⁴⁻ ions separated by metal cations – nesosilicates. Besides the temperature the solubility of an amorphous silica layer depends on pH and shows the minimum at pH 7. The accurate data are still missing because there is an extreme variation in the forms in which the amorphous silica can occur. The rate of dissolution is proportional to the concentration of H₃O⁺ and OH⁻ ions in the range from 0 to 2 and from 3 to 6, respectively. The rate of diffusion or desorption of the silicic acid from the surface limits the rate of dissolution if pH is higher than 6 (Iler, 1979). The dissolution mechanism of each multioxide silicate can be deduced from its structure. Note that in some cases, not all metal-oxygen bonds present in the structure need to be broken to completely destroy a mineral. Dissolution proceeds via the sequential equilibration of metal-proton exchange reactions until no further viable structure remains. The last of these sequential exchange reactions destroys the structure and it is irreversible in most cases. Assuming that at acidic conditions, the sequence of metal-proton exchange reactions during the dissolution of a multioxide silicate follow the order prescribed by the relative reactions rates of the single oxide dissolution as illustrated in Fig.1.1 (Oelkers, 2001).

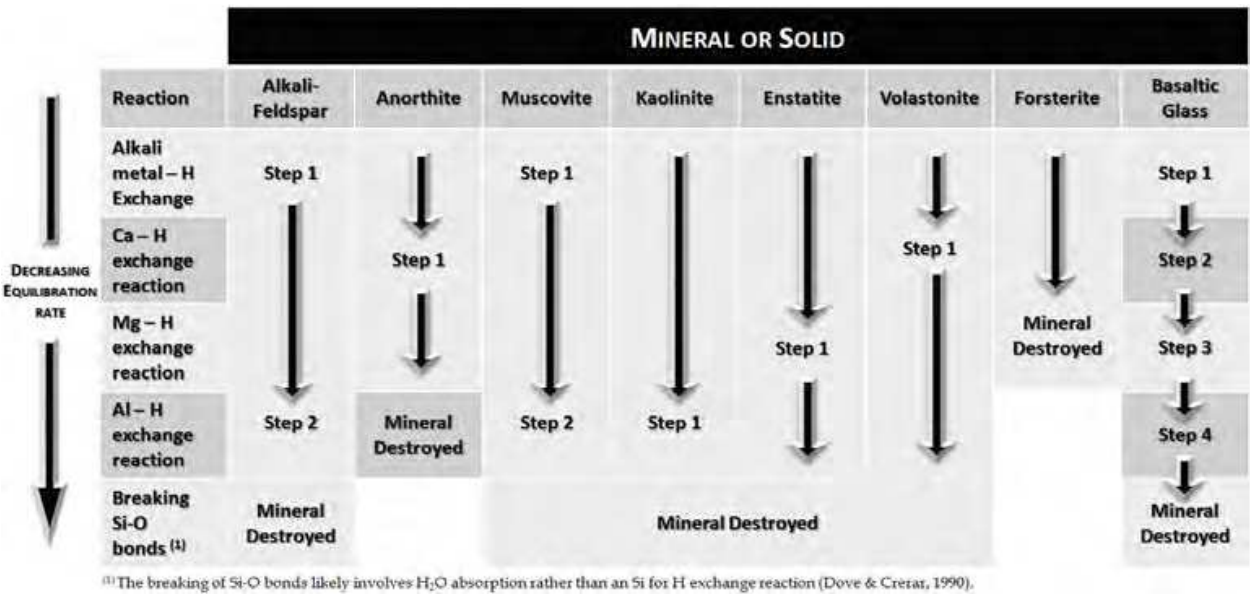
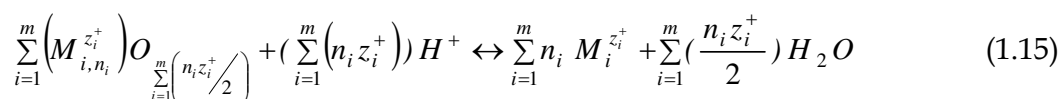
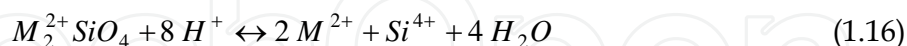


Fig. 1.1. Mechanism of dissolution of some minerals and basaltic glass at acidic condition according to Oelkers, 2001.

The dissolution rate of the clay minerals seems to be continuously decreasing with elapsed time due to the preferred dissolution of reactive edge surfaces. As edge surfaces are selectively dissolved, the percentage of these reactivity reactive sites decrease with time leading to a decrease in the average reactivity of the overall clay surface (Köhler at al., 2005). The derivation of rate law for congruent dissolution of silicate multioxides at close to equilibrium conditions will be derived using a general formula $M_{(1)}^{z_1}n_1 M_{(2)}^{z_2}n_2 M_{(3)}^{z_3}n_3 O_{\sum(n(i)z(i))/2}$, which is representative for oxide composition of nesosilicates related to phenakite ($M_{(1)}M_{(3)}O_4$, where $M_{(1)} = Li, Be, Zn...$ and $M_{(3)} = Si$), olivine ($M_{(1)}M_{(3)}O_4$, where $M_{(1)} = Ca, Mg, Fe^{2+}, Mn...$ and $T = Si$) and garnet ($M_{(1)}^{2+}M_{(2)}^{3+}M_{(3)}O_4$, where $M_{(1)} = Ca, Mg, Fe, Mn...$, $M_{(2)} = Al, Fe^{3+}, Cr^{3+}, V^{3+}, Ti^{4+} ...$, $M_{(3)} = Si, Fe^{3+}, Al...$) structural groups:



For example, the members of olivine subgroup such as calcio-olivine, forsterite, fayalite, tephroite... for that $M_{(1)} = \text{Ca, Mg, Fe}^{2+}, \text{Mn...}$, trivalent cations does not present and $M_{(3)} = \text{Si}$, are then dissolved according to following reaction scheme:



The kinetics of this reversible chemical reaction involving competition between two elementary - forward (+) and reverse (-) reactions, can be easily expressed by applying the Van't Hoff law such that:

$$r = r_+ - r_- = r_+ \left(1 - \frac{r_-}{r_+} \right) \quad (1.17)$$

The equilibrium constant K of forward and reverse Q reaction 1.15 can be then expressed as follows:

$$K = \frac{\prod_{i=1}^m a_{M_i^{z_i^+}}^{n_i}}{a_{H^+}^{\sum_{i=1}^m (n_i z_i^+)}} = \prod_{i=1}^m \left(\frac{a_{M_i^{z_i^+}}}{a_{H^+}^{z_i^+}} \right)^{n_i} \quad (1.18)$$

$$Q = 1/K \quad (1.19)$$

The saturation state of a fluid is often expressed in terms of the ratio (Q/K); if by common convention the dissolving mineral appears on the left side of the reaction, values of (Q/K) < 1 indicate undersaturation of the fluid with respect to the mineral, and conversely, (Q/K) > 1 is representative of supersaturation (Hellmann at al., 2009).

The dissolution rate can be described via combination of Eq.1.17 with law 1.18 and 1.19 by following kinetic equation:

$$r = r_+ - r_- = k_+ \prod_{i=1}^m a_{M_i^{z_i^+}}^{n_i} - k_- a_{H^+}^{\sum_{i=1}^m (n_i z_i^+)} = k_+ \prod_{i=1}^m a_{M_i^{z_i^+}}^{n_i} \left(1 - \frac{Q}{K} \right) \quad (1.20)$$

where the k represents the reaction rate constant. The chemical affinity of described reaction is defined as follow (Hellmann at al., 2009; Gérard at al., 1998):

$$A_r = -RT \ln \left(\frac{Q}{K} \right) \Rightarrow \Delta_r G = RT \ln \left(\frac{Q}{K} \right) \quad (1.21)$$

so that can be derived that:

$$\frac{Q}{K} = \exp \left(-\frac{A_r}{RT} \right) = \exp \left(\frac{\Delta_r G}{RT} \right) \quad (1.22)$$

The R is the universal gas constant (J·mol⁻¹·K⁻¹) and Δ_rG = -A_r denotes Gibbs energy (J·mol⁻¹) and chemical affinity (J·mol⁻¹) of reaction. The dissolution rate at near to equilibrium conditions when r₊ + r₋ ≈ 0 requires that Q ≈ K and the ratio k₊/k₋ ≈ K:

$$\exp\left(\frac{\Delta_r G}{RT}\right) = \frac{Q}{K} \quad (1.23)$$

The overall dissolution rate should through combination of Eq.1.22 with Eq. 1.23 expressed as:

$$r = k_+ \prod_{i=1}^m a_{M_i^{z_i^+}}^{n_i} \left(1 - \exp \frac{\Delta_r G}{RT}\right) \quad (1.24)$$

The temperature dependence of dissolution rate constant is given by Arrhenius law (Oelkers, 2001):

$$k_+(T) = A \exp\left(-\frac{E_a}{RT}\right) \quad (1.25)$$

The combination of Eq.1.24 and Eq.1.25 leads to equation:

$$r = \prod_{i=1}^m a_{M_i^{z_i^+}}^{n_i} A \exp\left(-\frac{E_a}{RT}\right) \left(1 - \exp \frac{\Delta_r G}{RT}\right) \quad (1.26)$$

where A is pre-exponential (frequency) factor and E_a is apparent activation energy. Under conditions that are not far from equilibrium conditions (please refer to Eq.1.23) where exp (Δ_rG/RT) ≈ 1 can be dissolution rate expressed as:

$$r \approx \prod_{i=1}^m a_{M_i^{z_i^+}}^{n_i} A \exp\left(-\frac{E_a}{RT}\right) \quad (1.27)$$

or

$$\ln r \approx \ln \prod_{i=1}^m a_{M_i^{z_i^+}}^{n_i} + \ln A - \frac{E_a}{R} \frac{1}{T} \quad (1.28)$$

The kinetic parameter of dissolution process can be then estimated from Arrhenius plot as the slope (-E_a/R) of the dependence of ln r on reciprocal temperature. Assuming information about ionic product of released cations (I_{aM(i)ⁿ⁽ⁱ⁾}), the value of A can be calculated from the intercept with y-axis.

A general scheme for the dissolution of a mineral or glass can be written as follow (Wieland et al.,1988):



The precursor complex has the same chemical formula as the activated complex, but the activated complex has more energy. Within the context of transition-state theory (TST), the activated complex is in equilibrium with other species that precede it in the reaction sequence. It follows that a mineral dissolution rate can be considered to be proportional to

the concentration of this “rate-controlling” precursor complex at the surface in accord with (Oelkers, 2001):

$$r_+ = k_+ X_p \quad (1.30)$$

where k_+ refers to a rate constant consistent with the P precursor complex and X_P stands for the mole fraction of the precursor complex at the surface.

The dissolution mechanism of this mineral or glass is often initiated by the formation of the precursor complex through one or more exchange reactions. The process leads to formation of the leached surface through the metal-proton exchange. The next part of the dissolution reaction is destruction of the leached surface (Oelkers, 2001), i.e. incongruent dissolution takes place. The overall mechanism then may consist of a series of “i” elementary steps:

$$r = r_+^i - r_-^i = \sigma_i r \quad (1.31)$$

The exponent σ is generally known as Temkin's average stoichiometric number, which is equal to the ratio of the rate of destruction of the activated or precursor complex relative to the overall dissolution rate. The σ value is related to the stoichiometric number of precursor complexes that can be formed from one mole of the commonly adopted chemical formula of a mineral or glass and it can have a value other than one (Aagaard & Helgeson, 1982). The average stoichiometric coefficient for the overall dissolution process that consists from i-steps can be defined as follows (Gin at al., 2008):

$$\sigma = \frac{\sum_{i=1} (\sigma_i \Delta_r G_i)}{\sum_{i=1} \Delta_r G_i} = \frac{\Delta_r G}{\sum_{i=1} \Delta_r G_i} \quad (1.32)$$

For reaction near to equilibrium we obtain:

$$\frac{r_+}{r_-} = \prod_{i=1} \frac{r_+^i}{r_-^i} = \exp \left(-\frac{\Delta_r G}{RT} \right) \quad (1.33)$$

and

$$r = r_+ \left(1 - \exp \left(\frac{\Delta_r G}{\sigma RT} \right) \right) \quad (1.34)$$

From the general law of mineral dissolution proposed by Aagaard and Helgeson, 1982 it can be derived by the same way as before:

$$r = k_+ \prod_{i=1}^m a_i^{n_i} \left(1 - \exp \frac{\Delta_r G}{\sigma RT} \right) \quad (1.35)$$

As it was pointed by Gin at al., 2008, the Eq.1.24 is often presented as direct application of transition state theory. In fact, this law may be derived using simple kinetic concepts (notably the Van't Hoff law) irrespective of any hypotheses concerning the reaction mechanisms. The notion of an activated complex associated with an elementary step is

theoretically compatible with the kinetic law 1.24, assuming an equilibrium existing between the activated complex and reactants in the forward and reverse directions. However, this notion is not required to obtain Eq.1.24 and indeed leads to a paradox that lies in the fact that equilibrium was assumed between the activated complex and reactants in the forward direction, but that a second equilibrium was also assumed between the activated complex and the product in the reverse direction. This implies equilibrium between the products and the reactants, so the net rate should be zero. This paradox, of course, does not call into question the expression of the kinetic constants: the forward rate simply offsets the reverse rate. Postulating equilibrium between the reactants forming the activated complex in both directions and the activated complex therefore implies that Eq.1.24 is valid only at equilibrium.

1.2 Clay minerals

Human life and the existence of many organisms on this planet are connected with clays. Clay minerals are the basic constituents of clay raw materials and clay raw material has always played the substantial role in human life (Table 1.3) due to their wide-ranging properties, high resistance to atmospheric conditions, geochemical purity, easy access to their deposits near the earth’s surface and low price. A majority of clays is known for its plasticity. However, many clay raw materials are not plastic, or they are semi-plastic such as clay stones, clay shales, talc, pyrophyllite, vermiculite and coarser mica. The properties of clay minerals also reflect the state and distribution of the electrostatic charge of the structural layers. The negative charge is a result of the ionic substitutions in the octahedral and tetrahedral sheets of clay minerals (Konta 1995; Murray; 2000).

Paper industry	Kaolinite,	Adsorbents	Bentonite, chlorites, palygorskite...	Bonding material	Kaolin, bentonite, bentonite...
Ceramics	Kaolinite, illite, talc, vermiculite...	Adhesives	Kaolinite,	Water purification	Vermiculite
Plastics and rubber	Kaolinite, pyrophyllite....	Pharmaceutic and cosmetics	Kaolinite, bentonite, pyrophyllite....	Waste treatment	Micas, bentonite...
Catalysts	Bentonite, palygorskyte...	Insulating material	Vermiculite, micas...	Agricultural and forestry	Palygorskyte, vermiculite, bentonite...
Dyes and paints	Kaolinite, micas, pyrophyllite....	Molecular sieves	Palygorskite, sepiolite...	Polishing materials	Bentonite

Table 1.3. Traditional application area of clay minerals (Konta 1995; Murray; 2000).

A significant role for clay minerals in the origin of life was postulated by Bernal, 1967. Clay surface could adsorb and concentrate organic substances and some hypothesis supposed that clay crystals could function as the earliest genetic information storing material (C.-Smith, 1966 and 1982) and iron-rich clay have significant importance in the origin of the

photosynthetic organisms (Hartman, 1975). Clay minerals, the essential constituents of argillaceous rocks, can be classified in seven groups according to their crystal structure and crystal chemistry. These groups are listed together with their properties and the most important members in the Table 1.4.

Group	Layer type	Length d ₀₀₁ [Å]	Interlayer charge	Interlayer contains ⁽¹⁾	Octahedral layer type:	Example
Kaolinite and serpentine	1 : 1 t-o		zero	---	Diocahedral	Kaolinite, dickite, nacrite...
					Triocahedral	Serpentine
Talc and pyrophyllite	2 : 1 t-o-t		zero	---	Diocahedral	Talc
					Triocahedral	Pyrophyllite
Smectites	2 : 1 t-o-t	9.6 – 21.0 ⁽²⁾	0.2 – 0.6	Na⁺, Ca²⁺ , K ⁺ , Li ⁺ , H ₃ O ⁺ and H ₂ O	Diocahedral	Montmorillonite
					Triocahedral	Saponite
Vermiculites	2 : 1 t-o-t	~14.3	0.6 – 0.9	Mg²⁺	Diocahedral	Diocahedral vermikulite
					Triocahedral	Triocahedral vermikulite
Micas	2 : 1 t-o-t	~10.0	0.9 – 1.0	K⁺, Na⁺, H₃O⁺ , Ca ²⁺ , □ ⁽³⁾ ...	Diocahedral	Muscovite, illite...
					Triocahedral	Biotite, flogopite...
Chlorites	2 : 1 + 1 t-o-t + o	~14.3	different	Di- or tri- octahedral layer	Diocahedral	Donbassite
					Triocahedral	Klinochlore
Palygorskite and sepiolite	other ⁽⁴⁾	---	different	other ⁽⁴⁾	other ⁽⁴⁾	Sepiolite, palygorskite
⁽¹⁾ Interlayer ions that are present predominantly are marked by bold.				⁽⁴⁾ Chanel containing water and exchangeable hydrated cations. Water can be withdrawn without structural lattice changes similar to zeolites.		
⁽²⁾ For untreated smectites is typical d ₀₀₁ ≈ 15 Å.						
⁽³⁾ Vacation.						

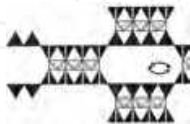
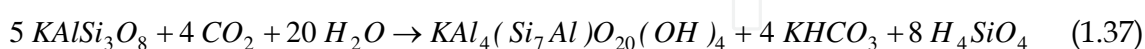
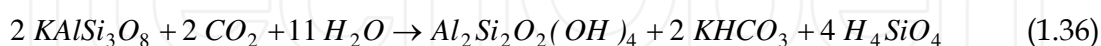


Table 1.4. Classification of phyllosilicates (Martin et al., 1991; Konta, 1995).

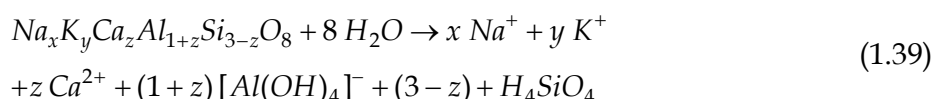
Clay minerals represent a large family of alumino-silicate structures with a range of chemical composition, structure and surface properties. Their crystal structure with a few exceptions consists of sheets firmly arranged in structural layers. Hence are these minerals termed as sheet silicates or phyllosilicates. The individual layers consist of two, three or four sheets. The sheets are formed either by tetrahedrons [SiO₄]⁴⁻ which are abbreviated as

“T” or by [AlO(OH)]⁶⁻ octahedrons which are signed as “O”. The interior of tetrahedrons and octahedrons contains smaller metal cations, their apices are occupied by oxygen’s from which some are connected to protons (as OH). All these fundamental structural elements are arranged to form a hexagonal network in each sheet (Caglar at al., 2008; Konta 1995).

Numerous rock-forming silicates (feldspars, granites, syenites, gneisses, arkoses, phonolites, rhyolites...) alter into clay minerals such as kaolinite (Eq.1.36), illite (Eq.1.37) and montmorillonite (Eq.1.38) through an intense hydrolysis, supported by natural acids (Konta, 1995):



Dissolution and precipitation of any feldspar can be described by the general formula (Hellmann at al., 2009):



where $x + y + z = 1$. The main factors affecting the rates and mechanisms of dissolution include the pH, temperature, composition of the liquid phase and feldspar, feldspar granulometry, the influence of atmospheric condition and vegetation (Chardon at al., 2006; Augusto at al., 2000).

1.3 Properties and mineralogy raw materials main minerals – montmorillonite and talc

Bentonite occurs in the form of lenses in other sediments mostly as a weathering product after igneous material settled in water. It also commonly occurs as a product of supergene or hydrothermal alteration of some volcanic rocks, e.g. rhyolites, porphyres, phonolites, dacites, andesites and basalts. Smectites are especially formed through the decomposition of volcanic glass. The chemical composition of smectite, the dominant mineral of bentonites, is variable. It varies between montmorillonite ($\text{Al}_{1.67}(\text{Mg}, \text{Fe}^{2+})_{0.33}\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot 0.5\text{Ca}_{0.33} \cdot n\text{H}_2\text{O}$) and beidellite ($\text{Na}_{0.5}\text{Al}_2(\text{Si}_{3.5}\text{Al}_{0.5})\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$). In the interlayer space of both smectites different cations are adsorbed, especially alkalis and alkaline earths (Konta 1995).

Smectites are an important class of clay minerals; they are utilized in many industrial processes due to their high CEC, swelling ability, and high surface area (Madejová at al., 2006). Montmorillonite was the name given to a clay mineral found near Montmorillon in France as long ago as 1874 (Grimshaw, 1971). Montmorillonite is classified as a dioctahedral clay mineral with the 2:1 type of layer linkage that is related to the group of smectites (Caglar at al., 2008).

Dioctahedral layered structure of 2:1 type represents T-O-T sheet layered mineral with two tetrahedral and one octahedral layer where the centre of octahedron are predominantly occupied by trivalent cations such as Al^{3+} , Fe^{3+} , Cr^{3+} , V^{3+} , etc. The structure of montmorillonite is shown in Fig.1.2.

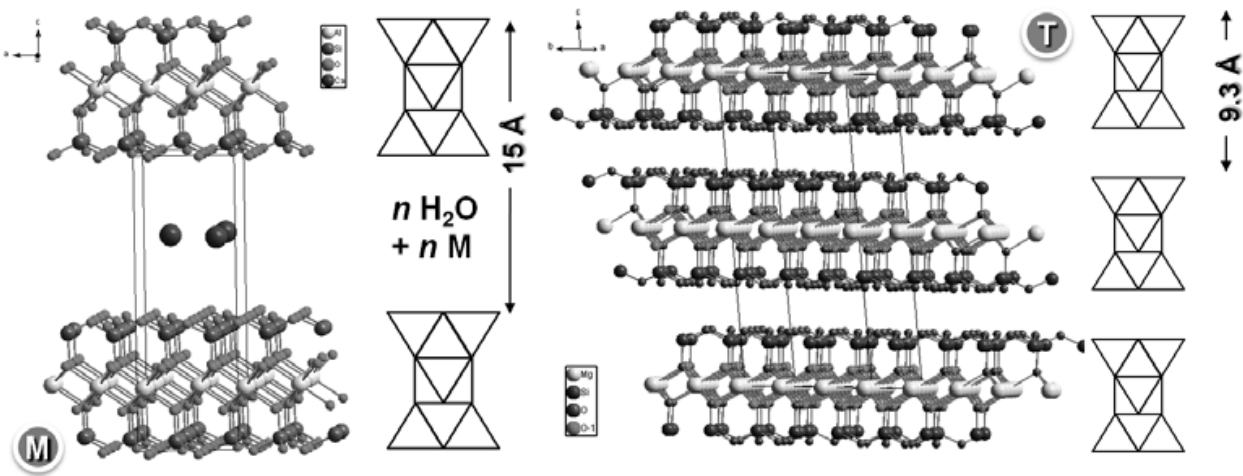


Fig. 1.2. The structure of montmorillonite (M) and talc (T).

Talc ($\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$) is a common 1:1 layer lattice silicate, the structure of which consists of two tetrahedral silicate sheets separated by an octahedral Mg-O(OH) sheet, i.e. it is the trioctahedral magnesian analogue of pyrophyllite ($\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$). Among its many uses, talc is an important raw material for magnesium ceramics (steatites, cordierite, enstatite and forsterite products). As the ceramic raw material, its thermal decomposition behaviour is of considerable interest (MacKenzie & Meinhold, 1994). Talc and pyrophyllite crystallize during metamorphic or hydrothermal processes (Konta, 1995). The structure of talc is shown in Fig.1.2.

2. Leaching experiment

All experiments reported in this work were performed on bentonite from locality Obrnice (Czech Republic) produced by the company Keramost a.s., that was used as the source of Na, Ca - montmorillonite, and talc produced by Združena v.d. Spišská nová Ves, plant Gelnica from locality Gemerská poloma (Slovak Republic). The composition of montmorillonite and talc can be expressed by the empiric formula $\text{Na}_{0.2}\text{Ca}_{0.1}\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2(\text{H}_2\text{O})_{10}$ and $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$, respectively.

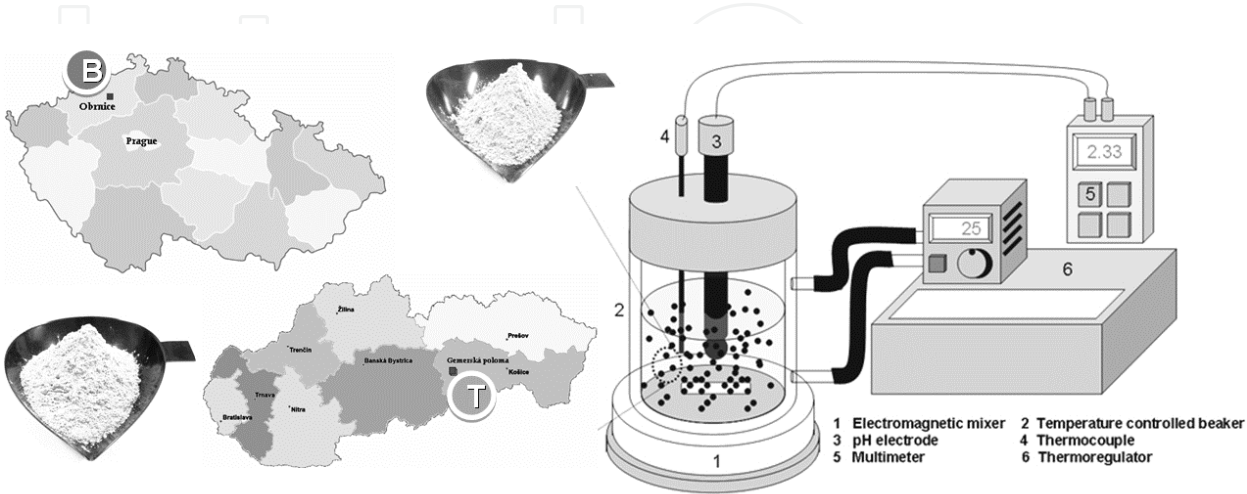


Fig. 2.1. Schematic illustration of the bentonite (B) and Talc (T) leaching experiment.

Leaching procedure was performed using the well stirred suspension of clay mineral in diluted solution of acetic acid (Lachema, p.a.) of concentration 3 dm³·mol⁻¹. Temperature of leaching bath ranged from 22 to 50 °C. The temperature of double wall glass reactor was adjusted using external water flow of temperature controlled water bath (thermostat). Sample was poured on by solution of acetic acid that was preheated to the applied leaching temperature in water bath of thermostat. Hence, the stirring of system by magnetic stirrer was used. Suspension contained 12.5 g of wollastonite per dm³ of leaching solution. The pH value of dispersing medium for 24 h leaching experiment was continuously measured by pH meter connected to PC (Fig.2.1).

Solid part of suspension was separated by filtration through dense filter paper (red strip) after leaching. Filter cake was washed three times by slightly acidified (acetic acid) distilled water. The quantities of ions in original sample and leachate were determined by the Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES; ICP IRIS Iterdip II XSP duo). Filter cake was dried at 110 °C; its properties and composition were subsequently investigated by simultaneous TG-DTA-EGA, FT-IR, BET and SEM.

Thermal analysis – simultaneous termogravimetry, differential thermal analysis and effluent gas analysis (TG-DTA and EGA) were performed with TG-DTA analyzer (Q600, Thermal Instruments) connected with FT-IR spectrometer (iS10, Thermo Scientific) through TGA/FT-IR interface (Thermo Scientific) heated to temperature 200 °C. That enables to study the composition of gas phase that was formed during processes which take place in heated sample. All experiments were performed with heating rate 20 °C·min⁻¹ using argon with flowing rate 100 cm³·min⁻¹ as the carrier gas, i.e. in the inert atmosphere.

Infrared spectra were collected upon mid-IR region via KBr pellets technique using FT-IR spectrometer iS10. Specimens were ground with dry spectroscopic grade KBr powder using the sample to KBr mass ratio of 1 : 100. The spectrum was obtained from 128 scans collected with resolution of 8 cm⁻¹. Scanning electron microscopy (SEM) was performed with a model BS 340 (Tesla). The X-ray diffractometer Siemens D500 with CuKα radiation at 40 kV and 40 mA was utilized for identification the phase composition of raw material and leached samples. Brunauer-Emmett-Teller (BET) analysis (Chembet 3000, Quantachrome Instruments) was used to determine of leached samples specific surface.

2.1 Evaluation of leaching test

The method applied for monitoring of the leaching process is the same as for study of leaching of calcium from wollastonite (Ptáček at al., 2010). The buffer system of weak acid (CH₃CO₂H) and its salt (Ca(CH₃CO₂)₂ or Mg(CH₃CO₂)₂) with a strong base, i.e. Ca(OH)₂ or Mg(OH)₂, was formed during dissolution of raw material. With respect to reaction stoichiometry, the amount of formed acetate ions was double to concentration of Ca²⁺ ions released from wollastonite. Hence following subform of well known Henderson buffer equation may be used for estimation of the course of leaching process:

$$pH(T) = pK_a(T) + \log \frac{2[Ca^{2+}]}{[CH_3CO_2H]} \quad (2.1)$$

where pK_a denotes dissociation constant of acetic acid at given temperature. All variables in Eq.2.1 depend on the temperature.

2.2 Evaluation of leaching process kinetics

The monitoring of the progress of leaching experiment reflects the following facts and presumptions:

1. The amount of calcium and magnesium released into the solution is much higher than other elements extracted from raw material during leaching experiments, i.e. the amount of other metals in the solution is negligible;
2. Large excess of acetic acid in the system ensures its stable concentration level;
3. Henderson-Hasselbach buffer equation (Eq.2.1) can be applied for the reaction mixture;
4. Leached calcium was instantaneously transported out of surface by intensive stirring of the system.

The steady-state dissolution rate for applied temperature $r_+(T)$ ($\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$) can be calculated using following equation (Oelkers, 2001):

$$r_+(T) = \frac{([M^{2+}]_i - [M^{2+}]_t) V}{v_{M(\text{Ac})_2} S (t - t_i)} = \frac{\Delta [M^{2+}] V}{S \Delta t} \quad (2.2)$$

where $[M^{2+}]_i$ and $[M^{2+}]_t$ are an initial t_i and general time t concentrations of $M^{2+} = \text{Ca}^{2+}$ and Mg^{2+} ions, respectively. The initial time of the process means the beginning of an induction period, so that the amount of Ca and Mg released during dissolution of calcite and dolomite can be excluded. The quantities V , $v_{M(\text{Ac})_2}$ and S are a volume of the system, stoichiometric number of $M(\text{Ac})_2$ ($v_{M(\text{Ac})_2} \approx 0,3$ for the Ca-montmorillonite and $v_{M(\text{Ac})_2} \approx 0,3$ for talc) and total surface area of sample introduced into the reactor, respectively. The term $\Delta [M^{2+}] / \Delta t$ of Eq.2.2 can be determined as the slope of the linear part of the plot of concentration vs. time (Cama, 1999). This method of $r_+(T)$ value estimation is in particular favourable for the systems with very complicated stoichiometry of ongoing reactions such as in studied montmorillonite clay.

The reached stage of the system during the leaching process can be characterized by fractional conversion (degree of conversion) as follows:

$$y = \frac{[M^{2+}]_i - [M^{2+}]_t}{[M^{2+}]_i - [M^{2+}]_\infty} \quad (2.3)$$

where bottom index i , t and ∞ denotes the initial (beginning of the induction period), currently measured and final value of M^{2+} ions concentration. The degree of conversion can hold values from 0 to 1 and its time dependence enables to estimate mechanism and kinetics of leaching process by linearization procedure. The method is based on the formula:

$$g(y) = k t \quad [T = \text{konst.}] \quad (2.4)$$

where k is the rate constant of the process. If the kinetic function $g(y)$ corresponding to the proper mechanism was chose, the dependence of $g(y)$ on t should be straight line with the slope k on wide interval of y . The mathematic expression of the kinetic function can be found in published literature (Vlaev at al., 2008; Duan at al., 2008; Saikia at al., 2002; Šesták, 1984). The variation of mineral dissolution rates with temperature is commonly described using the empirical Arrhenius law - Eq.1.25 (Oelkers, 2001; Cama at al., 1999). The estimation of the apparent activation energy and the pre-exponential (frequency) factor (A) is based on the logarithmic form of the Arrhenius law:

$$\ln r_{+}(T)=\ln A-\frac{E_a}{R} \frac{1}{T}$$

(2.5)

using values of r_{+} determined for several temperatures. The plot of $\ln k$ vs. T^{-1} (Arrhenius plot) should be straight line, where the slope $(-E_a/R)$ yields to the apparent activation energy of the process and y-axis intercept is then equal to the $\ln A$. For the early stage of dissolution process, the concentration of M^{2+} ions in leaching solution is increasing with time almost linearly. It stands to the reason that the initial part of dissolution process enables to estimate the dissolution rate constant as:

$$k=\frac{dy}{dt} \quad [s^{-1}]$$

(2.6)

3. Results and discussion

There are many factors affecting the course of experiment such as pH of leaching solution, kind and solvent composition, temperature, pressure, particle size distribution and particle shape, concentration of solid in the suspension and stirring intensity. Hence, the initial state of raw material serving as the source of clay mineral should be characterized. The survey of used raw materials composition and properties are listed in the Table 3.1.

Mineral		Montmorillonite			Talc		
Empirical formula		$Na_{0,2}Ca_{0,1}Al_2Si_4O_{10}(OH)_2(H_2O)_{10}$			$Mg_3Si_4O_{10}(OH)_2$		
Classification (Strunz)		VIII/H.19-20			VIII/H.09-40		
Colour		Light yellow	(14)		Light grey	(14)	
Composition	Na ₂ O	1.13 (1)	1.76 (2)	1.38 (3)	--- (1)	--- (2)	1.93 (3)
	K ₂ O	---	0.84	1.23	---	---	3.16
	CaO	1.02	0.45	11.88	---	---	3.35
	MgO	---	2.74	3.75	31.88	35.12	16.94
	Al ₂ O ₃ [%]	18.57	32.85	25.79	---	---	21.64
	Fe ₂ O ₃	---	13.72	11.29	---	---	1.68
	SiO ₂	43.77	41.50	36.63	63.37	58.43	51.29
	TiO ₂	---	---	1.65	---	---	---
	H ₂ O	36.09	6.14	6.39	4.75	6.45	6.65
X ₅₀ /X ₉₀ [μm] (4)		9.12/ 37.67			29.33/ 71.65		
SH (5) [g·cm ⁻³]		0.76			0.71		
SHS (6) [g·cm ⁻³]		0.81			0.73		
Moisture (7) [%]		7.68			0.51		
ZŽ (8) [%] / Colour		19.54 / red			12.71 / beige		
OH (9) [g·cm ⁻³]		2.23			2.80		
SS (10) [m ² ·g ⁻¹]		95.55			2.10		
ζ (11) [mV]		-13.5			-13.9		

Admixtures ⁽¹²⁾	Carbonates ⁽¹³⁾ , illite (3), clinochlore (2), fluorapatite (6), barite (7) and rutile (5).	Dolomite (1), calcite (2), albit (3), pyrite (4) and quartz (5)
⁽¹⁾ Stoichiometric composition of mineral according to pertinent empirical formula. ⁽²⁾ Determined composition of clay mineral (dry state of sample). ⁽³⁾ Analyzed composition of raw material (dry state sample). ⁽⁴⁾ Particle size analysis (Helos, Sympatec). ⁽⁵⁾ Pour density (according to standard ČSN EN 725-8). ⁽⁶⁾ Bulk density in the shaken state (according to standard ČSN EN 725-8). ⁽⁷⁾ Determined by humidity analyzer Kern MLS 50-3 (sample was dried at 110 °C to constant weight. ⁽⁸⁾ Loos on ignition (annealing at 1000°C to constant weight; according to standard ČSN 72 0103). ⁽⁹⁾ Bulk density (according to standard ČSN EN 993-17). ⁽¹⁰⁾ Specific surface (BET, Chembet 3000, Quantachrome Instruments). ⁽¹¹⁾ Electrokinetic “zeta” potential (suspension of 0.1 g · dm⁻³). ⁽¹²⁾ Main admixture mineral found by following method: XRD, FT-IR, SEM and TA. The content of crystalline phases was estimated by XRD in semi-quantitative mode. ⁽¹³⁾ Siderite (1), Ankerite (4) and Dolomite (7). ⁽¹⁴⁾ Monoclinic - prismatic class symmetry.		

Table 3.1. The composition and properties of clay raw materials.

3.1 Thermal analysis

Results of thermal analysis allow identification of main mineral phases and estimate their content in the clay raw material. The typical TG-DTA and EGA patterns of clay raw materials that were used as the source of montmorillonite and talc are shown in Fig.3.1. The DTG curve is plotted in order to reach higher sensitivity to distinguish between individual steps of thermogravimetric analysis.

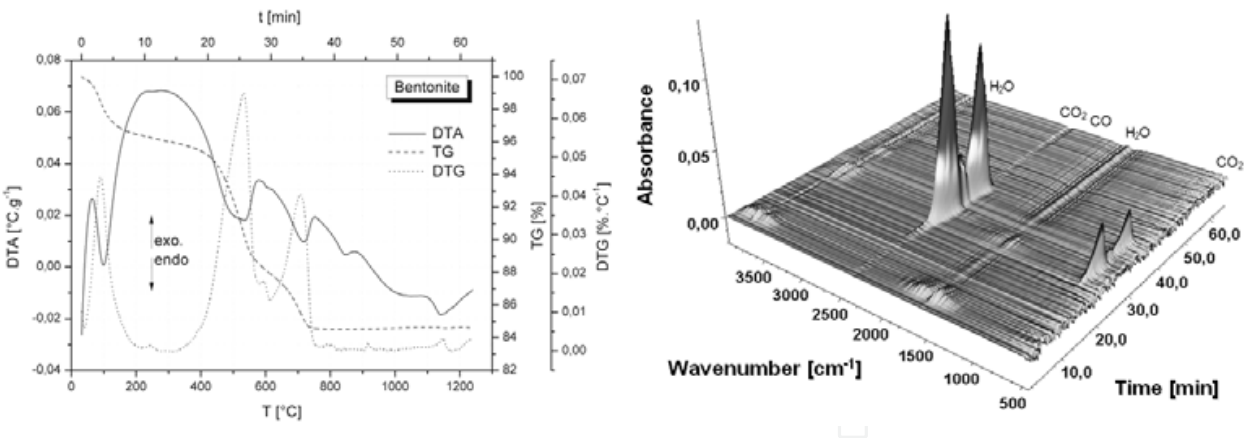
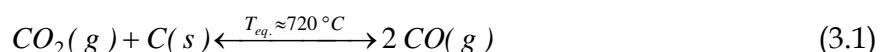


Fig. 3.1. TG-DTA and EGA pattern of montmorillonite clay.

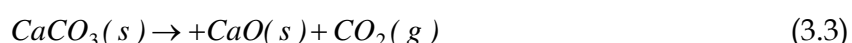
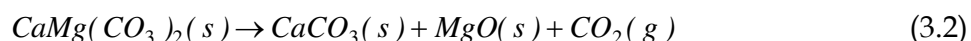
TA of bentonite performed up to 1250 °C shows that mass of sample is decreasing for about 15.42 % within to the series of six endothermic steps. Evaporation of adsorbed water leads to the first endothermic peak of the maximum at temperature about 99.4 °C. The mass of sample was up to 165.2 °C (ousted point of DTG peak) reduced at about 3.71 %. The water vapour released from the sample is also well visible on EGA. The water can be also detected in the spectrum of gas phase upon the temperature interval ranged from 225 to 260 °C, where water molecules has been ousted from the interlayer space of montmorillonite and admixture of illite. The process shows maximum rate at temperature 245.0 °C.

The dehydroxylation of clay minerals, decomposition of carbonates and burning of organic admixtures are the main overlapping processes whose take place within temperature interval from 380 to 600 °C. The DTA shows broad endothermic peak having a composed structure at temperature 533.9 °C. The bands of carbon dioxide and water are well visible on EGA plot. These processes are affected together via partial pressure formed gas species. For example the water formed by dehydroxylation of montmorillonite slows down the diffusion of oxygen into burning organic material and shifts the organic matter process to the higher temperatures, while water vapour formed by combustion of organic admixtures leads to increasing of partial pressure of water vapours. That results into decreasing rate of dehydroxylation of clay minerals (Ptáček at al., 2010). Oxygen deficiency leading to reduction condition during TA is indicated by bands of carbon monoxide on the results of EGA.

The effects of carbonates on the above mentioned processes should be explained using the Richardson's diagrams (Richardson, 1974) as follows. The Bell-Boudoir's reaction (Eq.3.1) shows thermodynamic equilibrium at temperature 720 °C, so that the carbon monoxide is the more stable at higher temperature than carbon dioxide. That means that CO₂ formed by the thermal decomposition of carbonates at temperatures near to temperature of equilibrium or higher facilitates the residual carbon removing process.



The two carbonates are identified in the analysis sample – siderite (FeCO₃) and dolomite (CaMg(CO₃)₂). Thermal decomposition of siderite that takes place at temperatures up to 410 °C are participate on the broad DTA endothermic effect at 533.9 °C. Annealing dolomite is decomposed within two steps that are represented by reactions 3.2 and 3.3. The first step takes place at 602.7 °C and second at 718.3 °C. The both processes are well visible on EGA.



The formation of SO₂ was detected on EGA upon temperature interval from 800 to 870 °C due to presence of traces of pyrite. The endothermic peak at temperature 848.2 °C is related to the formation of cordierite that is connected with destruction of the phyllosilicate structure of clay minerals. The eutectic melt was detected at temperature 1141.4 °C.

During thermal analysis of talc raw material performed up to temperature 1250 °C (Fig.3.2) is mass of the sample decreasing for about 13.12 %. The adsorbed water is removed up to 143 °C. The mass of sample was reduced for about 0.21 % during this process. The dehydroxylation of talc which takes place in temperature range from 720 to 970 °C and two steps of thermal decomposition of dolomite at 450 and 720 °C are the main occurring processes. The SO₂ bands in EGA plot indicate the presence of small amount of pyrite.

3.2 Infrared spectroscopy

The infrared spectrum of montmorillonite and talc clay is shown on Fig.3.3. The data published in literature (Eren & Afsin, 2008; Molina-Montes at al., 2008; Madejová at al., 2006; Tyagi at al., 2006; Klopogge at al., 2005) were used for interpretation of raw material

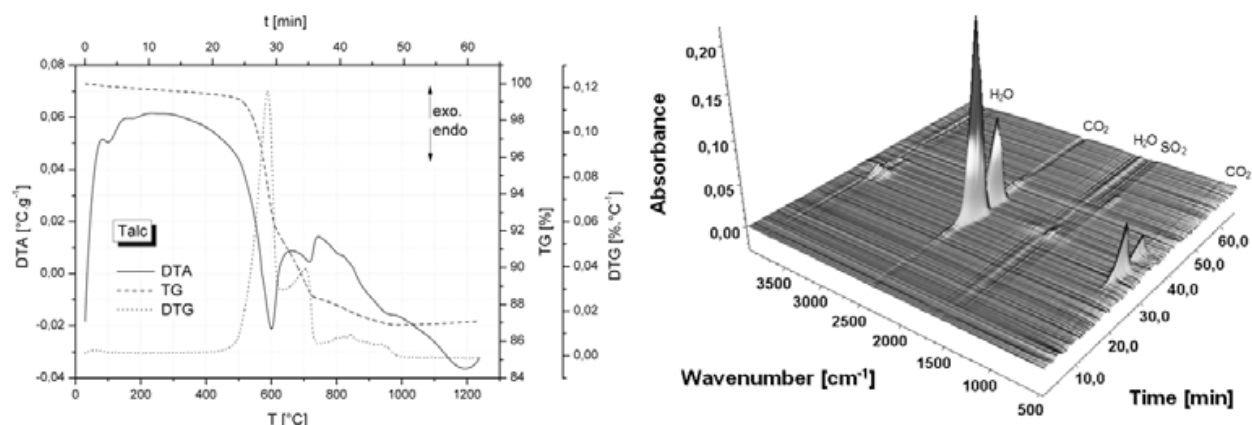


Fig. 3.2. TG-DTA plot and EGA pattern of talc raw material.

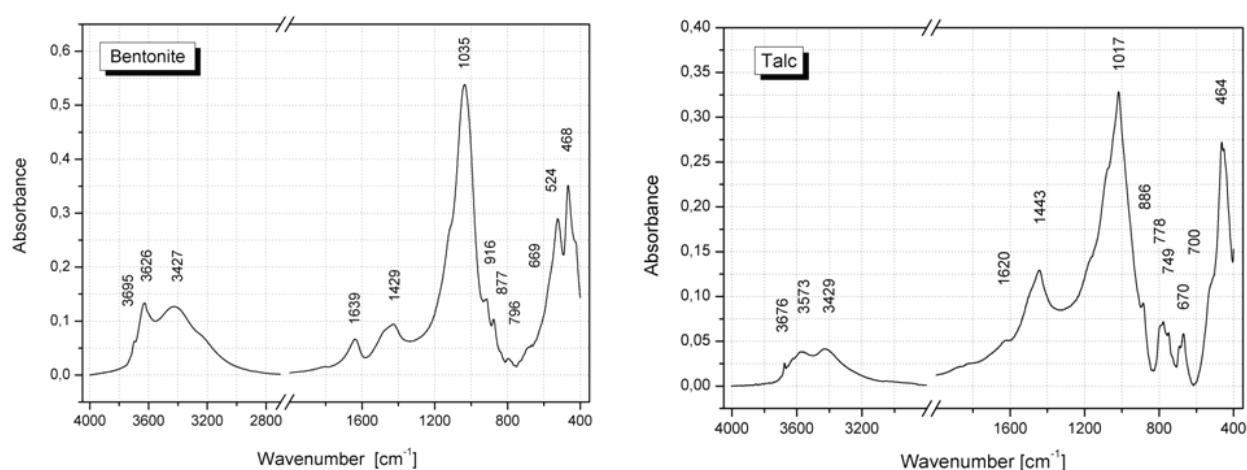


Fig. 3.3. Infrared spectrum of bentonite and talc raw material.

spectral features. The OH stretching bands are located at 3695 and 3626 cm^{-1} . The bending of AlAlO-H , AlFeO-H and AlMgO-H groups show bands at 916, 877 and 837 cm^{-1} . The stretching and bending band of physical adsorbed water are located at 3427 and 1639 cm^{-1} . The most intensive band at 1035 cm^{-1} is related to antisymmetric stretching of the $\equiv\text{Si-O-Si}\equiv$ bridge. The deformation mode is placed at 524 cm^{-1} . The dolomite and quartz are identified by infrared spectroscopy as the main admixtures of clay raw material that was used as the source of montmorillonite.

The infrared spectrum of talc (Fig.3.3) shows stretching of MgO-H groups at wavenumber 3626 cm^{-1} . The deformation modes are located at 670 and 646 cm^{-1} . The band of antisymmetric stretching and bending mode of $\equiv\text{Si-O}$ bond shows maximum absorption intensity at 1017 and 453 cm^{-1} , respectively. The other bands belong to admixture minerals - clinocllore and dolomite.

3.3 Clay material particle size distribution and morphology

The SEM and particle size distribution analysis of clays is shown in Fig.3.4. Bentonite consists of massive aggregates. The most important admixture minerals of montmorillonite clay (Fig.3.5) are siderite (FeCO_3) and carbonates from dolomite group such as dolomite ($\text{CaMg}(\text{CO}_3)_2$) and ankerite ($\text{CaFe}(\text{CO}_3)_2$), phyllosilicates illite ($((\text{K},\text{H}_3\text{O}^+)\text{Al}_2(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_2$)

and clinocllore ((Mg,Fe)₅Al(Si,Al)₄O₁₀(OH)₈). Further fluorapatite (Ca₅(PO₄)₃F), barite (BaSO₄) and rutile (TiO₂) are indentified in the clay. It's obvious that the carbonates serve as the source of Ca, Fe, Mg, Zn, Mn, etc. elements at the early stages of dissolution experiment. The particle size analysis of raw materials, i.e. bentonite clay and talc, used for leaching experiments are shown at Fig.3.4. The shape of particle size distribution curve of bentonite raw material reflects the complicate phase composition of sample that contains a significant amount of carbonates and other admixture minerals of different hardness compared to clay, i.e. minerals with different grindability. These admixtures are responsible for the right shoulders of the particle size distribution curve. The talc raw material with high content of clay phase shows almost ideal Gaussian profile of particle size distribution curve with median 29.33 μm (Table 3.1).

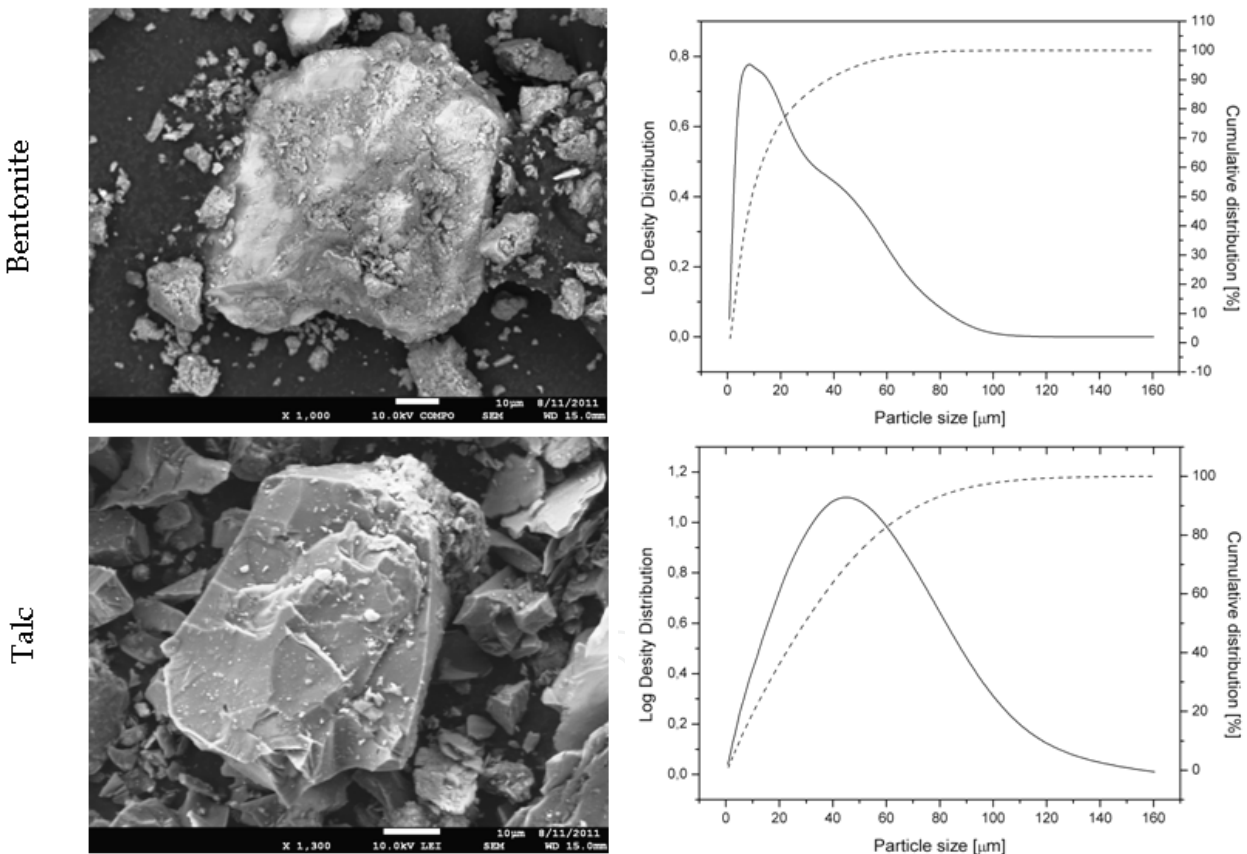


Fig. 3.4. SEM and particle size distribution analysis of clay raw material.

The layered structure of talc aggregates is shown at Fig. 3.6. The average size of (001) planes was via several measurements estimated on 200 μm. The calcite was identified as the main admixture mineral of talc raw material.

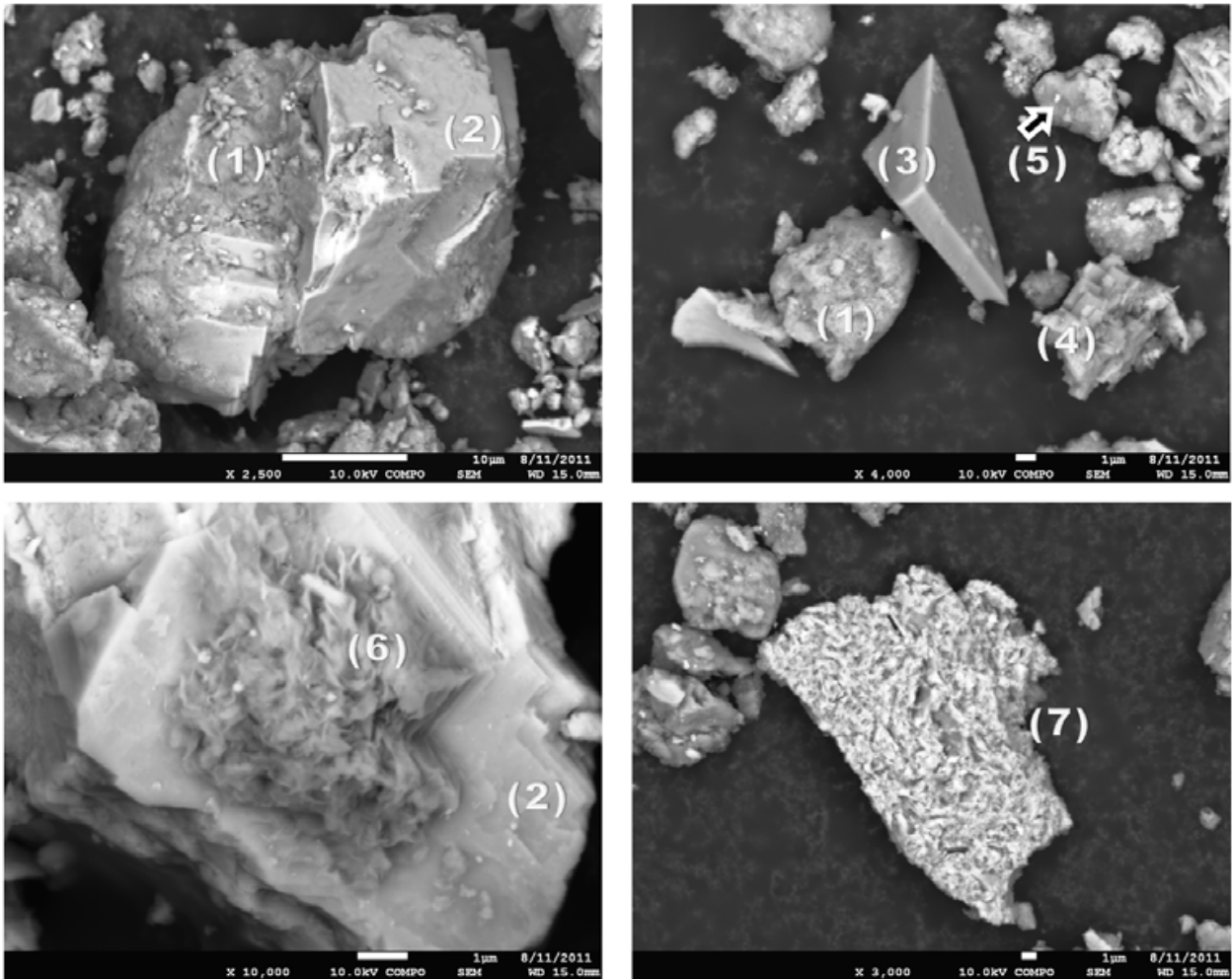


Fig. 3.5. The admixture mineral of montmorillonite clay (1): siderite (2), ankerite (3), illite (4), barite (5), clinochlore (6) and fluoroapatite (7).

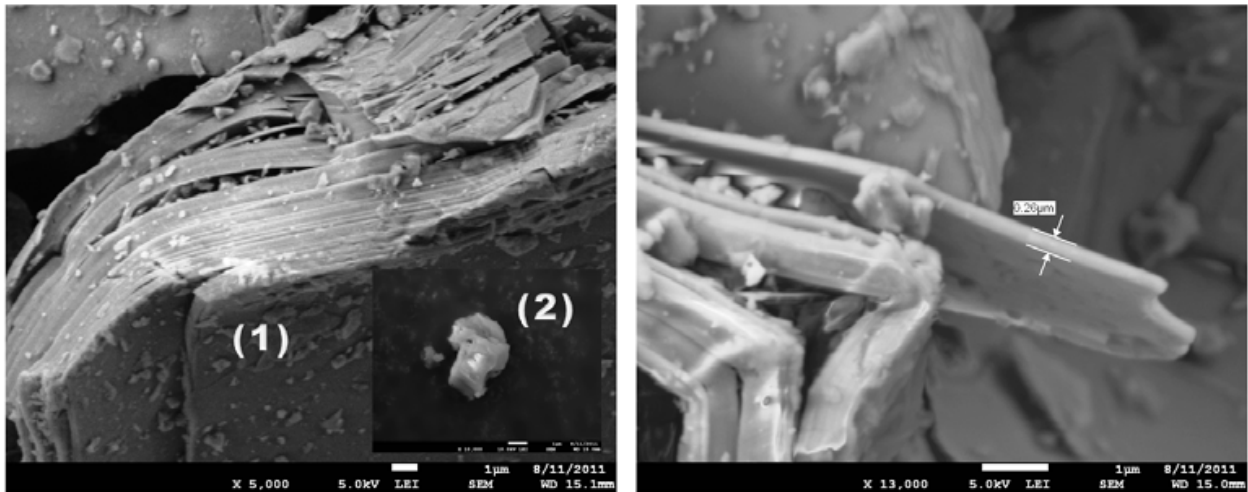
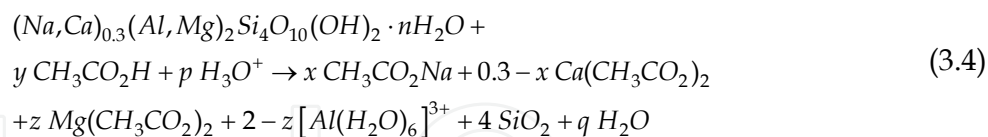


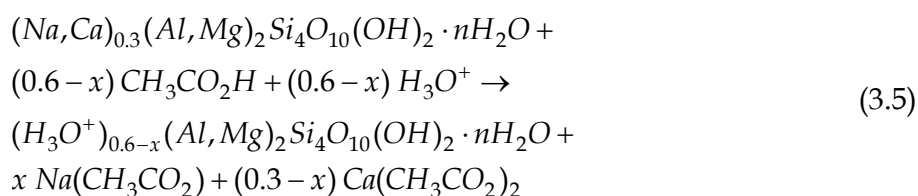
Fig. 3.6. Layered structure of talc (1) aggregate and grain of calcite (2).

3.4 Bentonite dissolution

The dissolution of main bentonite mineral, i.e. montmorillonite, in diluted solution of acetic acid should be expressed as following:



where $y = 2z - x + 0,6$, $p = 5,4 - 2z + x$ and $q = 6z + n - 6$. On the other hand, with regard to the montmorillonite structure that is described in chapter 1.3, the release of cations from interlayer space is participating on the process. These ions are being exchanged by H_3O^+ according to Eq.3-2.



It was found by (Adams, 1987; Jovanović and Janačković, 1991) that acid-activated (HCl or H₂SO₄ of different molar concentrations) bentonite leads to a dissolution or removal of the octahedral sheets and interlayer cations. Its resulting in an increase of the pore volume and pore diameter, an enrichment of residual amorphous SiO₂ and an increase of sorption properties.

The pH change of solvent during leaching process performed upon temperatures within range from 22 to 50 °C is shown in the Fig.3.7. The dependence of fractional conversion on the time was calculated according to formula 2.1 and 2.3 from measured pH on time dependence.

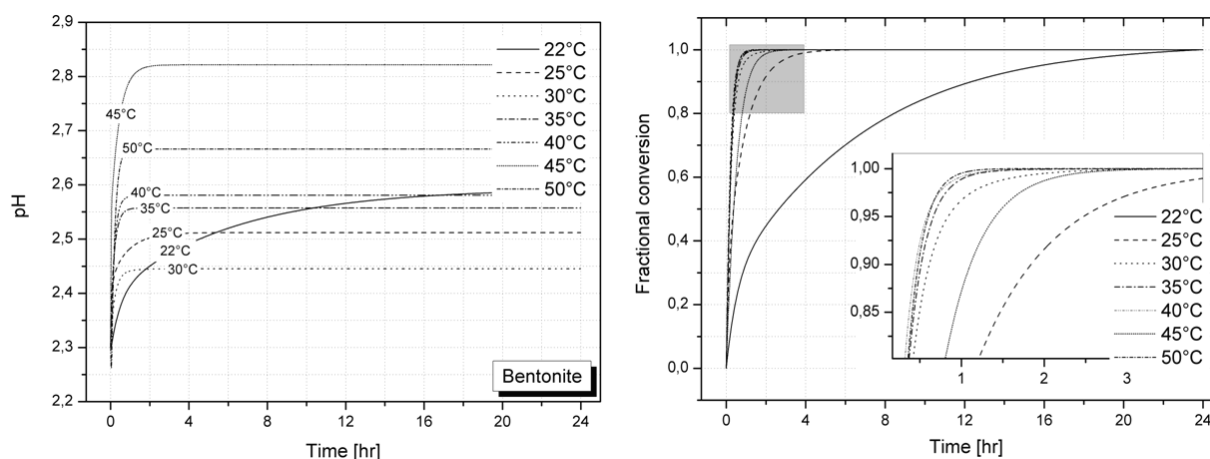


Fig. 3.7. The pH of leaching bath for experiment performed under different temperature and time dependence of fractional conversion.

The results of leaching experiment on montmorillonite clay show that mechanism of process is significantly affected by temperature. Linearization procedure leads to conclusion that the leaching process is handled by the stationary three-dimensional diffusion (D_4) at temperatures up to 25 °C, i.e. the course of leaching process can be characterized by Valensi-Ginstling-Brounstein (VGB) equation (Valensi, 1936; Ginstling and Brounstein, 1950):

$$g(y)=kt=1-\frac{2}{3}y-(1-y)^{2/3}$$

(3.6)

$$g(y)=kt=-\ln(1-y)$$

(3.7)

The Kolmogorov-Johnson-Mehl-Avrami (KJMA) equation shows the best results for experiments performed upon temperature interval from 30 to 40 °C. The kinetic function corresponding to the mechanism of random nucleation and subsequent growth of nuclei (F_1 or A_1) can be described by Eq.3.7. At temperatures higher than 40 °C the leaching process is forced by chemical reaction of $\frac{3}{4}$ th order ($F_{\frac{3}{4}}$), i.e. by mechanism non-invoking equation:

$$g(y)=kt=1-(1-y)^{1/4}$$

(3.8)

The Arrhenius plot is shown on Fig.3.8. The value of apparent activation energy that was determined upon the above mentioned temperature interval is listed in the Table 3.2.

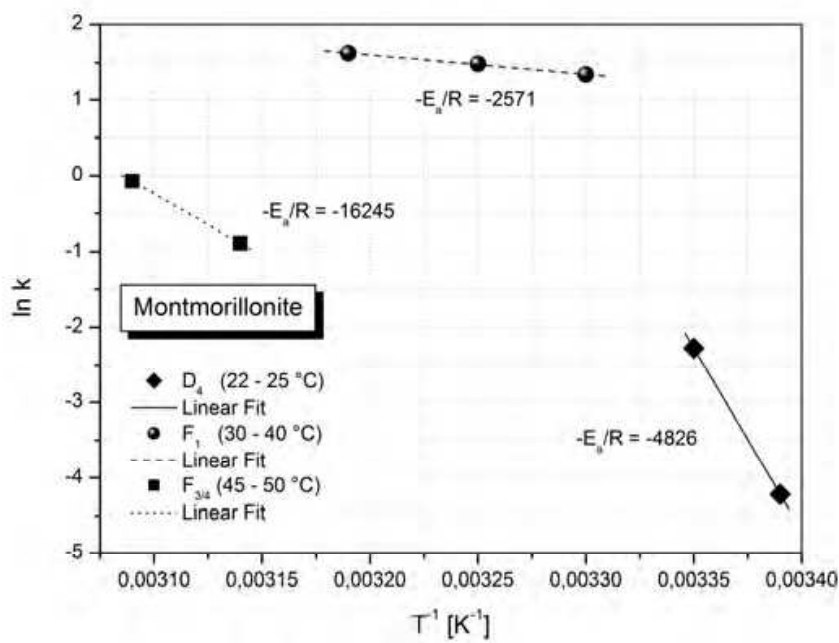


Fig. 3.8. The Arrhenius plot for the montmorillonite dissolved in diluted acetic acid.

T [°C]	Mechanism	k [s ⁻¹]	D = R ²	E _a [kJ mol ⁻¹]
22	D4: 1 - 2y/3 - (1 - y) ^{2/3}	1.47 · 10 ⁻²	0.999	388.9
25		1.02 · 10 ⁻¹	0.999	
30		3.82	0.999	
35	F1: -ln (1-y)	4.41	0.998	21.4
40		5.08	0.998	
45	F _{3/4} : 1 - (1-y) ^{1/4}	4.10 · 10 ⁻¹	0.997	135.1
50		9.23 · 10 ⁻¹	0.999	

Table 3.2. E_a of dissolution of montmorillonite clay. D=R² is the correlation coefficient of linear fit.

The results of ICP-OES analysis (Fig.3.9) of solvent after the leaching experiment show that predominantly extracted elements are Ca, Mg, Mg, Fe and Al. The amount of elements extracted per gram of clay raw material is listed in the Table 3.3.

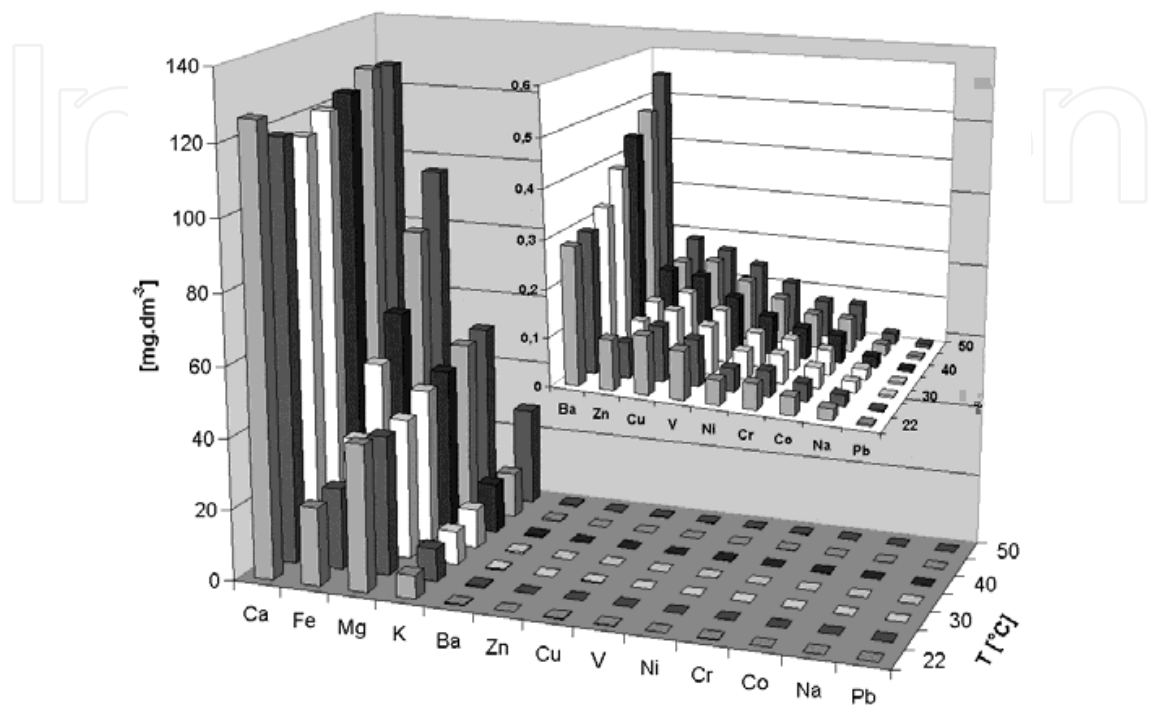


Fig. 3.9. Analysis of leaching bath composition.

With except of calcium where extracted amount is not correlated with temperature (Table 3.3), the amount of extracted elements is generally increasing with temperature. The higher temperature then enables to reach better activation of bentonite by acetic acid using higher temperatures due to increasing content of leached Fe and Mg. That behaviour results from the structure of mineral of smectite groups (Fig.3.2).

T	Element leached from the montmorillonite clay [$\mu\text{g.g}^{-1}$ of raw material]													
[$^{\circ}\text{C}$]	Al	V	Cr	Co	Ni	Cu	Zn	Ba	Pb	Na	Mg	K	Ca	Fe
20	751.84	20.112	10.758	7.558	10.19	24.33	21.082	57.054	0.778	4.838	8238	1320	25220	4410
25	743.18	19.642	10.484	7.522	9.526	23.194	14.552	58.856	0.76	4.628	7850	1844	23780	4576
30	722.36	20.326	11.992	8.546	11.608	25.148	18.97	65.142	0.778	4.496	7946	1892	23250	6560
35	775.7	22.356	13.164	10.596	14.396	28.098	22.522	77.964	0.828	4.596	8820	2232	24160	10088
40	807.03	23.064	13.37	11.738	16.662	30.824	31.928	88.106	1.042	4.624	9148	2786	24670	12260
45	824.9	25.888	14.446	14.152	19.832	33.072	31.434	96.29	1.06	4.662	9932	2570	25560	16336
50	845.88	28.826	15.622	15.776	22.384	33.866	37.566	109.69	1.588	4.542	10160	5550	25350	19284

Table 3.3. Influence of temperature on the extraction process.

While calcium is placed in place interlayer space and should be then easily replaced by sodium by cation exchange process, magnesium is bonded in brucite sheet of T-O-T complex and it can be released only after its dissolution. That is also the reason for observed correlation of Mg on the amount of extracted Al and other cation (Fe^{3+} , Cr^{3+} , V^{3+} ...) coordinated octahedrally in the "O" layer.

	T	Al	V	Cr	Co	Ni	Cu	Zn	Ba	Pb	Na	Mg	K	Ca	Fe
T	1.00														
Al	0.89	1.00													
V	0.94	0.94	1.00												
Cr	0.98	0.89	0.96	1.00											
Co	0.98	0.95	0.99	0.98	1.00										
Ni	0.97	0.95	0.98	0.98	1.00	1.00									
Cu	0.97	0.95	0.95	0.97	0.98	0.99	1.00								
Zn	0.89	0.95	0.93	0.92	0.94	0.95	0.96	1.00							
Ba	0.99	0.95	0.97	0.98	0.99	1.00	0.98	0.95	1.00						
Pb	0.85	0.87	0.94	0.86	0.90	0.90	0.84	0.90	0.91	1.00					
Na	-0.49	-0.08	-0.29	-0.42	-0.33	-0.32	-0.26	-0.15	-0.37	-0.31	1.00				
Mg	0.93	0.98	0.97	0.95	0.98	0.98	0.98	0.95	0.97	0.86	-0.14	1.00			
K	0.83	0.80	0.90	0.84	0.85	0.85	0.78	0.81	0.87	0.98	-0.46	0.79	1.00		
Ca	0.48	0.78	0.67	0.54	0.64	0.65	0.67	0.73	0.60	0.60	0.51	0.77	0.43	1.00	
Fe	0.98	0.95	0.98	0.98	1.00	1.00	0.98	0.94	1.00	0.90	-0.35	0.98	0.85	0.62	1.00

Table 3.4. Correlation table showing mutual relationships between temperature and amount of leached elements. The significant correlation is marked by bold.

The increasing efficiency of extraction process is shown in Table.3.5 as the calculated amount of carbon dioxide that may be captured by the extracted element in formed carbonate. The results indicate that extraction efficiency should be significantly improved by activation process performed at higher temperatures.

T [°C]		22	25	30	35	40	45	50
Ca	kgCO ₂ /	27.7	26.1	25.5	26.5	27.1	28.1	27.9
Mg	1000 kg	14.9	14.2	14.4	16.0	16.6	18.0	18.4
Fe	raw	3.5	3.6	5.2	8.0	9.7	12.9	15.2
Σ	clay	46.1	43.9	45.9	50.5	53.3	58.9	61.4
CaCO ₃	kg	63.6	60.0	58.6	60.9	62.2	64.5	63.9
MgCO ₃		28.6	27.2	27.6	30.6	31.7	34.5	35.3
FeCO ₃		9.1	9.5	13.6	20.9	25.4	33.9	40
Σ		101.3	96.7	99.8	112.5	119.4	132.8	139.2

Table 3.5. Bentonite clay activation efficiency.

The solid rest that is resulting from the leaching process was analysed by TA, IR and SEM to determine its properties for the usage in cements due to estimated pozzolanic activity or as absorption agents. Table 3.6 show that higher specific surface of leaching rest should be obtained for the sample prepared at temperature 35 °C.

T [°C]	22	25	30	35	40	45	50
SS [m ² /g]	91.4	96.8	96.0	106.6	102.5	97.1	97.8

Table 3.6. Influence the temperature of leaching bath on the specific surface of solid rest.

The results of infrared spectroscopy are shown in Fig.3.10. The results indicate that the raw material activation process is based mainly on the reaction 3.5. The increasing shift of the Si-O-Si stretching mode with temperature of leaching process indicate that the minerals are affected only by the formation of thin leached silica layer on the surface of aggregate, i.e. only the first step of incongruent dissolution process takes place.

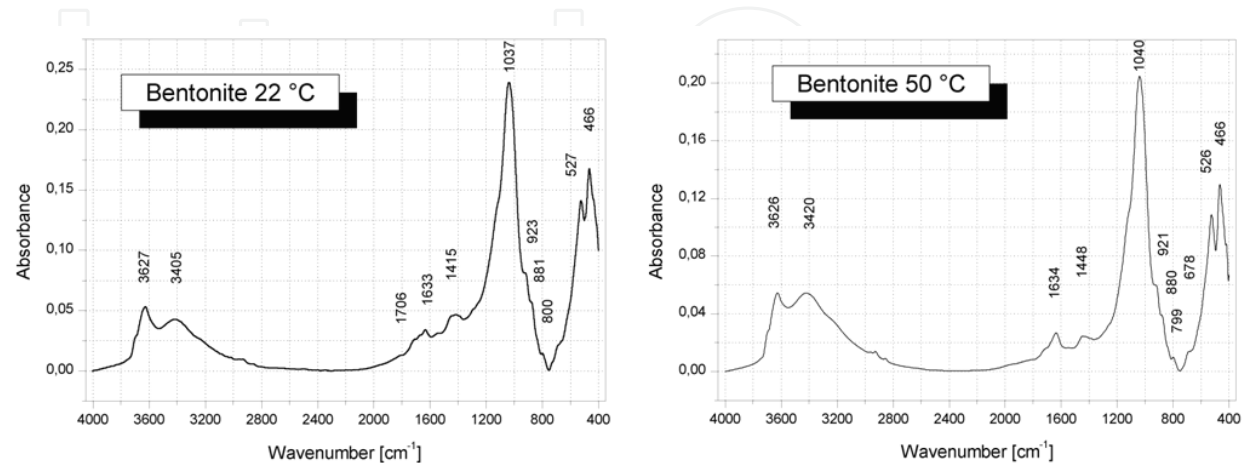
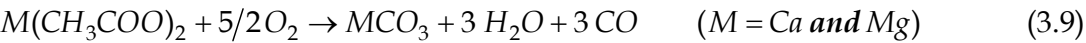


Fig. 3.10. Infrared spectrum of bentonite leached by acetic acid.

The results of thermal analysis (Fig.3.11) indicate introducing the salt of acetic acid into interlayer space of bentonite. The evaporation of acetic acid and burning of acetic salt are well visible on EGA. Thermal decomposition of acetates that is according to EGA connected with formation of acetone and carbon dioxide. Presence of carbon monoxide and dioxide bands upon the same temperature interval indicates the partially reduction condition of process that leads to formation of the calcium and magnesium carbonates:



Thermal decomposition of formed carbonates that takes place upon temperature interval from 700 to 900 °C is well visible on DTA as well as EGA pattern.

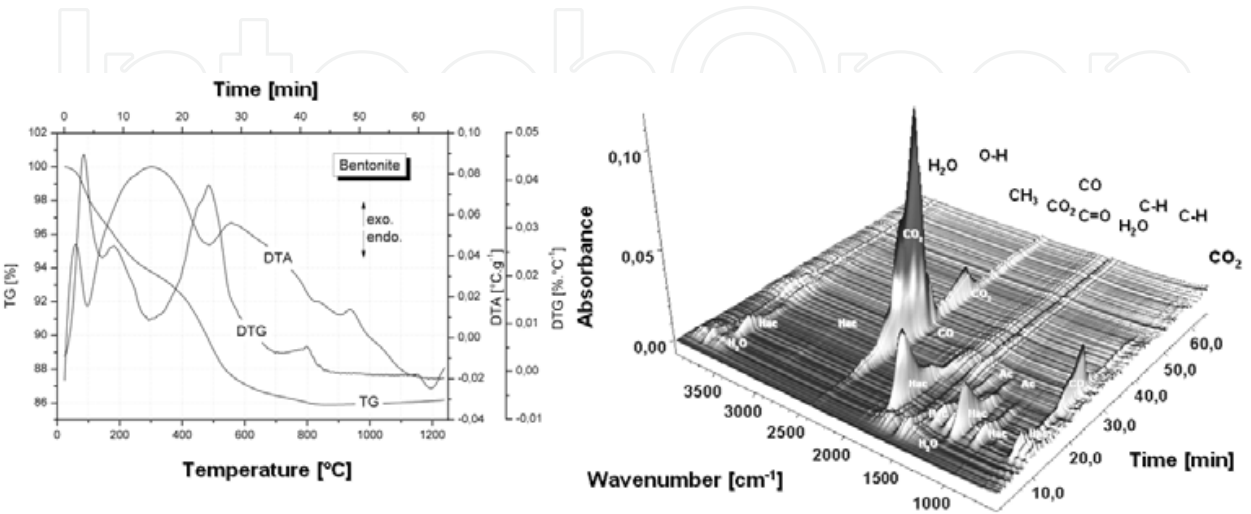


Fig. 3.11. Thermal analysis of solid rest after leaching process.

The SEM analysis of the clay after dissolution experiment is shown in Figure 3.12. The admixture of carbonate minerals (please see Fig.3.5) are dissolved at early stages of leaching process. The leached silica layer was formed on the surface of bentonite aggregates.

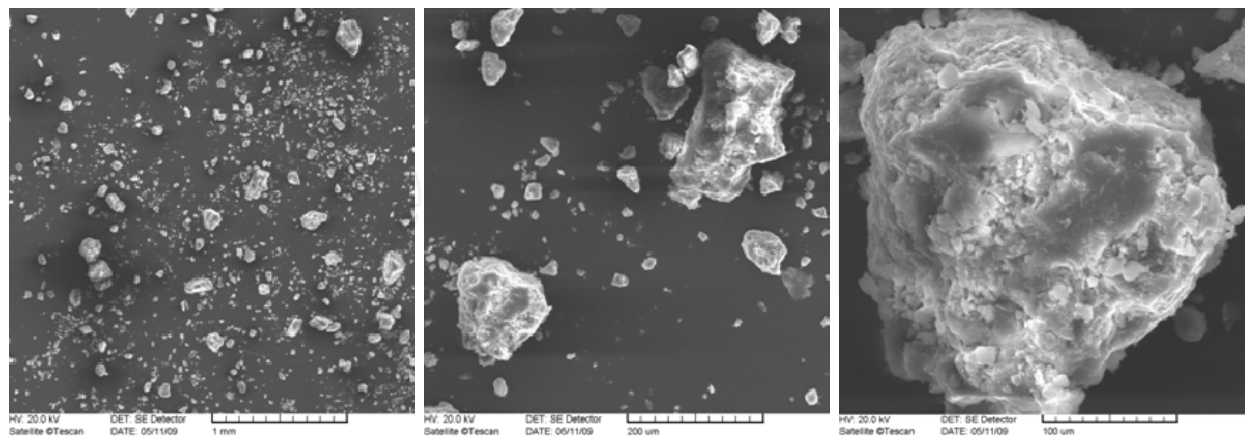
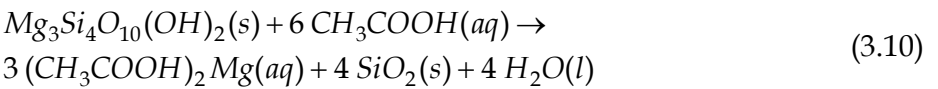


Fig. 3.12. The SEM of leached bentonite clay.

3.5 Dissolution of talc

The process of the dissolution of Talc in diluted solution of acetic acid should be described by following equation:



The measured dependence of pH on the time of dissolution and fractional conversion time dependence calculated according to Eq.2.1 and 2.3 is shown on Fig.3.13. To compare with bentonite clay, the course of talc activation process seems to be less affected by the temperature of leaching bath. Hence only the limit temperatures are plotted in the Fig.3.13.

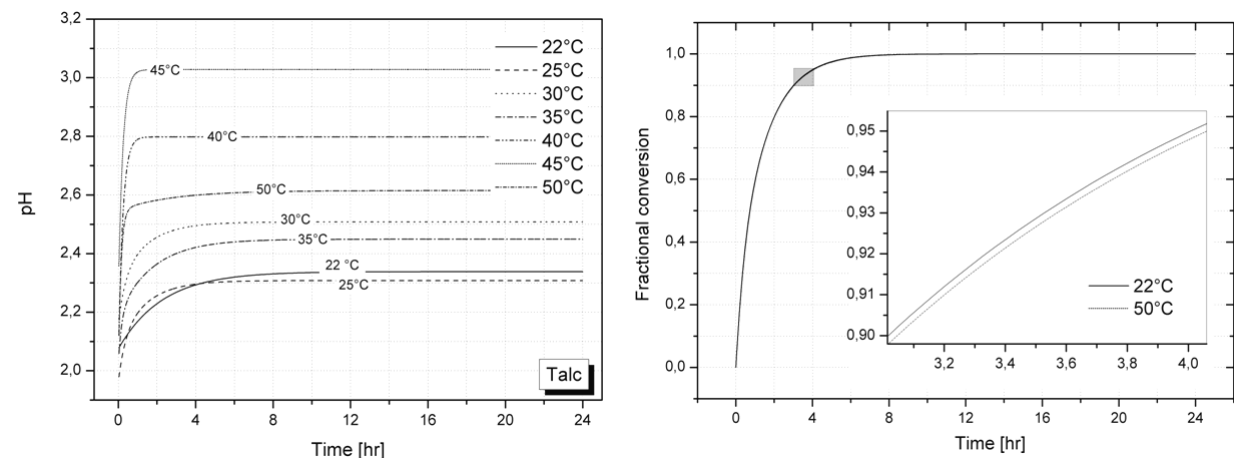


Fig. 3.13. The change of pH of leaching solution during activation of talc (a) and fractional conversion on time dependence (b).

The kinetic of leaching process should be described by the kinetic law:

$$y = 1 - \exp \left(- K t^{\frac{7}{6}} \right)$$

(3.11)

where kinetic exponent (Avrami’s factors) has value of 1.2.

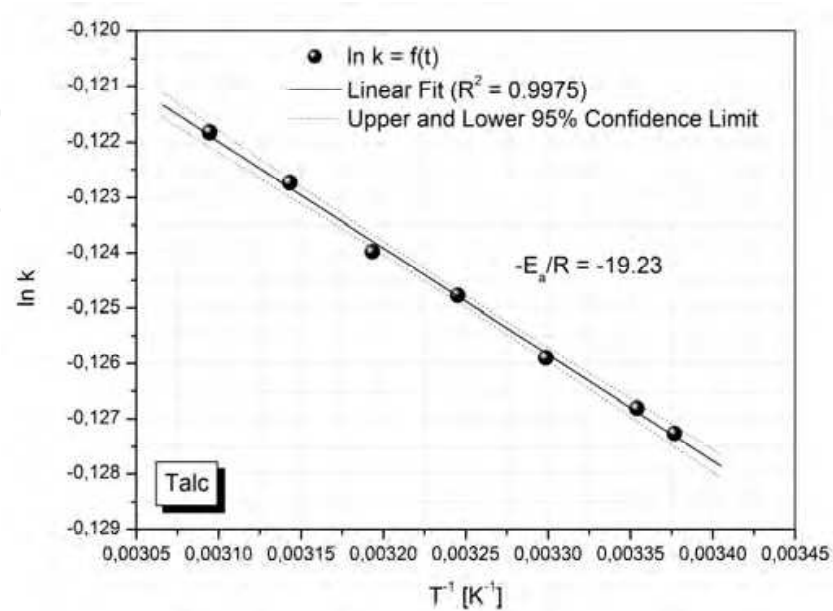


Fig. 3.14. The Arrhenius plot for the talc dissolved in diluted acetic acid.

The Arrhenius plot that is shown in Fig.3.14 was used for determination the apparent activation energy of the leaching test from the dependence of $160 \pm 3 \text{ J}\cdot\text{mol}^{-1}$. The results of ICP-OES analysis of solvent after leaching tests performed within the temperature interval from 22 to 50 °C are plotted in Fig.3.15.

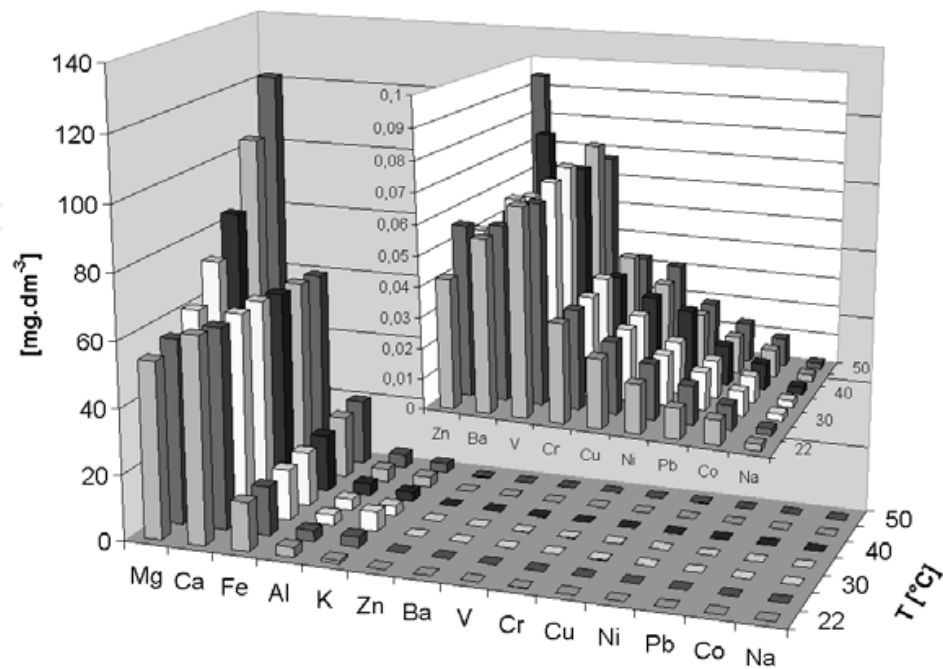


Fig. 3.15. The composition of leaching bath after leachig process.

There it is obvious that the amount of extracted magnesium and iron is strongly affected by the temperature while the calcium content is slightly decreasing with increasing temperature of solvent. It should be thus supposed that Ca come to solution in very short time after pouring the solvent during dissolution of the admixture of carbonates in the raw material. The negative temperature dependence is probably caused by absorption of calcium on leached layer that is formed on the surface of talc aggregates.

T [°C]	Element leached from the montmorillonite clay [µg·g ⁻¹ of raw material]													
	Al	V	Cr	Co	Ni	Cu	Zn	Ba	Pb	Na	Mg	K	Ca	Fe
20	612.55	13.53	6.44	1.6	3.17	4.51	8.48	11.29	1.96	0.4	10790	170	12580	2950
25	631.85	13.15	6.55	1.61	3.62	4.76	11.28	11.49	2.53	0.43	11330	620	12300	2970
30	661.65	13.93	6.67	1.62	3.38	4.79	10.38	12.63	2.53	0.44	12340	1190	12400	3100
35	696.86	14.39	7.16	1.71	3.4	4.94	9.6	12.21	2.49	0.44	14600	590	12450	3310
40	775.73	13.72	6.57	1.74	4.76	5.44	10.39	15.86	2.62	0.44	16870	540	12150	3460
45	804.73	14.82	7.28	1.85	3.75	5.63	10.79	12.2	2.48	0.46	20870	620	12100	3810
50	868.34	13.43	6.54	1.86	3.77	6.24	18.92	12.51	2.66	0.42	24300	570	11920	4050

Table. 3.7. Influence of temperature on the extraction process.

The increasing content of calcium in the leaching bath (please refer to Table 3.7) as well as the correlation between extracted amount of Al (Table 3.8) should be explained analogically with leaching test of montmorillonite clay.

	T	Al	V	Cr	Co	Ni	Cu	Zn	Ba	Pb	Na	Mg	K	Ca	Fe
T	1,00														
Al	0,98	1,00													
V	0,37	0,27	1,00												
Cr	0,38	0,26	0,93	1,00											
Co	0,96	0,97	0,43	0,44	1,00										
Ni	0,51	0,54	-0,05	-0,10	0,41	1,00									
Cu	0,96	0,99	0,14	0,16	0,94	0,50	1,00								
Zn	0,68	0,72	-0,31	-0,21	0,63	0,17	0,82	1,00							
Ba	0,42	0,43	0,04	-0,10	0,28	0,91	0,36	0,03	1,00						
Pb	0,69	0,61	0,05	0,19	0,51	0,57	0,62	0,55	0,50	1,00					
Na	0,43	0,30	0,70	0,71	0,34	0,41	0,21	-0,20	0,43	0,59	1,00				
Mg	0,97	0,98	0,28	0,29	0,98	0,40	0,98	0,76	0,27	0,54	0,23	1,00			
K	0,14	0,02	0,19	0,17	-0,06	-0,03	0,01	0,08	0,13	0,57	0,57	-0,02	1,00		
Ca	-0,89	-0,91	-0,01	-0,06	-0,85	-0,59	-0,95	-0,80	-0,38	-0,72	-0,27	-0,90	-0,11	1,00	
Fe	0,97	0,98	0,33	0,33	0,99	0,39	0,98	0,73	0,28	0,53	0,26	1,00	-0,01	-0,88	1,00

Table 3.8 Correlation table showing mutual relationships between temperature and amount of leached elements. The significant correlation is marked by bold.

The increasing efficiency of extraction process is shown in Table.3.9. The results indicate that extraction efficiency should be significantly improved by increasing of extracted Mg amount at higher temperatures.

T [°C]		22	25	30	35	40	45	50
Ca	kgCO ₂ / 1000 kg raw clay	13.8	13.5	13.6	13.7	13.4	13.3	13.1
Mg		19.6	20.5	22.4	26.4	30.6	37.8	44.1
Fe		2.3	2.3	2.4	2.6	2.7	3.0	3.19
Σ		35.7	36.4	38.4	42.7	46.6	54.1	60.3
CaCO ₃	kg	31.7	31.0	31.3	31.4	30.7	30.5	30.1
MgCO ₃		37.4	39.3	42.8	50.7	58.5	72.4	84.3
FeCO ₃		6.1	6.2	6.4	6.9	7.2	7.9	8.4
Σ		75.3	76.5	80.5	88.9	96.4	110.8	122.8

Table 3.9. Bentonite clay activation efficiency.

Table 3.10 show that higher specific surface of leaching rest after dissolution experiment.

T [°C]	22	25	30	35	40	45	50
SS [m ² /g]	3.2	3.3	2.9	3.1	3.1	3.1	3.6

Table 3.10. Influence the temperature of leaching bath on the specific surface of solid rest.

The infrared spectra of solid rest after leaching process are shown in Fig.3.16. The spectrum features indicate that the changes caused by leaching process are much lesser than in the case of bentonite.

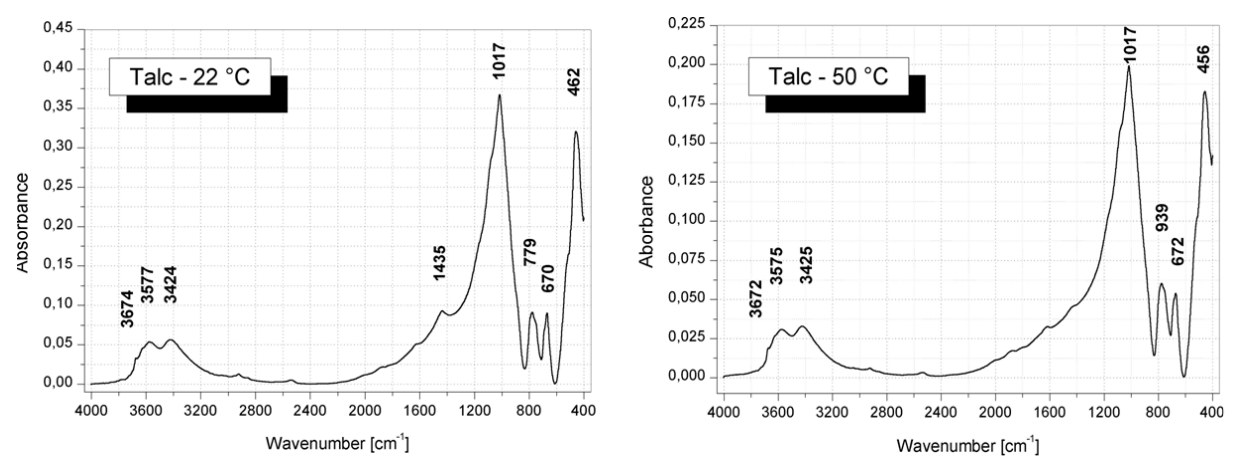


Fig. 3.16. Infrared spectroscopy of solid rest after activation of talc by acetic acid.

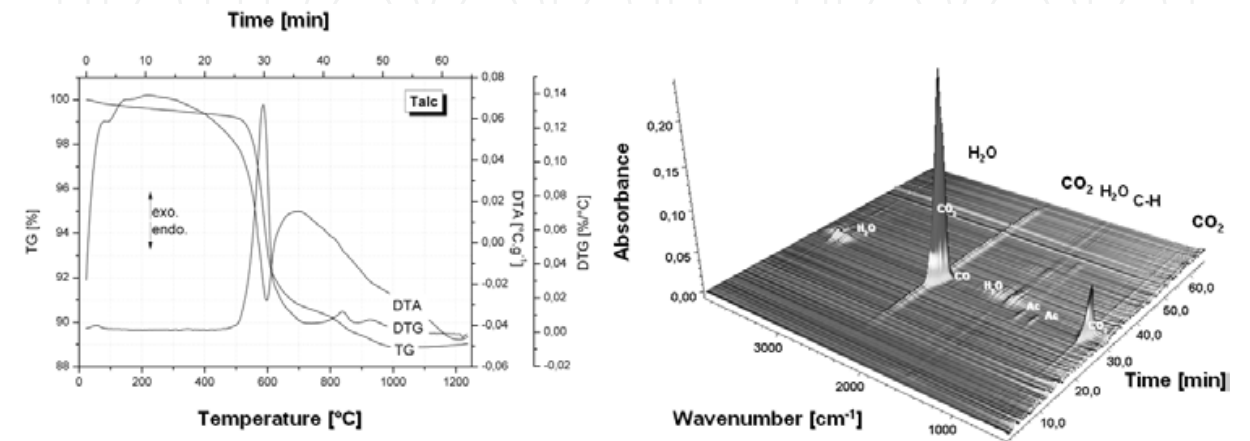


Fig. 3.17. Thermal analysis of solid rest after leaching process.

The typical results of thermal analysis shown on Fig.3.14. lead to the same conclusion. Thermal decomposition of acetates that is according to EGA connected with formation of carbon dioxide and acetone and dehydroxylation of talc are the main observed processes. With except of carbonate admixtures that were naturally dissolved, the results of SEM (Fig.3.18) do not show any significant changes in the activated talc material.

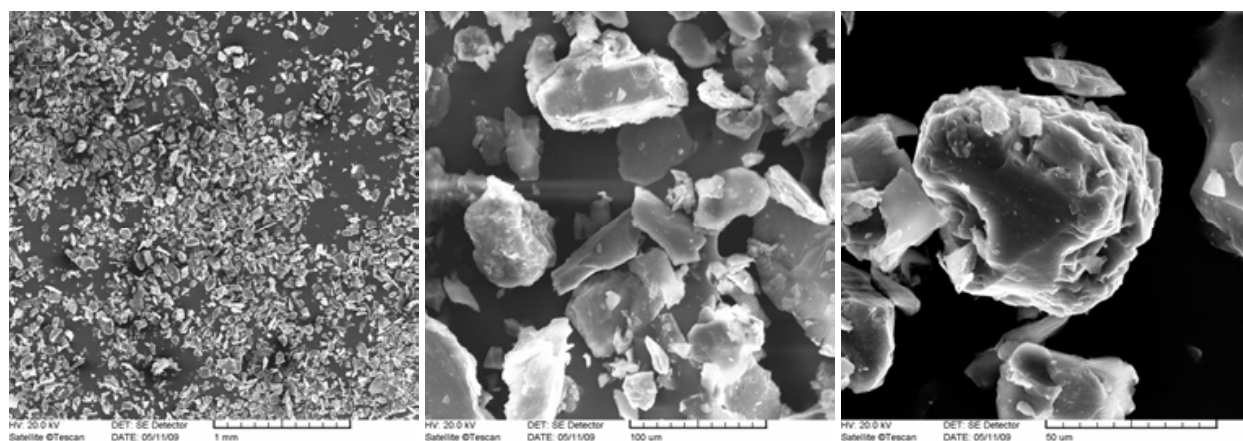


Fig. 3.18. Leached talc raw material.

4. Conclusion

The initial stage of bentonite leaching process is on exchange of Ca and K from the interlayer space of montmorillonite and illite. The dissolution of T-O-T complex that is promoted by higher temperature then leads to the release of Mg and other octahedrally coordinate ions. Storage capacity of bentonite clay for CCS should be then significantly improved by activation process performed at elevated temperature. Increasing temperature promotes the rate of incongruent leaching process. The process of activation of talc shows also significant influence of leaching bath on the process. While amount of extracted calcium remains constant or slightly decrease due to absorption phenomena, the amount of extracted calcium should be significantly improved with increasing temperature of leaching bath. The capacity for CO₂ caption is at about 35 % higher for the clay of montmorillonite. This difference is decreasing with increasing temperature of leaching bath.

5. Acknowledgment

This paper is supported by the research project of ERDF no. CZ.1.05/2.1.00/01.0012'' Centres for Materials Research at FCH BUT''.

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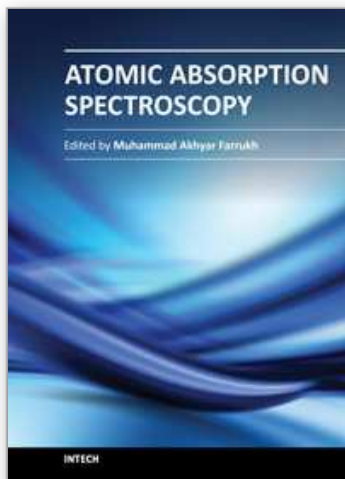
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Edited by Dr. Muhammad Akhyar Farrukh

ISBN 978-953-307-817-5

Hard cover, 258 pages

Publisher InTech

Published online 20, January, 2012

Published in print edition January, 2012

Atomic Absorption Spectroscopy is an analytical technique used for the qualitative and quantitative determination of the elements present in different samples like food, nanomaterials, biomaterials, forensics, and industrial wastes. The main aim of this book is to cover all major topics which are required to equip scholars with the recent advancement in this field. The book is divided into 12 chapters with an emphasis on specific topics. The first two chapters introduce the reader to the subject, its history, basic principles, instrumentation and sample preparation. Chapter 3 deals with the elemental profiling, functions, biochemistry and potential toxicity of metals, along with comparative techniques. Chapter 4 discusses the importance of sample preparation techniques with the focus on microextraction techniques. Keeping in view the importance of nanomaterials and refractory materials, chapters 5 and 6 highlight the ways to characterize these materials by using AAS. The interference effects between elements are explained in chapter 7. The characterizations of metals in food and biological samples have been given in chapters 8-11. Chapter 12 examines carbon capture and mineral storage with the analysis of metal contents.

How to reference

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Petr Ptáček, Magdaléna Nosková, František Šoukal, Tomáš Opravil, Jaromír Havlica and Jiří Brandštetr (2012). Activation of Bentonite and Talc by Acetic Acid as a Carbonation Feedstock for Mineral Storage of CO₂, Atomic Absorption Spectroscopy, Dr. Muhammad Akhyar Farrukh (Ed.), ISBN: 978-953-307-817-5, InTech, Available from: <http://www.intechopen.com/books/atomic-absorption-spectroscopy/activation-of-bentonite-and-talc-by-acetic-acid-as-a-carbonation-feedstock-for-mineral-storage-of-co>

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