



Modelling the solubility of sparingly soluble compounds depending on their particles size

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Abstract. The aim of the current study was to investigate and model particle size dependence of the dissolution process of $\text{Ca}(\text{OH})_2$, CaCO_3 , and oil shale ash. In the samples of the self-regulating equilibrium system H_2O –dissolved CO_2 –solid CaCO_3 filtered through a 0.45 μm filter no nanoparticles were detected. The nanoparticles appeared when the pH had been increased to 12.3 and the value of the product of the molar concentrations of the Ca^{2+} and OH^- ions reached the value of the solubility product constant K_{sp} . When different amounts of $\text{Ca}(\text{OH})_2$ were added to degassed water, the pH increased and nanoparticles started to appear in the solution containing 0.5 g/L of solid $\text{Ca}(\text{OH})_2$ (pH = 12.3). Up to this value of the pH all particles had dissolved. Due to the better solubility of small particles connected to the rise of the value of the solubility product constant K_{sp} for nanoscale particles, the solubility of $\text{Ca}(\text{OH})_2$, the concentration of Ca^{2+} ions, and the pH increased. The pH of oil shale ash leachate increased with the increasing of the amount of ash, as the quantity of nanoparticles increased in a similar manner as described for the solubility of $\text{Ca}(\text{OH})_2$.

Key words: calcium carbonate, calcium hydroxide, carbon dioxide, solubility, particle size.

1. INTRODUCTION

The systems containing dissolved CO_2 and limestone, which mainly consists of CaCO_3 , have a great importance in the environmental and technological processes. Limestone containing oil shale is used in power plants applying either pulverized oil shale or circulated fluidized bed combustion technologies. The lower combustion temperature in the latter technology reduces the decomposition of CaCO_3 . Thus, the emission of CO_2 is reduced in comparison with the pulverized firing technology [1,2].

Proton-centred models have been developed for the open [3] and closed self-regulating systems [4] H_2O –

dissolved $(\text{CO}_2)_\text{w}$ –solid CaCO_3 . We earlier showed that if solid CaCO_3 is added to an initial equilibrium system H_2O – $(\text{CO}_2)_\text{w}$, the pH will increase and the achieved constant value will be dependent on the initial concentration of $(\text{CO}_2)_\text{w}$. The formation of a new closed equilibrium system leads to a decrease of the concentrations of carbon dioxide $(\text{CO}_2)_\text{w}$ in the water phase [4]. The final value of pH does not depend on the amount of added CaCO_3 and corresponds to the model-predicted one. However, this results in a faster rise of the pH due to the larger specific surface area of the particles [4].

According to Zumdahl [5], the aqueous solubility of sparingly soluble compounds in equilibrium with the solid phase is constant and corresponds to the value of the solubility product constant K_{sp} . The product of molar concentrations of the ions formed in the dissolution has

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a infinite number of possible values, depending on the conditions, such as presence of a common ion and temperature [5].

The Kelvin equation is also applied to determine the equilibrium solubility of solids in a liquid. In this case the ratio of vapour pressures is changed to the solubility of the spherical and flat particles but the surface tension μ used for the gas–liquid interface can not be applied for an interface involving solids. The thermodynamic approach makes it clear that the curvature of the surfaces of particles has an essential effect on the solubility in the case of small particles [6]. The surface free energy interpretation is more plausible for solids than surface tension, which is useful for gas–liquid interfaces. Although the increase in the solubility of small particles is unquestionably a real effect, using it quantitatively as a means of evaluating μ is fraught with difficulties [6]. It is generally accepted that neither the amount of excess solid nor the size of the particles present in the system will change the position of the equilibrium. This concept is still popular in many current textbooks [7].

The aim of the current study was to examine the role of nanoparticles in the process of the dissolution of sparingly soluble compounds such as CaCO_3 , Ca(OH)_2 , and also oil shale ash.

2. MATERIALS AND METHODS

In the experiments with CaCO_3 (Sigma-Aldrich, 99.95%) the used demineralized water was purged with ambient air before CaCO_3 was added to establish the equilibrium concentration of CO_2 in the water phase. In the

experiments with Ca(OH)_2 (Acros, 99.995%) and oil shale ash from an electrostatic precipitator, the demineralized water was purged to remove dissolved CO_2 with pure N_2 gas at 25 °C for 30 min. During the purging with N_2 gas or air, the samples were mixed at 500 rpm. The pH was measured with an Evikon pH meter E6115. The samples were filtered through 0.45 μm membrane filters. The concentration of Ca^{2+} ions was determined by titration with EDTA and the concentration of OH^- ions by titration with HCl. To measure the particles sizes and count nanoparticles, nanoparticle tracking analysis was carried out by applying standard measurements of a NanoSight LM10 Viewing Unit (Malvern Instruments Ltd., United Kingdom).

3. RESULTS AND DISCUSSION

In the filtrated samples of the closed self-regulating system H_2O –dissolved $(\text{CO}_2)_\text{w}$ –solid CaCO_3 no particles were detected by nanoparticle tracking analysis. Nanoparticles of Ca(OH)_2 appeared in the solution when the pH was increased by the addition of NaOH to 12.3 as the value of K_{sp} was exceeded (Fig. 1a). According to the literature data, the pH of the saturated solution of Ca(OH)_2 is about 12.4, used as a standard of highly alkaline pH [8], which well corresponds to the results of the present research.

When different amounts of solid Ca(OH)_2 were added to water, nanoparticles were detected in samples starting from the amount 0.5 g/L ($\text{pH} \geq 12.3$). Up to this value of the pH all particles dissolved. Due to the better solubility of small particles in the nanoscale region, the

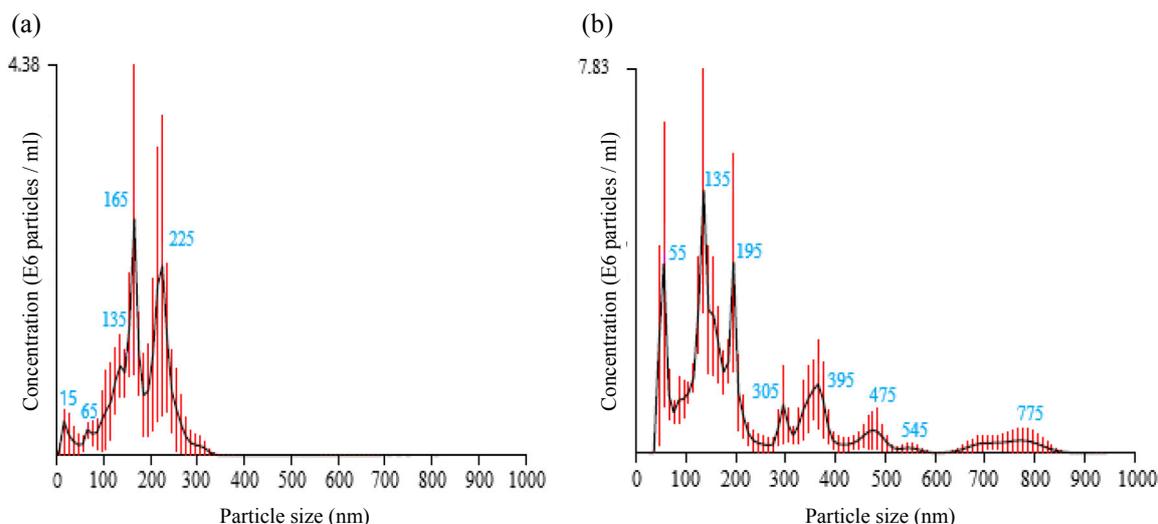


Fig. 1. Size distribution of nanoparticles in the filtrated CaCO_3 solution where the pH had been increased to a value of 12.3 (a) and suspension of oil shale ash from an electrostatic precipitator (3 g/L) (b). Red error bars indicate ± 1 standard error of the mean.

solubility of $\text{Ca}(\text{OH})_2$, the concentration of Ca^{2+} ions, and the pH increased. When the added amount of $\text{Ca}(\text{OH})_2$ was raised till 10 g/L, the pH value approached 12.9. This phenomenon can be explained by an increase in the solubility of nano-size particles and the value of the solubility product K_{sp} .

The size distribution of particles in the filtrated suspension of oil shale ash from an electrostatic precipitator (3 g/L) is shown in Fig. 1b. The average pH values of 12.7 of oil shale ash suspensions are primarily attributable to the high content of metal oxides in the ash, which will react with water, and hydroxides will be formed. As it prevails over other metal oxides [2], CaO gives an essential contribution to the formation of an equilibrium system upon the dissolution of $\text{Ca}(\text{OH})_2$.

4. CONCLUSIONS

In the filtrated samples of the closed self-regulating system H_2O –dissolved $(\text{CO}_2)_\text{w}$ –solid CaCO_3 , no particles were found at pH values below 12.3. When this value of the pH had been achieved, nanoparticles appeared in the liquid phase. When different amounts of $\text{Ca}(\text{OH})_2$ were added to the water, the pH rose but nanoparticles were detected in samples when the amount of added solid $\text{Ca}(\text{OH})_2$ was 0.5 g/L and higher ($\text{pH} \geq 12.3$). The quantity of nanoparticles rose with the increasing of the amount of added $\text{Ca}(\text{OH})_2$ to water. At 10 g/L of added $\text{Ca}(\text{OH})_2$, the pH value reached 12.9. This phenomenon can be explained by an increase in the solubility of nano-size particles and also the rise of the value of the solubility product K_{sp} . The average pH value 12.7 of oil shale ash suspensions is primarily attributable to metal oxides in the ash, which react with water forming hydroxides.

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Vähelahustuvate ühendite lahustuvuse modelleerimine sõltuvalt osakese suuruselt

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Käesoleva uurimistöö eesmärk oli modelleerida CaCO_3 , $\text{Ca}(\text{OH})_2$ ja põlevkivi põletamisel tekkiva elektrifiltritua lahustumisprotsessi sõltuvalt nanoosakeste suuruselt vedelfaasis. Tasakaalulise süsteemi H_2O – lahustatud CO_2 – tahke CaCO_3 filtreerimisel läbi 0,45 μm membraanfiltrit ei leitud lahuses nanoosakesi. Nanoosakesed ilmusid, kui lahuse pH-d suurendati väärtuseni 12,3. Tahke faasi moodustumine algab, kui $\text{Ca}(\text{OH})_2$ lahustuvuskorrutise (K_{sp}) väärtus on ületatud. Kui degaseeritud veele lisati erinevad kogused $\text{Ca}(\text{OH})_2$, suurenes süsteemi pH. Alates lisatud tahke $\text{Ca}(\text{OH})_2$ kogusest 0,5 g/L suurenes pH 12,3-ni ja lahusesse hakkasid ilmuma nanoosakesed. Kui suurendati lisatud tahke $\text{Ca}(\text{OH})_2$ hulka, Ca^{2+} -iooni kontsentratsioon ja pH tõusid, mis on tingitud K_{sp} väärtuse suurenemisest lisandunud $\text{Ca}(\text{OH})_2$ sisaldavate nanoosakeste tõttu. Põlevkivitua pH väärtus tõuseb tuha koguse suurenemisega, sest nanoosakeste kogus kasvab analoogiliselt $\text{Ca}(\text{OH})_2$ lahustumisega.