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Determination of the reactivity of $CaSO_4 \cdot 2H_2O$

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Abstract: Reactivity of energy gypsum was investigated. The method is based on the conversion reaction of aqueous suspension of gypsum with ammonium carbonate solution. Rate of the conversion of all investigated samples, including gypsum originating from flue gas desulphurization (FGD), was high and 80 % conversion was achieved during one hour. It was found that there is a correlation between BET specific surface and the rate of the conversion reaction.

Keywords: FGD gypsum, reactivity of $CaSO_4 \cdot 2H_2O$, ammonium carbonate, BET surface

Introduction

Gypsum ($CaSO_4 \cdot 2H_2O$) occurs in nature as a mineral and it is also formed as a side product from desulphurization processes. When it originates from a coal power plant, we call it flue gas desulphurization (FGD) gypsum. Because of desulphurization process; acid rains do not bring such amount of sulphur species into the nature like in the past. From a general environmental view, this is a positive phenomenon. However, plants require sulphur species for their development and these species have to be supplied by fertilizers containing ammonium sulphate (AS) or other sulphate containing compounds. A typical representative of fertilizer containing AS is ammonium sulphate nitrate fertilizer (ASN) that is produced for example by YARA, BASF, and Duslo in Slovakia. The main classical sources of AS are productions of caprolactame, methylmetacrylate, pyrolysis of coal in the production of coke and from various desulphurization processes using ammonia. In Slovakia, ammonium sulphate used to be a side product (waste material till 1980) was from the production of caprolactame and methylmetacrylate in PCHZ Žilina. Nowadays that manufacture is closed and Duslo as the producer of ASN fertilizer takes AS from foreign suppliers, or AS is generated by the reaction of sulphuric acid with ammonia directly in the reactor for the preparation of ASN slurry (Horváth et al., 2015).

One of the possibilities (besides the reaction of sulphuric acid with ammonia) is the production of ammonium sulphate by the so called conversion reaction between gypsum and the mixture of carbon dioxide and ammonia:

$$CaSO_4(s) + 2NH_3(g) + CO_2(g) + H_2O(l) = (NH_4)_2SO_4(aq) + CaCO_3(s) \quad (1)$$

Tab. 1. The enthalpy and Gibbs energy of the reaction (1).

t/°C	$\Delta H°/kJ \cdot mol^{-1}$	$\Delta G°/kJ \cdot mol^{-1}$
0	–178.3	–51.8
20	–178.5	–42.5
40	–178.8	–33.3
60	–179.0	–24.0

The reaction scheme (1) does not describe exactly the conversion reaction because it contains anhydrous calcium sulphate instead of dihydrate. It is shown here only for illustration that the Gibbs energy of the conversion reaction at ambient temperature is negative. At higher temperatures the standard Gibbs energy is less negative. Besides, at temperatures higher than ca 60 °C compounds like NH_2COONH_4 and/or $(NH_4)_2CO_3 \cdot 2NH_4HCO_3$ can be formed (Blouin et. al., 1970). When ammonium carbonate is used instead of ammonia and carbon dioxide, it is necessary to be aware of its decomposition when the temperature is increased. As a result the temperature of the conversion reaction should not exceed 60 °C.

The discussed conversion process of gypsum is not new. It was carried out for the first time in industrial scale in Merseburg (Germany) in 1909. That's why it is often called the Merseburg process. The economy of this process is crucial, and it is derived from a relatively sophisticated reactor system, the price for ammonia (rather high) and CO_2 (low). The price for gypsum was also very low because it was a side product from the production of phosphate components from apatites (Gowariker et al., 2009). The conversion of gypsum might be economically viable today because of growing expenses related to the deposition of FGD-gypsum and the price for

release of CO_2 which is captured as $CaCO_3$ in the Merseburg process. Moreover, as it has been mentioned above, ammonium sulphate is more desired product today than in the past, which positively influences its price.

For design of the industrial process it is necessary to know the kinetics of the conversion reaction. This problem is widely discussed in the papers (Elkanzi and Chalabi, 1991; Ganz et al., 1959).

E.M. Elkanzi and M.F. Chalabi investigated kinetics of the reaction between suspension of gypsum and the solution of ammonium carbonate. According to their opinion, kinetics in the three phase system (suspension of gypsum in water + mixture of gases NH_3, CO_2) depends on the following steps:

1. mass transfer gas/liquid,
2. chemical reaction of formation of solution of ammonium carbonate,
3. transport of ammonium carbonate through the film "liquidus/solidus",
4. diffusion of ammonium carbonate through the layer of calcium carbonate, which is the solid product of the conversion reaction,
5. chemical reaction on the surface of unreacted calcium sulphate.

They carried out the experiments in the temperature range 10—20 °C (interval 5 °C). Suspension contained 5 mass % of gypsum. Saturated solution of ammonium carbonate was added in excess to the stoichiometry of the conversion reaction. Size of gypsum particles was lower than 50 μm and rotation of stirrer was 2200 min^{-1}. The authors came to the conclusion that the first two steps do not influence kinetics of the reaction. On the basis of the literature and their own experimental data they proposed a pseudo-first-order kinetic model describing the conversion process. The activation energy was determined to be 72 $kJ \cdot mol^{-1}$. It is important to stress that the mass transport effects were eliminated by the vigorous stirring.

G.M. Blouin et al. (1970) claim that the optimal temperature of the conversion reaction is in the range (50—60) °C. After 2 h the conversion of gypsum was from 95 % to 98 %.

Experimental

In this work, we tested two methods used for the determination of the rate of the conversion reaction.

Chemicals

The method proposed for the determination of the rate of the conversion reaction was tested using 4 samples of gypsum. One was FGD gypsum (gypsum A), the other three samples were of purity *pro analysis* supplied by different companies. Merck, pro analysis grade (gypsum 1); Mikrochem, pro analysis grade (gypsum 2) and Riedel de Haen, extra pure grade (gypsum 3). Other chemicals: $(NH_4)_2CO_3$ p.a., LACH-NER, CZ; HCl p.a., Centralchem, SK; NaOH p.a., Mikrochem, SK.

Characterization of gypsum

The BET specific surface was calculated from nitrogen adsorption isotherms at –196 °C using ASAP-2400 (Micromeritics, Norcross, USA). The problem is that for this measurement the sample has to be evacuated. Unfortunately, gypsum is a dihydrate and it partly decomposes when exposed to vacuum. Therefore, pressure of about (20—30) Pa was used instead of a common value 2 Pa, and evacuation was carried out for 24 h at 80 °C.

Particle size distribution was measured using a laser particle size distribution analyser CILAS 930 Liquid from CILAS (France). Water or various organic solvents, mainly methanol and ethanol, can be used as a dispersing medium. A typical amount of the sample (ca 100 mg) is poured into the container filled with the liquid (approx. 400 ml), slightly stirred and closed. Exact amount of sample depends on the particle size and it has to be determined from testing measurements. Measurements without ultrasound and with ultrasound should be performed to estimate the existence of agglomerates. Data were treated using the SizeExpert V9.08 SW. It was found that slightly higher values of mean size diameter were obtained using methanol as a dispersing medium instead of water. Explanation for such behaviour is that the water free methanol probably extracts water from gypsum and consequently agglomerates of gypsum are more stable and they are not disintegrated to such extent as in the case of water used as dispersing medium.

Procedure 1

This procedure is based on the determination of unreacted ammonium carbonate entering the reaction

$$CaSO_4(s) + (NH_4)_2CO_3(aq)) = \\ = (NH_4)_2SO_4(aq) + CaCO_3(s) \quad (2)$$

Starting concentration of the solution of ammonium carbonate was ca 0.8 $mol \cdot dm^{-3}$. The exact concentration of ammonium carbonate in the solution was determined by adding known amount of excess HCl solution (1 $mol \cdot dm^{-3}$) and its back titration with solution of NaOH (1 $mol \cdot dm^{-3}$). Methyl orange was used as an indicator.

The reaction between gypsum and ammonium carbonate was carried out in a 400 ml beaker placed into a water bath heated to the desired temperature. 250 ml of the solution of ammonium carbonate was

put into the beaker and well dispersed suspension of gypsum (stoichiometric amount (34.4 g) according to the reaction (2)) was added. Prior to mixing, all the reagents had the same temperature. It was found out that for good reproducibility of the data, thorough dispersion of gypsum was necessary. The mixture of reagents was stirred (200 rpm) with a single-impeller stirrer (VEB MLW Prüfgeräte, Medingen, Germany). From the reaction mixture, 10 ml of suspension was sampled in chosen intervals. Pure liquid was quickly separated from solid particles using a centrifuge. 10 ml of HCl solution was added to 5 ml of pure liquid obtained from the centrifuge. The solution was shortly heated (CO_2 bubbles escaped) and after cooling it was back titrated with NaOH solution using methyl orange as the indicator.

Procedure 2

This procedure is based on the determination of sulphates generated according reaction (2). 25.00 g of gypsum dried at 60 °C for 48 h is carefully dispersed in 50 ml of deionized water. 30 % solution of ammonium carbonate is added in 10 % excess with respect to stoichiometry. The suspension is stirred and kept at the desired temperature in the water bath as mentioned above. At the end of the experiment, the reacting suspension is filtrated and filtration cake is washed with 25 ml deionized water. Sulphates are precipitated with excess of barium chloride solution. Besides barium sulphate, also barium carbonate can precipitate. This has to be decomposed by HCl solution. After washing, the amount of sulphates is determined by gravimetry. This method can be used as a supplement to the first procedure.

Results and Discussion

For quantitative evaluation of the rate of the conversion reaction, the following parameters were chosen:

i) Initial rate of the reaction. This parameter can be determined by the extrapolation of the conversion curve (see figures) to zero time, $\tau = 0$.
ii) Half-time of the reaction.
iii) Conversion reached after certain time. On the basis of obtained results, we chose 25 min as the most reliable time for estimation of this parameter.
iv) Maximum conversion achieved.

Initial rate estimated by extrapolation of the conversion curve is not a reliable parameter, because it is influenced very much by the disintegration of agglomerates formed by gypsum particles. Half-time of the reaction is also determined from the conversion curve. It is reliable parameter if approximately 65 % conversion is reached at the half-time of the reaction. Definitely it is a better parameter for estimation of the reaction rate than the initial rate of the reaction.

Our tests showed that the conversion reached after a chosen time (25 min in this work) is the most reliable parameter characterizing the rate of the reaction. As illustrated bellow, this parameter has a good reliability. During 25 min, agglomerates are already disintegrated. Maximum conversion has also to be related to a specific reaction time. However, it is less sensitive to the experimental conditions than the degree of conversion reached after 25 min.

Reactivity of the industrial sample was measured six times using procedure 1 (Fig. 1) and two times

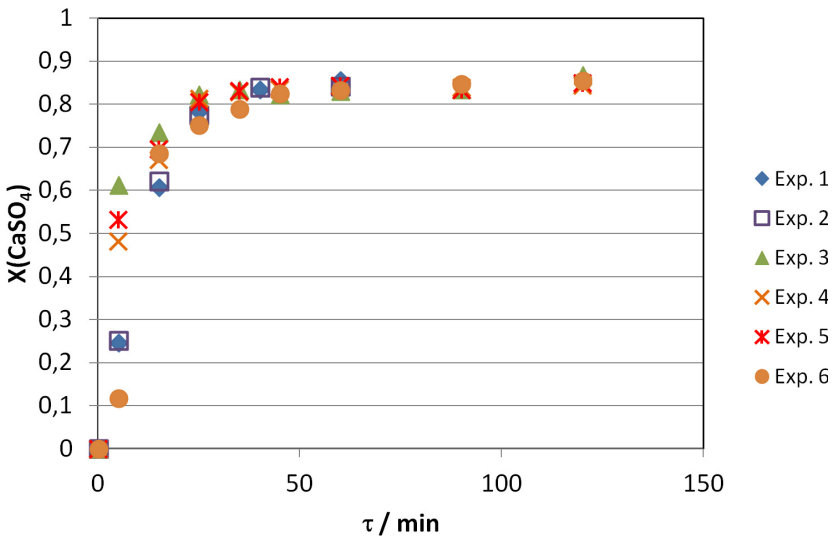

Fig. 1. Reproducibility of the time dependence of the conversion of FGD gypsum A at 20 °C. (Exp.1 to Exp. 6 were conducted under the same conditions – see Experimental).

by procedure 2 (Table 2). These data can be used for the estimation of the accuracy of the method used.

As follows from Fig. 1, FGD gypsum (gypsum A) is rather reactive. It is also obvious that after 25 min the conversion has a good reproducibility (uncertainty 5 %), while this parameter is rather scattered for lower duration of the reaction.

In Table 2, the data obtained by the precipitation of sulphate by barium chloride are shown. This method yields a higher degree of conversion, probably because of the presence of barium carbonate in the precipitate.

Tab. 2. The degree of conversion of FGD gypsum at 25 °C obtained by the procedure based on the precipitation of sulphates.

Time (min)	Conversion of FGD gypsum A	
0	0	0
10	0.936	0.926
30	0.969	0.983
60	0.992	1.036

For characterization of reactivity of gypsum samples 1–3, a determination of unreacted ammonium carbonate using procedure 1 was chosen as the most reliable and comfortable. Two or three parallel tests were carried out with the each sample. The results are represented in Figure 2. One can see that sample 3 differs from samples 1 and 2. X-ray analysis revealed that this sample is a mixture of dihydrate and hemihydrate of calcium sulphate.

The parameters used for characterizing the reactivity of four samples of gypsum are summarized in Table 3. Specific surface and mean size of particles are also presented in this Table. It can be seen that the maximum conversion reached after 2 h is in the limits of error the same for all samples. This parameter has no relation either to the specific surface or to the mean size of the particles. The same holds for the initial rate and/or half-time of the reaction. Conversion achieved after 25 min of the experiments exhibits the best correlation with the BET specific surface (Fig. 3). We assume that the initial rate is strongly influenced by moisture of samples and agglomerates of gypsum particles. From the reproducibility measurements (Figs. 1, 2)

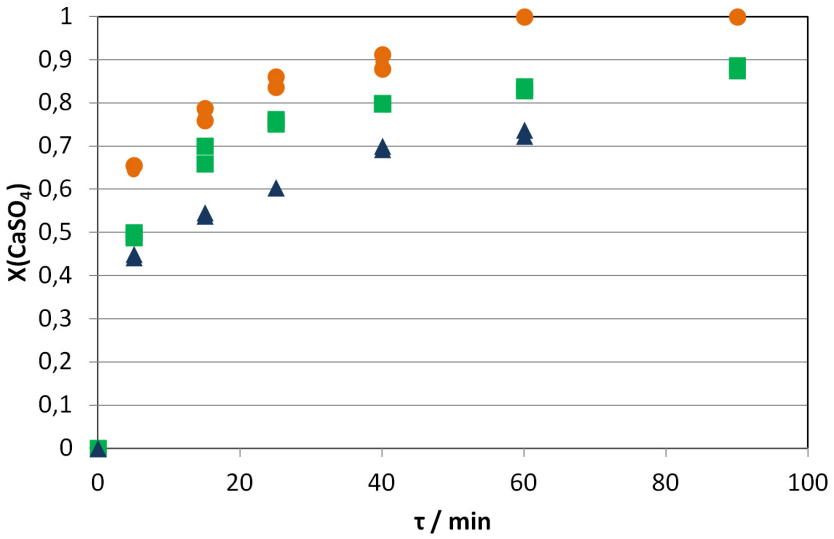

Fig. 2. The conversion of three samples of gypsum (samples of analytical grade), t = 20 °C. Circles – gypsum 1; squares – gypsum 2; triangle – gypsum 3.

Tab. 3. Comparison of the parameters characterizing the rate of the conversion of gypsum.

Sample	S_{BET} ($m^2 \cdot g^{-1}$)	Mean size of particles (μm)	$x_v(t = 0)$ ($mol \cdot dm^{-3} \cdot min^{-1}$)	$\tau(X_A=0.5)$ (min)	X_A (25 min)	$X_{A,\,max}$
A	13.2	38.91	0.049	4.0	0.792	0.854
1	17.2	31.04	0.051	3.8	0.845	1.000
2	13.4	54.27	0.045	5.1	0.757	0.931
3	13.0	14.19	0.036	5.6	0.604	0.731

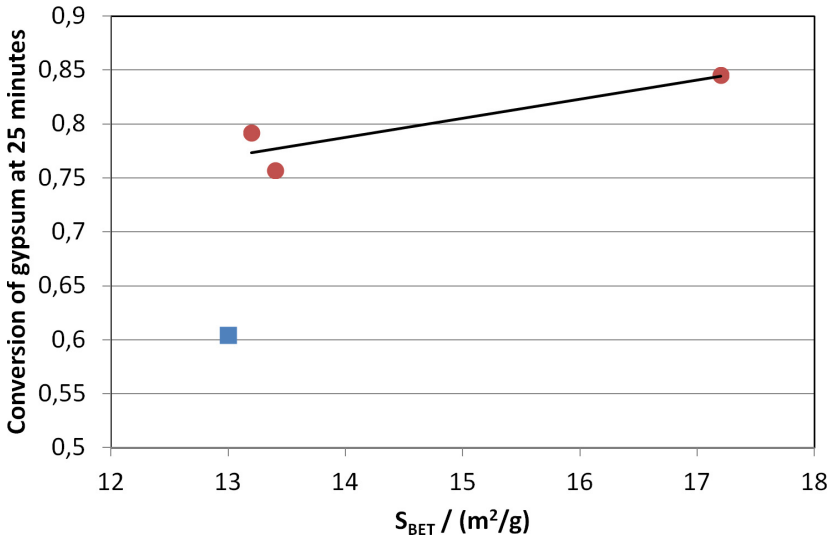

Fig. 3. The dependence of the conversion reached after 25 min *vs.* specific surface of gypsum. t = 20 °C. Circles — gypsum A, 1 and 2; square — gypsum 3.

it follows that all agglomerates are destroyed after ca 25 min.

Conclusion

Study of the rate of the reaction of gypsum with ammonium carbonate in water environment at defined temperature and stirring has proved to be a good tool for estimation of the reactivity of gypsum. The method was tested using four gypsum samples, one being FGD gypsum and three other samples were analytical grade chemicals. It has been shown the conversion reaction is rather fast; after 2 h the conversion achieved 84—92 %. For characterization of the reactivity, the most predictive parameter seems to be the conversion reached after 25 min from the beginning of the experiment. This parameter is in good correlation with the specific surface of the samples determined by the BET method.
The described method can be involved into the characterization techniques for FGD gypsum.

Acknowledgement
This work was supported by the Slovak Research and Development Agency under the contract NO. APVV-14-0217 (Exploitation of gypsum into valuable chemical products and intermediates – EGYVACHEP) and funding by VUCHT a.s.

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