

Precipitation of calcium carbonate in the presence of urea at 293K

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The results of the precipitation of calcium carbonate from waste distillation liquor (DS) from the Solvay method and sodium bicarbonate saturated solution in the presence of urea were presented. The investigation was carried out at 293K. The influence of the time of reagents dosage to the solution of urea on the physicochemical character of obtaining product was studied. The time of reagents dosage: 1, 5, 10, 20, 30 min and the concentration of the urea applied: 0.5, 1, 2 and 4 mol/dm³. The granulometric composition, the values of bulk and packing densities and the absorptiveness sorption of water and paraffin oil of the obtaining calcium carbonate were investigated.

Keywords: calcium carbonate, waste distillation liquor (DS), sodium bicarbonate, urea, bulk density, packing density.

INTRODUCTION

Calcium carbonate is commonly used in various branches of industry and belongs to one of the most plentiful minerals in nature. CaCO₃ exists in three polymorphic forms: calcite, aragonite and vaterite. At room temperature and under pressure conditions, calcite is the most stable phase of calcium carbonate. Aragonite and vaterite are obtained at high temperature. These two phases are thermodynamically less stable than calcite's nature¹⁻⁴.

The natural chalk used in construction industry and other branches of economy for years, was processed and modified⁵. Processing of chalk includes its crushing, washing, drying and softening. However, despite the processes performed to improve the quality, the product frequently does not fulfill the requirements of many branches of industry. Therefore, calcium carbonate, obtained from the natural source, is frequently replaced by the synthetic product.

Crystallization of calcium carbonate depends on many factors, including the temperature, the pH of the solution, supersaturation, the way and time of the reagent dosage, hydrodynamic conditions in the reaction mixture, time of the contact between the sediment and the mother liquor, as well as the presence of additional substances in the reaction mixture^{6,7}.

The reported research is focused on obtaining the calcium carbonate precipitates possessing the properties required by industry, using waste such as the post-distillation liquor called DS liquor or the saturated solution of sodium bicarbonate from the soda production process with the Solvay method⁷⁻⁹.

The data presented regard the precipitation of calcium carbonate from waste distillation liquor (DS) with the Solvay method and sodium bicarbonate saturated solution in the presence of urea. The investigation was carried out at 293K. The influence of dosage reagents time to the solution of urea on the physicochemical character of obtaining product was studied. The time of the reagent dosage was 1, 5, 10, 20, 30 min, respectively and the concentration of the applied urea was: 0.5, 1, 2 and 4 mol/dm³. The granulometric composition, the values of bulk and packing densities and absorption of water and paraffin oil of the obtained calcium carbonate were investigated.

EXPERIMENTAL

Materials

Post-distillation liquor (DS), Sodium Bicarbonate (Inowrocławskie Zakłady Chemiczne „Janikosoda” S.A.) and CO(NH₂)₂ (purity of 99.5%, POCh Gliwice S.A., Poland) were used for all the experiments.

The saturated solution of sodium bicarbonate was prepared from the raw sodium bicarbonate obtained from the filtration node. The concentration of HCO₃⁻ ions in that solution was approximately 1.2 mol/dm³.

The post-distillation liquor DS is generated in the ammonia regeneration node during soda production with the Solvay method. In the process conducted on the industrial scale that liquor contains approximately 10 m³ of the liquid waste per one ton of soda and 20 kg/m³ of solid waste. The major components of the DS liquor are calcium chloride and sodium chloride, while the additional components are sulfates and solid waste. The technical requirement necessary to use the post-distillation liquor with the view to obtaining the precipitated chalk is its separation from the solid impurities by clarification and filtration. The concentration of calcium ions in that liquor was approximately 1 mol/dm³, the concentration of iron ions 0.017 g/dm³.

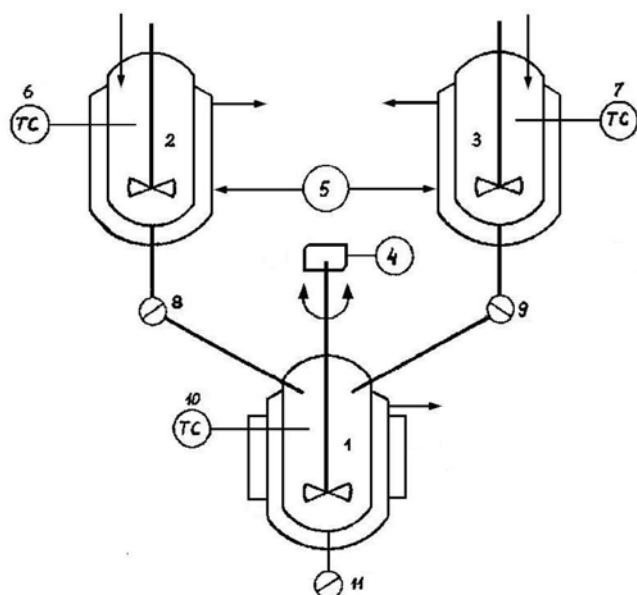
Experimental Procedure

A research on the precipitation of calcium carbonate was conducted at 293K by dosing the substrates into 250 cm³ of urea solution demonstrating the following concentrations: 0.5, 1, 2 and 4 mol/dm³. The time of reagent dosage varied, namely: 1, 5, 10, 20 and 30 min.

The precipitation was performed in the apparatus, presented in Figure 1.

The apparatus enabled the total control of the process parameters. The temperature was controlled with the mercurial thermometers, the rate of the reagent dosage was regulated with the pre-calibrated peristaltic pumps. During the experiments the reaction mixture was stirred with the precisely controlled speed of 500 revolutions per minute.

For the precipitation of each portion of calcium carbonate, 400 cm³ of DS liquor was used with the corresponding amount of NaHCO₃ according to the reaction equation:
$$\text{CaCl}_2 + 2\text{NaHCO}_3 \rightarrow \text{CaCO}_3 + 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2 \quad (1)$$



1 – lower reactor
2, 3 – upper reactors
4 – stirrer
5 – thermostat
6, 7, 10 – thermometers
8, 9 – peristaltic pumps
11 – outlet valve

Figure 1. Schematic diagram of the apparatus used for calcium carbonate precipitation

The required amount of substrates was put into the supply reservoir (upper) and thermostated. After reaching the required temperature, the DS liquor and NaHCO_3 were proportioned during a specified period of time into the thermostated main reactor (lower) containing 250 cm³ of the urea solution of a selected concentration.

After the reagent dosage, the reaction mixture was kept in the reactor for 15 minutes with the constant stirring speed. After that time the mixture was transferred to the clarifier, where it was stabilized. The obtained calcium carbonate was filtered with the sintered glass crucible and the vacuum pump. The precipitate was washed with the distilled water to remove chloride ions, and subsequently dried at 378 K and subjected to the physicochemical analysis.

Each synthesis was repeated to obtain the amounts of CaCO_3 necessary for the physicochemical analyses.

Basic physicochemical parameters of the obtained calcium carbonate were determined, such as bulk density, packing density, water absorptiveness, paraffin oil absorptiveness and the kind of the obtained crystals. The scanning electron microscopic and IR analyses were performed to determine the morphology and microstructure of the particles.

The morphology of the obtained crystals of calcium carbonate was determined by microscopic investigation with the Biolar 2308 microscope.

Analytical Method

The concentration of calcium ion in the distillation liquor (DS) was determined by complexometric titration with a known EDTA solution, using a fully automatic titrator 716 DMS TITRINO by Methrom, Switzerland¹⁰. The average relative error was estimated to be $\pm 1\%$.

The concentration of bicarbonate ion in the sodium hydrogen carbonate saturated solution was determined by the potentiometric method titrated with a known HCl solution^{10, 11}. The analysis was performed with the use of the fully automatic titrator 716 DMS TITRINO, equipped with a com-

bined glass electrode supplied by Methrom, Switzerland. The relative error was less than 1%.

The urea concentration was determined by the Kjeldahl method^{12, 13}. The sample is heated to reach the boiling temperature in the presence of concentrated sulfuric(VI) acid and catalyst agents (CuSO_4). In order to increase the boiling temperature of the sample, potassium sulfate(VI) was added. The NH_4^+ ions concentration was determined by the distillation method, using a fully automatic distillation apparatus Vapodest 30 (Gerhardt, Germany). The average relative error was estimated to be $\pm 2\%$.

The concentration of ferric(III) ion in the distillation liquor was determined with the help of a spectrophotometric method¹⁴. The analysis was performed using a double-beam UV-VIS spectrophotometer (Hitachi U-2000). The formation effect of colored complexes by Fe^{3+} with sulphosalicylic acid was employed. The relative error was less than 2%.

The concentration of sulphuric(VI) ion in the DS liquor was determined by the gravimetric analysis of barium sulphate formed in the acidic solution¹⁵. The average relative error of the measurement was estimated to be $\pm 1.5\%$.

RESULTS AND DISCUSSION

Calcium carbonate was obtained in a reaction of calcium ions from the post-distillation liquor with the hydrogen carbonate ions from the bicarbonate solution under the following conditions:

- temperature 293K
- concentration of sodium bicarbonate: approx. 1.2 mol/dm³
- concentration of calcium ions in the DS liquor: approx. 1 mol/dm³
- stirring intensity: 500 rev/min
- reagent dosing time: 1, 5, 10, 20 and 30 minutes

The parameters defining the quality of the precipitated calcium carbonate are: purity, bulk and packing density, as well as water and paraffin oil absorptiveness.

Water absorptiveness by the surface of calcium carbonate defines the degree of particle aggregation and characterizes the hydrophilicity of the sample. Paraffin oil absorptiveness defines the hydrophobicity of the obtained product.

The results of the precipitation of CaCO_3 at 293K for a different rate of the reagent dosage are presented in Table 1. The changes of water and paraffin oil absorptiveness by the samples of calcium carbonate are presented in Figures 2 – 5.

The results revealed the increase of bulk and packing density of the obtained calcium carbonate with the elongation of the time of the reagents dosage (Table 1).

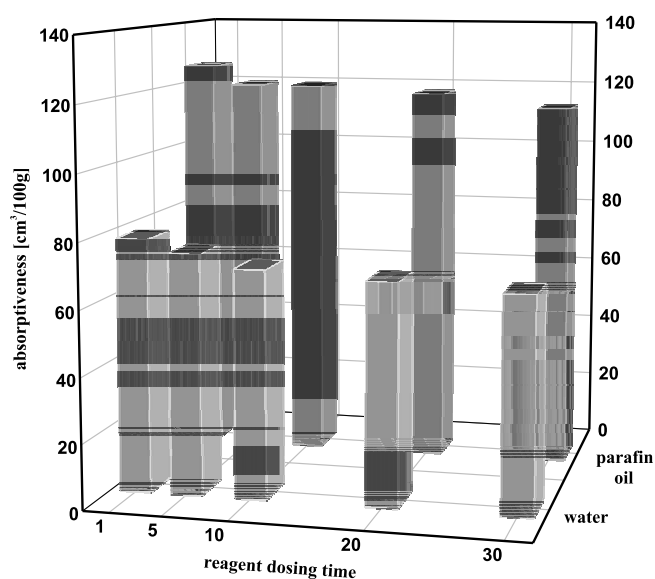
The bulk density of the precipitated calcium carbonate ranged from 364 to 500 kg/m³, while the values of packing density are from 728 to 900 kg/m³. The lowest values of bulk density (364 kg/dm³) are detected for the experiments in which the DS liquor and NaHCO_3 solutions were added to the urea solution of 0.5 mol/dm³ concentration during 1 and 5 minutes.

The increase of the urea concentration from 0.5 to 4 mol/dm³ resulted in only a small increase of bulk and packing density for all the times of the reagent dosage.

The analysis of the changes of water and paraffin oil absorptiveness (Fig. 2 – 5) revealed the decrease of these values with the increase of bulk density of the obtained calcium carbonate. The decreasing bulk density of calcium

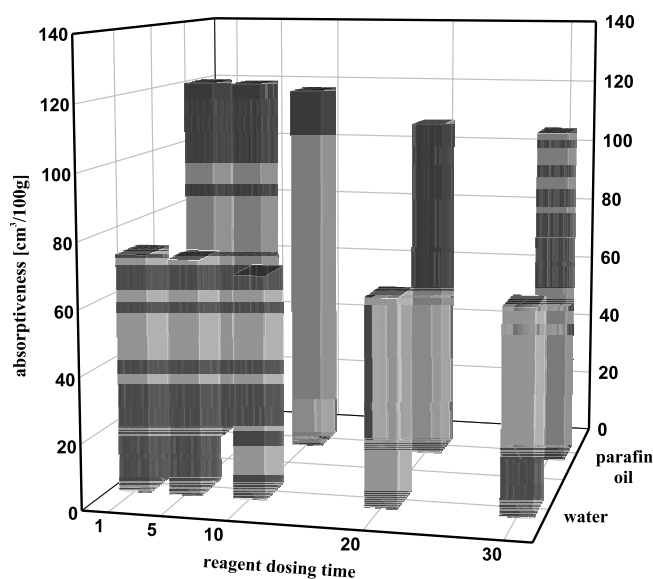
Table 1. The results of the precipitation of calcium carbonate in the presence of urea at 293K

reactor		density [kg/m ³]		
Upper		lower	bulk	packing
1	2			
time of reagents dosage t = 1 min				
DS	NaHCO ₃	0.5 M urea	364	728
		1 M urea	364	750
		2 M urea	370	784
		4 M urea	378	790
time of reagents dosage t = 5 min				
DS	NaHCO ₃	0.5 M urea	364	742
		1 M urea	400	769
		2 M urea	408	788
		4 M urea	420	796
time of reagents dosage t = 10 min				
DS	NaHCO ₃	0.5 M urea	366	769
		1 M urea	420	780
		2 M urea	435	794
		4 M urea	444	800
time of reagents dosage t = 20 min				
DS	NaHCO ₃	0.5 M urea	392	786
		1 M urea	430	800
		2 M urea	457	830
		4 M urea	465	850
time of reagents dosage t = 30 min				
DS	NaHCO ₃	0.5 M urea	416	800
		1 M urea	455	835
		2 M urea	474	870
		4 M urea	500	900

**Figure 2.** Absorptiveness of water and paraffin oil by calcium carbonate precipitated in the 0.5 M urea solution

carbonate corresponded to the increasing water and paraffin oil absorptiveness. Water absorptiveness of the obtained samples of the precipitated chalk are approximately 60 – 73 cm³/100g, while paraffin oil absorptiveness is approximately 104 – 120 cm³/100g.

To determine the dependence between the crystal size and bulk and packing density the microscopic analysis of the obtained calcium carbonate was performed. A small amount of single crystals was detected. In all the analyzed samples most of the crystals occurred in a form of aggregates. The samples characterized by large values of packing density

**Figure 3.** Absorptiveness of water and paraffin oil by calcium carbonate precipitated in the 1 M urea solution

revealed developed or intermediate aggregation and the crystal size below 8 μm.

The structure of the crystals was also investigated with the Scanning Electron Microscopy. The uniform distribution of calcium carbonate particles can be noticed, with the significant trend to form a dense system of agglomerates. That is not so noticeable for the samples of calcium carbonate with lower bulk density. X-ray diffraction analysis of calcium carbonate crystals revealed the presence of only one polymorph – calcite.

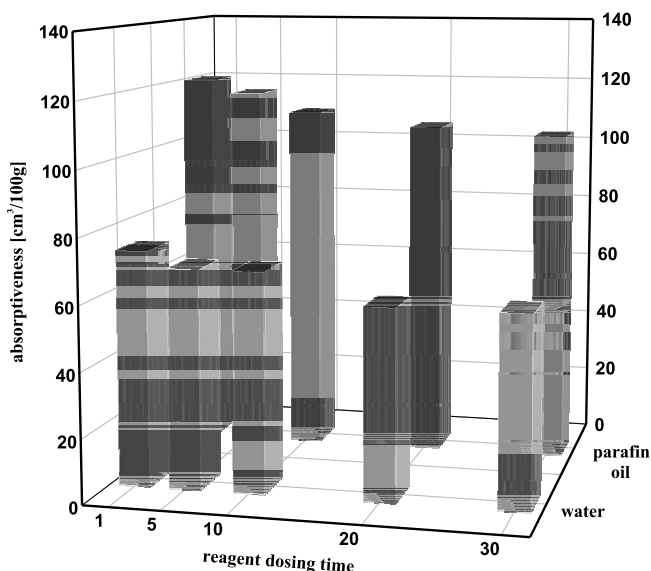


Figure 4. Absorptiveness of water and paraffin oil by calcium carbonate precipitated in the 2 M urea solution

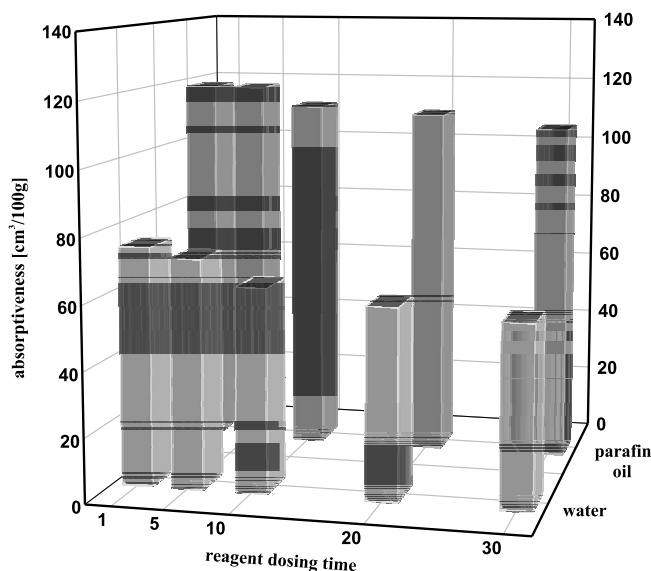


Figure 5. Absorptiveness of water and paraffin oil by calcium carbonate precipitated in the 4 M urea solution

LITERATURE CITED

1. Bolewski, A. & Manecki, A. (1993). *Detailed Mineralogy* (in Polish). Warsaw, Poland: PAE S.A.
2. Sohnle, O. & Mullin J. W. (1982). Precipitation of calcium carbonate. *J. Crystal Growth*. 60, 239 – 250. DOI: 10.1016/0022-0248(82)90095-1.
3. Tai, C.Y. & Chen P-C. (1995). Nucleation, agglomeration and crystal morphology of calcium carbonate. *AIChE Journal*. 41, 68 – 77. DOI: 10.1002/aic.690410108.
4. Tai, C.Y. & Chen F-B. (1998). Polymorphism of CaCO₃ precipitated in a constant composition environment. *AIChE Journal*. 44, 1790 – 1798. DOI: 10.1002/aic.690440810.
5. Domka, L. (1997). Comparison of physicochemical properties of natural chalks from Polish deposits and their significance for elastomer processing (in Polish). *Fizykochemiczne Problemy Metalurgii*. 31, 83 – 88.
6. Sawada, K. (1997). The mechanisms of crystallization and transformation of calcium carbonates. *Pure Appl. Chem*. 69, 921 – 928.
7. Walton, A.G. (1967) *The Formation and Properties of Precipitates*. New York, USA: Intersc. Publishers.

8. Niederliński, A., Bukowski A. & Koneczny H. (1978). *Soda and accompanying products* (in Polish). Warsaw, Poland: WNT.

9. Bortel, E. & Koneczny H. (1992). *Outline of Chemical Technology* (in Polish). Warsaw, Poland: PWN.

10. Hermanowicz, W. (1999). *Physico-chemical investigation of water and wastes* (in Polish). Warsaw, Poland: Arkady.

11. Minczewski, J. & Marczenko Z. (2004). *Analytical Chemistry* (in Polish). Warsaw, Poland: PWN.

12. Kiełkowska, U., Trypuć, M., Mazurek, K. & Drużyński S. (2007). The influence of urea on the KHCO₃ and NH₄VO₃ solubility in the KHCO₃ + NH₄VO₃ + H₂O system. *Pol. J. Chem. Tech.* 9 (2), 23 – 26. DOI: 10.2478/v10026-007-0018-7.

13. Houben, J. & Weil Th. (1974). *Methoden der organischen Chemie*. Stuttgart: Georg Thieme Verlag.

14. Dojlido, J. (1997). *Instrumental method of water and wastes investigation* (in Polish). Warsaw, Poland: Arkady.

15. Struszyński, M. (1982). *Quantitative and technical analysis* (in Polish). Warsaw, Poland: PWT.

16. Trypuć, M. & Buczkowski R. (1990). The investigations on obtaining of calcium carbonate from waste distillation liquid and sodium hydrogen carbonate solution (in Polish). *Przemysł Chemiczny*. 69/3, 131 – 133.