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INTERNATIONAL MINERAL PROCESSING & RECYCLING CONFERENCE

XIV INTERNATIONAL MINERAL PROCESSING AND RECYCLING CONFERENCE

Editors:
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May 12-14, 2021, Belgrade, Serbia

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APPLICATION OF MECHANOCHEMICALLY ACTIVATED SODIUM CARBONATE IN ENVIRONMENTAL PROTECTION

Nataša Đorđević[1#], Slavica Mihajlović[1], Milica Vlahović[2], Sanja Martinović[2]
[1] Institute for Technology of Nuclear and Other Mineral Raw Materials, Belgrade, Serbia
[2] University of Belgrade, Institute of Chemistry, Technology and Metallurgy, Belgrade, Serbia

ABSTRACT – Sodium carbonate samples were mechanicaly activated in a vibro mill. The increase in the free surface area of the activated samples was monitored by the BET method, and the state of the crystal lattice by the diffraction method. The analysis of the results showed a significant increase in the free surface of the activated material as well as significant changes in the crystal structure of the samples due to grinding in a vibro mill. Such activation of sodium carbonate would enable a significant increase in the sorption properties of sodium carbonate and thus its application in environmental protection.

Keywords: Air Protection, Sodium Carbonate, Mechanochemical Activation.

INTRODUCTION

Due to the increasing pollution of the environment, there is a need for fast and efficient methods of prevention and solving the problem of ecological protection. Increasing the concentration of carbon dioxide in the atmosphere is one of the key parameters of nature pollution, which has multiple negative consequences for life on Earth. One of the most effective ways to maintain the concentration of CO_2 in the air is the natural absorption of carbon dioxide by plants. Unfortunately, deforestation in the world is in expanding, and the problem of greenhouses and rising temperatures worldwide contributes to the growing problem. The reduction of the Earth's green mantle, especially in Brazil and Argentina in order to increase livestock is one of the causes of the increase in the amount of CO_2 in the air.

Possibilities of improving CO_2 intake by polyethyleneamines were investigated, using zinc-silicate supports [1], as well as other methods [2-4]. It is known that different models have been tested in order to absorb carbon dioxide, either in industrial plants or directly exposed to air (since carbon dioxide is obtained as a by-product of many industrial plants, its release greatly affects environmental pollution). A special problem is the exhaust gases from cars, where carbon dioxide and water vapor are obtained as a product in the process of fuel combustion. All the carbon dioxide that goes into the atmosphere as a result of human activities has a great impact on environmental pollution, creating a greenhouse effect and raising the average temperature, which directly affects the climate. At least its partial elimination from industrial plants would already significantly

[#] corresponding author: n.djordjevic@itnms.ac.rs

reduce its concentration and slow down the process of environmental pollution. It is of great importance to monitor the level of carbon dioxide in the air, whether it is natural disasters that contribute to disturbances of the atmosphere, water and soil, or human impact through heavy and automotive industry and life in big cities [5-14].

EXPERIMENTAL

In order to investigate the possibility of improving the absorption capacity of sodium carbonate, Na_2CO_3 was mechanochemically activated in a high-energy mill with torsion springs and ring working elements "KHD HUMBOLDT WEDAGAG". The mill consists of a housing in which there is a mechanism with a horizontally placed working vessel. The working vessel of the mill has a cylindrical shape of small height and is located on a specially constructed bearing with a cap. Under the working vessel of the mill, which has a vibrating oscillatory movement, there is a drive mechanism with an elastic shaft. The eccentric flywheel and torsion springs convert the circular motion of the elastic shaft into the vibrating oscillatory motion of the working vessel of the mill. The working vessel has two massive annular working elements of different diameters, with a total weight of 3 kg, which occupy one third of the working volume of the mill. The lid of the working vessel of the mill has a felt seal around the perimeter. The base of the working vessel of the mill is placed horizontally on the body of the mill.

The volume of the working vessel of the mill is 2 dm^3, and the mass of material that can be activated under optimal conditions is 200 g. Engine power is 0.8 kW. The device works discontinuously in an air atmosphere. Intense vibrating movement of the working vessel of the mill with massive rings, leads to heating of the vessel to a temperature of 80 °C.

A sample of Na_2CO_3, weighing 50 g, was activated by mechanochemical procedure for 1, 3, 5, 7, 14 and 28 minutes. The activated samples are then disposed of in order to absorb carbon dioxide. Exposure to activated sodium carbonate depends on the current needs of the environment in terms of carbon dioxide absorption (industrial plant, laboratory conditions, closed or open system, atmospheric conditions, already existing equipment using CO_2 absorbent). The standing time of the samples was from 1 to 85 days. The temperature at which the samples were deposited was room temperature. As a function of the activation time in the mechanochemical reactor, the residence time of the sample after activation and the atmosphere in which the sample is located (carbon dioxide content in the atmosphere), it is necessary to monitor changes in CO_2 in the atmosphere and activated sodium carbonate using different methods. was followed by the BET method. Crystallographic tests of activated Na_2CO_3 were performed. X-ray diffraction of polycrystalline samples was performed on a PHILIPS PW-1700, an automated diffractometer with a copper tube, which operates at 40 kV and 35 mA. The device is equipped with a graphite monochromator and a proportional counter filled with xenon. Shooting angle (2Θ) of 4-15 °.

The bond energy values represented in sodium carbonate are as follows [9]:

a) Na - O (364 kJ/mol)
b) C - O (1076.4 kJ/mol)
c) C = O (532.2 kJ/mol)

The decomposition temperature of sodium carbonate is 851 °C. Sodium carbonate has a monoclinic crystal lattice (a = 8.907; b = 5.239; c = 6.043), specific gravity 2500 kg/m3. The chemical composition of sodium carbonate according to the catalog MERCK index 11.8541, and the content of Na_2CO_3 was 99.5%. A chemical analysis was performed on a representative sample, which is in full agreement with MERCK's characterization.

RESULTS AND DISCUSSION

The increase in the specific surface area of Na_2CO_3 determined by the BET method as a function of the time of mechanochemical activation is shown in Figure 1. The highest degree of fragmentation and increase of free surface area was achieved in the first 40 minutes of activation, from 6.8 m^2/g of inactivated sample to 8.25 m^2/g. In the period from 40 to 100 minutes of activation, the free surface area continues to increase slightly, so that the free surface area of ground sodium carbonate for 28 minutes is 8.6 m^2/g. An increase in the free surface area of activated sodium carbonate indicates the possibility of a significant increase in the adsorption capacity of CO_2 from the air.

Mechanochemically activated Na_2CO_3 samples were submitted for X-ray diffraction analysis. The samples were isolated from the outside atmosphere, so that no additional influence on the already activated samples could occur. The aim of this analysis was to establish how the structure of sodium carbonate behaved as a function of the grinding time in the vibro mill. Table 1 shows the intensities of diffraction peaks of activated Na_2CO_3 depending on the activation time. Figure 2 shows the diffractograms of Na_2CO_3 activated for 1-21 min in a vibro mill.

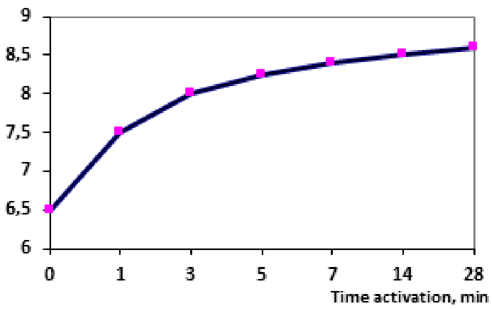

Figure 1 Change of specific surface of Na_2CO_3 as a function of time of mechanochemical activation by BET method

Table 1 Values of the intensity of diffraction maxima at a certain diffraction angle as a function of the activation time of Na_2CO_3 samples

	Peak intensities I (cts) depending on the activation time, min					
Diffraction angle, 2Θ	1 min	3 min	5 min	7 min	14 min	28 min
30	350	193	199	276	177	193
34.165	146	128	125	142	106	108
35.225	222	166	164	228	144	154
37.965	310	196	174	228	146	156
40	154	194	83	106	72	86
Middle value 35.471	236	155	149	196	158	139

As a function of the time of activation of sodium carbonate, the crystal lattice is disturbed at all diffraction angles and the free surface of the activated material is increased. During the first five minutes of activation, there is a sharp decrease in the value of the intensity of diffraction maxima. Between the fifth and seventh minutes of grinding, the values of the maximum intensity increase, also at all diffraction angles. The increase in the intensity of diffraction maxima can be explained by the fact that after five minutes of grinding, after the collapse of the crystal structure, the mechanical energy supplied to the system allows a certain recrystallization of the existing system, the partial arrangement of the destroyed structure. After the fifth minute, the intensities decrease again until the fourteenth minute of grinding, after which the change in the intensity of the maximum has a steady flow with a slight tendency to increase in function from the time of grinding. This stationary flow of the curve can be explained by the assumption that after the collapse of the newly formed structure, after 14 minutes of grinding, no changes in the structure of the activated sample occur. It can also be concluded that by further extending the grinding time after 28 minutes, no further change in the structure of the activated material would be achieved.

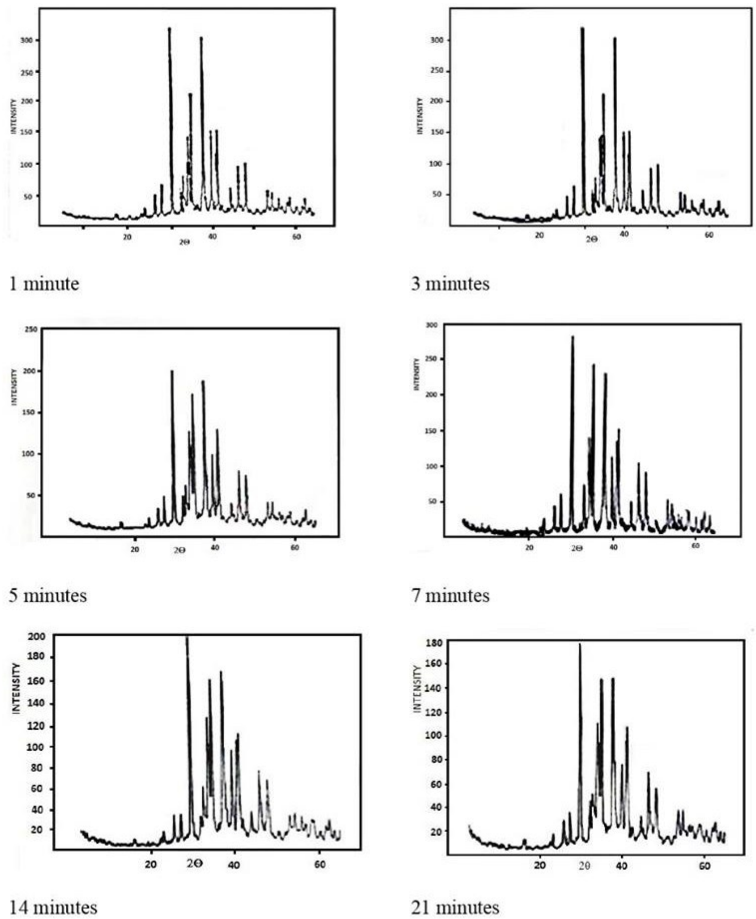

Figure 2 Diffractograms of Na_2CO_3 activated 1-21 min in a vibro mill

The results of the BET method after activation indicate the fact that due to grinding there was a significant increase in the free surface area of the activated sodium carbonate powder. As sodium carbonate is a known sorbent of carbon dioxide from the air, increasing the free surface area of the activated powder significantly increases the possibility of CO_2 sorption.

Comparing the results of the diffractograms of the activated samples in relation to the inactivated sample, it can be noticed that the grinding of sodium carbonate led to a disturbance of the crystal structure. In order to monitor the change in the intensity of diffraction maxima as a function of the activation time, five characteristic peaks at certain values of diffraction angles were selected from the data given with the diffractograms. Based on the analysis, it can be concluded that during 28 minutes of activation there is a sudden and significant decrease in the value of the intensity of diffraction maxima, ie the collapse of the crystal structure, at all angles of diffraction. This is due to the fact that the invested mechanical energy is spent on the comminution of existing grains of sodium carbonate, and then leads to the collapse of the internal structure of Na_2CO_3 crystals.

Based on the results, it can be seen that during the first five minutes of activation, there is a sharp decrease in the value of the intensity of diffraction maxima, the collapse of the crystal structure, at all angles of diffraction. This is a consequence of the fact that the invested mechanical energy is spent on crushing the existing grains of sodium carbonate, and then it leads to the destruction of the internal structure of the Na_2CO_3 crystal. Between the fifth and seventh minutes of grinding, the values of the maximum intensity increase at all diffraction angles. The increase in the intensity of diffraction maxima can be explained by the fact that after five minutes of grinding, after the collapse of the crystal structure, the mechanical energy supplied to the system allows a certain recrystallization of the existing system, partial arrangement of the destroyed structure.

As sodium carbonate is an effective carbon dioxide absorption agent, based on the attached research results, it can be concluded that mechanochemical activation can significantly contribute to an additional increase in the absorption capacity of sodium carbonate. In the next course of experiments, it is important to determine the increase in the degree of CO_2 absorption on sodium carbonate as a function of activation time, by monitoring the change in sample mass during relaxation in atmospheres with increased CO_2 concentration and humidity, and spectrophotometric analysis of activated samples after relaxation time.

CONCLUSION

Based on the results of the BET method of samples of sodium carbonate activated from 1 to 28 minutes, it can be concluded that grinding the samples leads to a significant increase in the free surface area of activated material, which increases the possibility of adsorption and absorption (sorption by surface area and volume) of CO_2. From the results obtained by diffractometric analysis, a significant destruction of the crystal lattice of the ground sample is observed, which enables not only the sorption of CO_2, but also the hemisorption of gas on the activated sample. The results of further tests will be presented in the next paper. Increasing the sorption capacity of CO_2 on sodium carbonate opens up great possibilities for its application in environmental protection, especially in industrial conditions.

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