The Effect of Forced Carbonation on the Change in the Structure of Lime-Containing Systems over Time

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Abstract. The paper presents the results of experimental research on establishing the possibility of using furnace gasses and sodium manufacturing waste as low-activity lime dust in the solid building materials manufacturing technology. Research on the changes of physical and mechanical properties and structure of the material based on lime-calcareous compositions that solidify in the environment with increased carbon dioxide concentration after being stored in the natural environment for 24 months were conducted. Material samples constitute semidry-pressed cylinders (compacting pressure – 30 MPa), made of a mixture of low-activity lime dust and a filler, which is waste material from extraction of limestone of Crimean deposit. Conducted research of physical and mechanical properties, of structure and characteristics of material’s porosity had shown that an increase of samples’ strength could be observed both as a result of portlandite changing into calcite upon forced carbonation, as well as a result of repeated crystallization of scalenohedral calcite into rhombohedral shape after storing samples in the natural environment.

1. Introduction

Recently the issue of preserving the natural resources and decreasing the atmosphere pollution level due to various technogenic waste becomes more and more concerning. Analysis of the state of the issue shows that for most of industrial production the formation of waste with their low utilization degree is characteristic, which affects the increase of the areas of dump and sludge pits.

There are several large industrial companies on the territory of Crimean Peninsula that contribute yearly to shaping the anthropogenic stress in the region by forming millions of tons of waste and harmful substances emission into the atmosphere.

Calcined sodium is not an exemption. The chemical process of manufacturing calcined sodium with ammoniac technology is based on five reactions, one of which is obtaining calcium oxide and carbon dioxide by calcinating calcium carbonate in lime burning furnaces [1,2,3]. As a result of purifying carbon dioxide for its further use, a byproduct known as lime dust, which is characterized by low activity and high calcium carbonate impurity content. It is possible to organize its partial implementation as low-activity quick lime. However, it does not allow to avoid the issue of accumulation of this byproduct in dump pits and negative influence on environment.

The issue of mineral waste reclamation can be solved by using them in such material-intensive field of national economy as manufacture of building materials and products [4,5,6]. This predefines the necessity of developing the research in the field of obtaining cost-effective and environmentally friendly building materials, as well as implementation of developed resource-saving technologies in the manufacturing process.
2. Analysis of publications, materials, and methods

Based on the aforesaid, it is important to study the issue of using CO₂ in the building materials technology based on industrial bonding lime and calcareous waste for manufacture byproduct recovery and decrease carbon dioxide emissions into the atmosphere.

As a result of hydrated lime changing into calcium carbonate, the material becomes harder, its water and cold resistance increases. The service life of lime materials is time-proven (the palaces of the ancient city of Knossos XVII – XV cen. B. C. on the island of Crete, Saint Sophia’s Cathedral in Kyiv, XI cen. C. E., ancient defensive structures and buildings on the shore of Lisbon etc. [7]). However, this process is lengthy and may take years or even decades. It can be intensified by forced carbonation of materials on the lime basis through recovery with specially-treated smoke fumes from lime furnaces [8,9,10,11].

The authors of the paper have received optimal parameters for obtaining carbonated lime-carbonate wall building materials with necessary physical and mechanical properties [12,13,14,15]. However, the issues of change of properties of materials based on low-activity bonding lime forced carbonated solidification over time remain unexplored.

According to contemporary views, the structure of the material does not remain unchanged, it constantly changes in space and time under the influence of both external and internal factors [16]. A lot of attention was always paid to researching the changes of physical and mechanical properties of building materials over time to increase their service durability and longevity [17,18,19]. Numerous research projects were directed towards researching carbonation’s impact on the structure and durability of materials. Specifically, the scientists from Jinan University in China have uncovered certain rules of porosity structure change of the building material when it goes through carbonization. It was established that over time porosity of carbonized layer decreases because of new crystal formations [20]. Due to the fact that recrystallization of Ca(OH)₂ happens within relatively short technological terms [21], it is necessary to study the changes of structure and properties of carbonated lime-carbonate materials over time, which will give an idea about preservation of mechanical properties as one of those that define the longevity of materials and products.

The aim of this paper is to study the changes of physical and mechanical properties and structure formation kinetics of forcibly carbonated samples based on industrial low-activity lime and quarrying waste of Crimean limestones after prolonged storage. The term of storage constituted 2 years.

The study of properties of lime-carbonate compositions was conducted on the semidry-pressed cylinder samples (specific compacting pressure – 30 MPa) 30 mm in diameter, solidification of which was conducted in the carbonation chamber [21] under conditions of 30% concentration of carbon dioxide with variation of processing time equal 1, 3, 6 and 9 hours.

The research of formation of porous structure was conducted on samples by using the reference porosimetry method. Tablet samples were produced for the study, their diameter being 23 mm, thickness – 1.9÷2.0 mm by sawing-out from the samples of lime-carbonate compositions, as well as on purpose-made lime tablet samples. Air-slaked lime was used to produce the latter.

To produce cylinder samples as a bonding component, a calcium air-slaked lime was used, which is low-activity lime dust that sinks in the electric filters of mine furnaces when limestone undergoes calcination, as well as fresh drowned lime to study formation of porous structure in samples of pure lime. Limestone of Belgorod deposit of the Republic of Crimea with fractionated composition was used as carbonate filler.

Research of samples’ material structure depending on carbon dioxide processing conditions was conducted with the help of X-ray phase analysis on the X-ray diffractometer Bruker ASX D8ADVANCE. Analysis of samples’ porous structure was conducted on the automated reference porosimeter (version 3.2, manufactured by MPM&P RESEARCH INC). Physical and mechanical properties of samples were obtained through standard laboratory testing.

Solidification of test samples was organized in the following way: samples obtained through semidry compression underwent carbon dioxide processing for 1, 3, 6 and 9 hours respectively, after which a portion of samples was tested with to define physical and mechanical properties, while another portion of samples was weathering under normal conditions (decreased concentrations of carbon dioxide) in the laboratory for 24 months. To study the formation of porous structure in tablet samples made of pure lime, the time of carbon dioxide processing constituted 1, 3, 5, 20, 60 and 180 minutes. After the
first measurement of the porous structure the tablet samples were also weathering under normal conditions within the laboratory for a week.

3. The main section with the results and their analyses

Initial raw mixture constituted a composition of calcium air-slaked lime with its mass amounting at 45% and the limestone filler amounting at 55%. Humidity of the raw mixture constituted 8% of the dry composition mass. Based on the composition of the raw mixture of samples and activeness of carbon dioxide processing time, it can be assumed that the approximate lime content constitutes 18% by mass.

To define the dynamics of changes of physical and technical properties of obtained material, the test samples were tested in different time intervals: 1 full day, 1 month, 6 months, 24 months. Changes of compression strength ($R_{\text{comp}}$), density ($\rho$) and mass gain ($\Delta m$) of samples depending on their age and carbon dioxide processing time were tabulated in Table 1, from which it appears that the durability of all samples increases over time. Also an increase in density and mass gain of samples can be observed. Mass gain indicates that the process of changing Ca(OH)$_2$ into CaCO$_3$ continues even after carbon dioxide processing – the remaining free portlandite recrystallizes into calcite, while the crystals of scalenohedral calcite themselves [20] become bigger and rhombohedral in shape.

Table 1. Change of physical and mechanical properties of material test samples over time depending on carbon dioxide processing time.

| Time of treatment with CO$_2$ | $R_{\text{comp}}$ (MPa) Samples age | $\Delta m$ (g) Samples age | $\rho$ (kg/m$^3$) Samples age |
|-----------------------------|-------------------------------------|--------------------------|-------------------------------|
|                             | 1 day                               | 1 month                  | 24 months                     |
| 1 hour                      | 35.76 37.56 48.31 44.59 2.564 2.821 3.071 3.172 1772 1820 1838 1855 |
| 3 hours                     | 36.52 42.75 49.63 50.96 2.155 2.586 2.864 3.027 1771 1818 1836 1856 |
| 6 hours                     | 42.54 44.07 54.26 51.38 2.212 2.628 2.762 3.049 1791 1827 1841 1864 |
| 9 hours                     | 34.80 36.52 43.88 44.59 2.332 2.792 2.924 3.046 1788 1814 1812 1838 |

Results of material X-ray phase analysis of obtained test samples depending on carbon dioxide processing time at end points of time intervals that are being researched (1 full day and 24 months) show that the number of free portlandite decreases with an increase of processing time, which is caused by calcium hydroxide changing into carbonate.

The X-ray pictures of samples that are being studied themselves are of similar nature (Figure 1). Percentage content of main portlandite and calcite phases depending on carbon dioxide processing time and weathering under normal conditions is shown in Table 2.

Figure 1. X-ray picture of the material sample 1 full day (a) and 24 months (b) after forced carbonation for 3 hours.

Unstable compressive strength increase of cylinder samples may be caused by an emergence of destructive processes that develop in relation to overburned unslaked particles of lime dust within the composition of raw mixture. Because of using high-quality high-activity lime as a bonding agent the durability of carbonated samples during storage under natural conditions for 6 years increases by 145% and decrease of compressive strength indexes throughout the entire interval is not observable [22], and also with increased carbon dioxide processing duration of samples (6 and 9 hours) a decrease...
in durability can be observed, which is possibly related to dilution (corrosion) of scalenohedral calcite crystals with availability of sufficient amount of liquid phase in the system [20].

**Table 2.** Percentage content of portlandite and calcite depending on carbon dioxide processing time and weathering under normal conditions.

| Mineral  | Time of treatment with CO₂ | Exposure time under normal conditions |
|----------|-----------------------------|---------------------------------------|
|          |                             | 1 day | 24 months |
| Portlandite | 1                           | 2.9   | 2.7       |
|           | 3                           | 2.2   | 1.2       |
|           | 6                           | 1.8   | 0.8       |
|           | 9                           | 0.6   | 0.3       |
| Calcite  | 1                           | 97.1  | 97.3      |
|          | 3                           | 97.8  | 98.8      |
|          | 6                           | 98.2  | 99.2      |
|          | 9                           | 99.4  | 99.7      |

Analysis of porous structure of samples that underwent 1, 6 and 9 hours of carbon dioxide processing respectively and weathered under normal conditions for 24 months is shown in Figure 2.

**Figure 2.** Integral curves of pores’ volume distribution by their radiuses (a – within the range of 0.01 – 22 µm, b – within the range of 0.01 – 1.5 µm) in material samples after 24 months of weathering under normal conditions after forced carbonation for 1, 3, 6 and 9 hours.

Based on porogramms obtained and percentage content of calcite in the study samples it can be assumed that provisional ending of the lime carbonation process may be ascribed to the term of weathering the samples under normal conditions at the age of 6 months. Samples porogramms at the age of 24 months are essentially identical. Maximum pore size constituted 20÷22 µm for samples with 1, 3, and 9 hours of weathering in carbon dioxide respectively and 10 µm for sample with 6 hours of carbon dioxide treatment. However, the percentage content of pores at the size of 1 – 22 µm constitutes 0.5 – 2%. Additionally, porosity of samples constitutes approximately 26-28% in all cases. Main pores volume (25%) lies within the 0.5 – 1 µm range.

The results of researching the formation of porous structure on the samples made of pure slaked lime with repeated measurement of porous structure after 1 week of weathering under normal conditions are presented on porogramms on Figure 3 and Figure 4. It can be seen on the graphs that samples porosity changes depending on carbon dioxide environment processing time. As such, porosity of a sample without processing with carbon dioxide constitutes 42.7%. Later on after carbon dioxide processing for 1, 5, 20, 60 and 180 minutes porosity constitutes 38.7, 33.4, 31.6, 31.1 and
29.7% respectively. It is possible that porosity of samples decreases as a result of recrystallization of portlandite into calcite, as well as in its variety of aragonite and vaterite, which later on in turn change into calcite [24]. The basic pore size range for samples made of pure lime constitutes 0.01 – 0.15 µm. Porogramms show that the main porous structure of such samples mostly forms in first 5 minutes of carbon dioxide processing (for 2mm-thick samples). It is worth noting that sample carbonation continues even after weathering under normal conditions. In this vein, the porosity of samples that were stored under normal weather conditions of the laboratory within 7 full days decreases from 38.7 to 34.8% (Figure 4).

Thus, it can be concluded that formation of durability of test samples at the starting stage of their forced carbonate solidification mostly depends on reaction of lime carbonation and emergence of calcite in the system, and later of the defining processes are recrystallization and growth of calcite crystals that form a more dense material structure.

![Figure 3](image1.png)  
**Figure 3.** Integral curves of pores volume distribution by their radiuses (a – within the range of 0.01 – 25 µm, b – within the range of 0.01 – 0.25 µm) in pure lime samples immediately after carbon dioxide processing within 1, 5, 20, 60 and 180 minutes.

![Figure 4](image2.png)  
**Figure 4.** Integral curves of pores volume distribution by their radiuses (a – within the range of 0.01 – 25 µm, b – within the range of 0.01 – 0.2 µm) in pure lime samples immediately after carbon dioxide processing within 1 min and after 7 full days.
4. Conclusion

General analysis of tested samples indicates that over time the compositions made of lime furnace dust and calcareous filler gain durability both during carbon dioxide processing and under natural conditions due to calcite recrystallization. In this vein, the durability of samples that underwent carbon dioxide processing for 1, 3, 6 and 9 hours increased after 24 months of storage under natural conditions by 18.5, 39.5, 21.8 and 21% respectively. An insignificant decrease of durability that could be observed from 6 to 24 months is related to the presence of overburned unslaked particles of lime dust in the composition of raw mixture.

The research of porous structure shows that the carbonation process is finite and is reached approximately within 6 months of weathering under normal conditions after formed carbonation. The research of porous structure of samples made of pure lime shows that the main porous structure of the material forms within first 5 minutes of the carbon dioxide processing. Obtained results allow us to conclude that low-activity lime dust may act as bonding component in the composition with calcareous filler to obtain solid semidry building materials, the durability gain of which is achieved through carbonate solidification within the environment with increased carbon dioxide concentration. However, it is necessary to pay close attention to the content of overburned CaO particles within it and use various technological methods to decrease and reduce their number to a minimum.

References

[1] Bikbulatov I Kh, Nasyrov R R, Daminov R R, Voronin A Yu 2007 Method of utilization of the main waste of soda ash production *Electronic scientific journal Oil and gas business* 2 1-16
[2] Kurbangaleev M H, Khasanova A A, Yanbekov L F 2015 The use of solid solid waste soda production as a raw material for commercial products *Collected papers CITIES OF RUSSIA: PROBLEMS OF CONSTRUCTION, ENGINEERING, LANDSCAPING AND ECOLOGY* pp 59-62
[3] Dzhandullaeva M, Adilova M, Aliyeva Z, Kholmukhamatova F 2018 The use of carbonate waste soda production as a raw material in the production of silicate bricks *Universum: Technical Sciences* 12 77-80
[4] Latifa M A, Naganathanb S, Razakc H A, Mustaphab K N 2015 Performance of lime kiln dust as cementitious material *Procedia Engineering* 125 780 – 787
[5] Arulrajah A, Mohammadinia A, D’Amico A, Horpibulsuk S 2017 Effect of lime kiln dust as an alternative binder in the stabilization of construction and demolition materials *Construction and Building Materials* 152 999–1007
[6] Jitsanigam P, Biswas W K, Compton M 2018 Sustainable utilization of lime kiln dust as active filler in hot mix asphalt with moisture damage resistance *Sustainable Materials and Technologies* 17 E00071
[7] Borges C, Santos Silva A, Veiga R 2014 Durability of ancient lime mortars in humid environment *Construction and Building Materials* 66 606–620
[8] Pöllmann H 2015 Mineralogical Strategies to reduce CO₂ in the fabrication of alternative cements *Proc. IBAUSIL* 1 pp 11-129
[9] Moorehead D R 1986 Cementation by the carbonation of hydrated lime *Cement and Concrete research* 16 700–708
[10] De Silva P, Bucea L, Moorehead D R, Sirivivatnanon V 2006 Carbonate binders: Reaction kinetics, strength and microstructure *Cement & Concrete Composites* 28 613–620
[11] Van Balen K, Van Gemert D 1994 Modelling lime mortar carbonation *Materials and Structures* 27 393-398
[12] Lyubomirskiy N V, Fedorkin S I, Bakhtin A S, Bakhtina T A, Lyubomirskaya T V 2017 Research in influence of regimes of forced carbonate hardening on properties of materials on the basis of lime-limestone compositions of semidry pressing *Stroiitel'nye materialy* 8 7–12
[13] Fedorkin S I, Lyubomirskiy N V, Lukyanenko M A 2008 System based on lime of carbonizing hardening *Constr. Mater.* 11 45-47
[14] Lyubomirskiy N V, Fedorkin S I 2016 The influence of carbon dioxide pressure on the kinetics of forced carbonation of limestone semi-dry pressing and the formation of its strength *Construction and technogenic safety* 3 28-38
[15] Lyubomirskiy N V, Bakhtin A S, Bakhtina T A, Nikolaenko E Yu, Nikolaenko V V 2016,
Influence of calcium bicarbonate on the structure and properties of materials based on lime carbonation hardening. "International research journal" 11-4 86-93

[16] Folmer M 1986 Kinetics of formation of a new phase. FIZMATLIT (Moscow)

[17] Neves-Juniora A, Ferreira S R, Toledo Filhoc R D, Rego Fairbairnd E M, Dweck J 2019 Effect of early age curing carbonation on the mechanical properties and durability of high initial strength Portland cement and lime-pozolan composites reinforced with long sisal fibres. Composites Part B 163 351–362

[18] Borges C, Santos Silva A, Veiga R 2014 Durability of ancient lime mortars in humid environment. Construction and Building Materials 66 606–620

[19] Abed M, Nemes R 2019 Long-term durability of self-compacting high-performance concrete produced with waste materials. Construction and Building Materials 212 350–361

[20] Cizer O, VanBalen K, Elsen J, VanGemert D 2008 Crystal morphology of precipitated calcite crystals from accelerated carbonation of lime binders. 2nd Int. Conf. on Accelerated Carbonation for Environmental and Materials Engineering pp 149-158

[21] Fedorkin S I, Lyubomirskiy N V, Nosatov V G, Loktionova T A 2007 Automatic installation and technique of studying of process of carbonization of lime. Construction and technogenic safety 19-20 74-78

[22] Lyubomirskiy N V, Bakhtin A S, Bakhtina T A 2017 Change of physical and mechanical properties of lime-carbonate calcium materials of forced carbonate hardening in time. Construction and technogenic safety 8 67-73

[23] Volkovich Yu M, Bagotzky V S, Sosenkin V E, Blinov I A 2001 The standard contact porosimetry. Colloids and Surfaces A: Physicochemical and Engineering Aspects 187–188 349–365

[24] Ghouleh Z, Rodrick Guthrie I L, Shao Y 2015 High-strength KOBM steel slag binder activated by carbonation. Construction and Building Materials 99 175–183

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