The antifungal efficiency of carbide lime slurry compared with the commercial lime efficiency

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Abstract. The article deals with studying the antifungal efficiency of carbide lime slurry compared to industrially manufactured commercial lime. Antifungal efficiency expressed as mould proofness properties was tested on the fungi using the procedure given in standard CSN 72 4310. A mixture of fungi Aspergillus niger, Chaetomium globosum, Penicillium funiculosum, Paecilomyces variotii and Gliocladium virens was utilized for testing. The scale for evaluating mould proofness properties according to CSN 72 4310 is from 0 to 5 in degree of fungi growth, where 0 means that no fungi growth occurs and the building products and materials possess fungistatic properties. The study confirms the fungistatic properties of carbide lime slurry as well as industrially manufactured commercial lime. However, carbide lime slurry and industrially manufactured commercial lime possess no fungicidal effect.

1. Introduction

Calcium carbide CaC₂ is industrially produced in an electric arc furnace with graphite electrodes from a mixture of lime and coke at approximately 2000°C by reaction (1) [1, 2]. The carbide product produced generally contains around 80 wt.% CaC₂. Calcium carbide is generally used for the generation of acetylene gas (C₂H₂) by the reaction (2).

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CaO + 3 C \rightarrow CaC_2 + CO \quad (1)
\]

\[
CaC_2 + 2 H_2O \rightarrow C_2H_2 (g) + Ca(OH)_2 \quad (2)
\]

Carbide lime (CL) is high quality hydrated lime slurry produced as a by-product of acetylene production, composed mainly of calcium hydroxide Ca(OH)₂ with minor portions of CaCO₃, and the presence of carbon as graphite particles and amorphous films in the waste [3, 4]. Carbide lime has been used for decades as an alternative source for hydrated lime in such applications as municipal and industrial wastewater treatment, flue-gas desulfurization, sludge conditioning, road stabilization and other applications where normal commercial lime is used. The Ca(OH)₂ content of the dry solids is in the 90% range. Ca(OH)₂ (hydrated lime) slurry produced as, and delivered, in a slurry form. The study [5] was aimed at the possibility of using the carbide lime waste as an alternative material to the conventional lime used for cement-lime mortar. Specimens were tested for mechanical properties and
the results have shown that the carbide lime waste can be readily used for masonry cement mortar work.

Calcium carbide lime is practically used for various chemical and industrial uses such as pH control, industrial water and as sewage treatment, stabilization and agricultural purposes [6]. It is solid or liquid with white-gray colour. Lime is non-toxic, however, it may cause skin and eye irritation and burns. The irritant effects of lime are due primarily to its alkalinity, but dehydrating and thermal effects may be contributing factors. Due to the alkalinity of lime it may be subject to different regulations in different locations.

Monopoly producer of calcium carbide CaC$_2$ is company Fortischem a.s. Novaky (former NCHZ a.s. Novaky) in Slovakia [7]. The manufactured CaC$_2$ is ground, sorted and supplied in number of qualitative types. It is used as a raw material for the production of acetylene, calcium cyanamide, in metallurgy for metal desulphurization. Lime fine powder, lime powder and lime hydrates are supplied in various qualities. Lime powders and dust regulate soil pH. They are also used to adjust water pH in waste water treatment plants [7]. The industrial wastes including carbide lime slurry Ca(OH)$_2$ are separately deposited at the waste dump - landfill site in the vicinity of Novaky. However, several hundred thousand - millions tons of carbide lime slurry Ca(OH)$_2$ are landfilled till now, without any utilization, which is serious environmental load and burden.

The ordinary commercial limes are extensively utilized throughout the world according to the technical standards and regulations. They can be applied as building lime EN 459-1, as a part for masonry cement EN 413-1, for rendering and plastering mortar EN 998-1, for masonry mortar EN 998-2, for unbound and hydraulically bound mixtures - soil treated by lime, for hydraulically bound mixtures - hydraulically stabilized soils EN 14227-11, for calcium silicate masonry units EN 711-2 and for autoclaved aerated concrete masonry units EN 711-4, respectively.

The disinfective effect of lime at hygienisation is very good known for centuries and it is very well utilized at sanitisation (hygienisation) till now, as well. Disinfection by lime in the wastewater reclamation plant reduced number of microorganisms extensively when operated at pH 11.2 [8]. Lime enables the destruction of all pathogens due to the pH effect, which provides alkaline hydrolysis, combined with the temperature increase - thermolysis, that quicklime hydration brings [9]. Of course, the thermolysis effect can be decreased in the case of slaked, hydrated lime Ca(OH)$_2$, however, the alkaline hydrolysis can be considered as the main antimicrobial potential of lime. Alkaline hydrolysis (OH-) results in the destruction of protein-based cellular walls and of enzymes, the destruction of proteins at polypeptide bonds to amino acids and oligopeptides, the destruction of nucleic acids (RNA), the destruction of carbohydrate cell constituents and lipids and the denaturing of enzymes [9]. Therefore, this article aims at the studying the antifungal effect of carbide lime slurry in comparison to the industrially manufactured commercial lime with emphasis on increasing its potential application.

2. Materials and methods

2.1. Materials
Following lime samples were tested: carbide lime slurry (CLS) and comparative industrially manufactured commercial lime (IMCL) as the reference material. The chemical composition of tested samples was performed by XRF according to EN 196-2 using apparatus SPECTRO X-LAB 2000. The semi-quantitative chemical composition of the samples is given in table 1.

The mineralogical composition of the samples was determined by XRD technique using BRUKER AXS D8 Advance device and it is given in table 2.
Table 1. The chemical composition of tested carbide lime slurry (CLS) and industrially manufactured commercial lime (IMCL) in wt.%. 

| Comp.   | Unit       | CLS   | IMCL  | Comp.   | Unit       | CLS   | IMCL  |
|---------|------------|-------|-------|---------|------------|-------|-------|
| L.O.I*  | [wt.%]     | 27.70 | 22.22 | V₂O₅    | [ppm]      | 88.0  | 96.0  |
| SiO₂    | [wt.%]     | 2.243 | 1.079 | Cr₂O₃    | [ppm]      | 30.96 | 25.49 |
| Al₂O₃   | [wt.%]     | 1.317 | 0.424 | CoO      | [ppm]      | 3.30  | 3.41  |
| Fe₂O₃   | [wt.%]     | 0.1503| 0.262 | NiO      | [ppm]      | 6.85  | 7.68  |
| CaO     | [wt.%]     | 66.642| 65.278| CuO      | [ppm]      | 0.51  | 7.07  |
| TiO₂    | [wt.%]     | 0.0501| 0.023 | ZnO      | [ppm]      | 27.3  | 11.79 |
| MgO     | [wt.%]     | 0.375 | 9.883 | As₂O₃    | [ppm]      | 3.04  | 5.15  |
| K₂O     | [wt.%]     | 0.0812| 0.143 | Cd       | [ppm]      | 1.69  | 0.79  |
| Na₂O    | [wt.%]     | 0.926 | 0.406 | SnO₂     | [ppm]      | 28.0  | 20.69 |
| SO₃     | [wt.%]     | 0.4177| 0.127 | Sb₂O₃    | [ppm]      | 7.27  | 6.64  |
| MnO     | [wt.%]     | 0.0043| 0.0065| Hg       | [ppm]      | 1.18  | 1.83  |
| P₂O₅    | [wt.%]     | 0.0239| 0.029 | Ti       | [ppm]      | 2.37  | 2.88  |
| Cl      | [wt.%]     | 0.0101| 0.0058| PbO      | [ppm]      | 0.93  | 13.01 |

*L.O.I: Loss on ignition

Table 2. The mineralogical composition of tested carbide lime slurry (CLS) and industrially manufactured commercial lime (IMCL) in wt.%. 

| [wt.%]    | portlandite | calcite | quartz | periclase | graphite | hydrocalumite Friedel’s salt♦ |
|-----------|-------------|---------|--------|-----------|---------|-------------------------------|
| IMCL      | +           | +       | +      | +         | -       | -                             |
| CLS●      | 70.10       | 22.40   | -      | -         | 2.37    | 5.13                          |

♦ – the hydrocalumite phase Ca₄Al₂(OH)₁₂(Cl,OH)_₂.4H₂O (Ca₄Al(OH)₂Cl₂H₂O, β-Ca₄Al₂O₆Cl₂.10H₂O, or Ca₄Al₂(OH)₁₂(Cl,CO₃,OH)₂.4H₂O) is structurally like as Friedel’s salt 3CaO.Al₂O₃.CaCl₂.10H₂O and so it is adequately attributed to Friedel’s salt phase, as well.

● – the quantitative mineralogical composition determined by XRD analysis connected with Rietveld computation of quantitative analysis.

2.2. Method of testing the resistance of building products and materials to filamentous fungi (moulds) according to standard CSN 72 4310

The antifungal activity of carbide lime slurry (CLS) and comparative industrially manufactured commercial lime (IMCL) was tested using the procedure given in the Czech standard CSN 72 4310 – The testing of mould proofness of building products and materials [10]. The mould proofness properties expressed as the intensity of fungi growth on building products and materials are determined by both artificial and natural contamination, with exposure to the selected testing moulds under the prescribed conditions presented in the standard [10]. The testing method is fully described [11], in detail. The scale of evaluation of the mould proofness properties of building products and materials according to CSN 72 4310 [10] is given in table 3. The degree of the fungi growth is expressed by a value from 0 to 5, where the value 0 is attributed to no occurring fungi growth and the building products and materials possess fungistatic properties; in some cases, fungicidal properties also occurred after the formation of an inhibiting zone in the broth around the sample. The final evaluation was carried out by microscopic examination of the intensity of mould growth on the sample surface. The intensity of mould growth was evaluated according to the scale from 1 to 5 given in table 3. The mould proofness properties of the building products and materials were evaluated according to CSN 72 4310 [10] as follows:

| Comp. | Unit | CLS   | IMCL  | Comp. | Unit | CLS   | IMCL  |
|-------|------|-------|-------|-------|------|-------|-------|
| L.O.I*| [wt.%] | 27.70 | 22.22 | V₂O₅ | [ppm] | 88.0  | 96.0  |
| SiO₂  | [wt.%] | 2.243 | 1.079 | Cr₂O₃ | [ppm] | 30.96 | 25.49 |
| Al₂O₃ | [wt.%] | 1.317 | 0.424 | CoO  | [ppm] | 3.30  | 3.41  |
| Fe₂O₃ | [wt.%] | 0.1503| 0.262 | NiO  | [ppm] | 6.85  | 7.68  |
| CaO   | [wt.%] | 66.642| 65.278| CuO  | [ppm] | 0.51  | 7.07  |
| TiO₂  | [wt.%] | 0.0501| 0.023 | ZnO  | [ppm] | 27.3  | 11.79 |
| MgO   | [wt.%] | 0.375 | 9.883 | As₂O₃| [ppm] | 3.04  | 5.15  |
| K₂O   | [wt.%] | 0.0812| 0.143 | Cd   | [ppm] | 1.69  | 0.79  |
| Na₂O  | [wt.%] | 0.926 | 0.406 | SnO₂ | [ppm] | 28.0  | 20.69 |
| SO₃   | [wt.%] | 0.4177| 0.127 | Sb₂O₃| [ppm] | 7.27  | 6.64  |
| MnO   | [wt.%] | 0.0043| 0.0065| Hg   | [ppm] | 1.18  | 1.83  |
| P₂O₅  | [wt.%] | 0.0239| 0.029 | Ti   | [ppm] | 2.37  | 2.88  |
| Cl    | [wt.%] | 0.0101| 0.0058| PbO  | [ppm] | 0.93  | 13.01 |
The building products and materials are fungicidal – mould does not develop on the sample. An inhibiting zone forms on the agar around the sample;

- the building products and materials are fungistatic – mould does not develop on the sample. Mould growth on the agar is not affected;
- the building products and materials are not mould-proof (the intensity of mould growth on the sample surface itself is from 1 to 5).

Table 3. The scale of evaluation of the mould proofness properties of building products and materials according to standard CSN 72 4310 [10].

| Degree of fungi growth | Description                                                                 |
|------------------------|-----------------------------------------------------------------------------|
| 0                      | No growth of fungi                                                          |
| 1                      | The growth of fungi is negligible (the colonies of fungi are dispersed)     |
| 2                      | The growth of fungi is gradual (numerous small fungi colonies which cover 25% of the sample surface) |
| 3                      | The growth of fungi is intensive (fungi colonies cover up to 50% of the sample surface) |
| 4                      | The growth of fungi is very intensive (fungi colonies cover up to 75% of the sample surface) |
| 5                      | The sample surface is fully covered by fungi (fungi colonies cover 100% of the sample surface) |

The testing was realized in the accredited microbiological laboratory of Testing Institute for Textiles (Textilní Zkusebni Ustav, s.p.) in Brno, Czech Republic. The test conditions are as follows: sample size Ø 5.5 cm; temperature in the incubator 28±1°C; rel. humidity in the incubator 95%; incubation period 3 months; standard broth media.

A mixture of fungi Aspergillus niger (CCM 8155), Chaetomium globosum (CCM 8156), Penicillium funiculosum (CCM F-161), Paecilomyces variotii (CCM F-566) and Gliocladium virens (CCM 8042) was applied for the testing. The tested samples were exposed to the contamination by the chosen microorganisms in the broth medium according to exactly defined conditions given in CSN 72 4310 [10] during the incubation period of 3 months, after which their mould proofness was evaluated.

3. Results and discussion

After the 3 months incubation period according to standard CSN 72 4310 [10], the mould proofness properties of carbide lime slurry (CLS) and comparative industrially manufactured commercial lime (IMCL) were evaluated as the degree of fungi growth.

Generally speaking, the CLS and IMCL (reference material) are suitable for reaching 0 degree of fungi growth according to CSN 72 4310 [10]. On the basis of the experimental results, it can thus be stated that the CLS and IMCL are defined as the fungistatic building materials according to CSN 72 4310 [10]. The degree of fungi growth 0 means that no growth of fungi occurs and the building products and materials possess fungistatic properties.

The inhibiting zone did not form on the agar around all of the tested samples. This means that CLS and IMCL (reference material) possess no fungicidal effect. However, the results unambiguously showed that CLS and IMCL have a fungistatic effect. Moulds did not develop on the samples, but the mould growth on the agar was not affected.

The fungistatic effect of CLS and IMCL is declared on the basis of reference testing, which was carried out in an accredited microbiological laboratory at the Textile Testing Institute (Textilní Zkusebni Ustav, s.p.) in Brno, Czech Republic, which is an approved certification body, as well. CLS and IMCL complying with the requirements of CSN 72 4310 [10] can be used for the production of
fungistatic building materials and products. An application of CLS and IMCL into the building materials and products increase their mould proofness and antimicrobial properties.

According to the results, the addition of fungistatic CLS and IMCL (reference material) into the building products and materials is suitable for increasing the antimicrobial effects and for achieving fungistatic protection, as well. From a practical point of view, fungistatic CLS and IMCL are suitable for achieving a mould-free environment. CLS and IMCL potentially offer wide application possibilities in the building industry from preventive use to the purposes of repairing and reconstruction. However, the mechanism of the antimicrobial effects of CLS as well as IMCL should be the subject of further study.

4. Conclusion
The main conclusions that can be drawn from this experimental study are summarized as follows:

- carbide lime slurry (CLS) and comparative industrially manufactured commercial lime (IMCL) is a fungistatic building material according to the requirements of standard CSN 72 4310 with 0 degree of fungi growth;
- no growth of fungi is observed in CLS and IMCL, with mould proofness property 0;
- the inhibiting zone did not form on the agar around the tested samples, which means that CLS and comparative IMCL possess no fungicidal effect;
- fungistatic CLS as well as IMCL (reference material) are suitable for use in a wide scope of applications aimed at eliminating fungal growth, starting with preventive purposes and ending with repairing and reconstruction works.

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