

Comparative study of antimicrobial efficiency of metallurgical slags suitable for construction applications

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Abstract. The article deals with comparative study of antimicrobial efficiency of metallurgical slags suitable for construction applications. The tested slags were as follows: granulated blast-furnace slag (GS1), air cooled blast-furnace slag (AS2), demetallized steel slag (DS3), calcerous ladle slag (LS4), slag from copper refining (CS5). The antimicrobial activity was tested on selected representatives of bacteria, yeasts, and filamentous fungi. The highest antibacterial activity possessed LS4, which intensely inhibited growth of bacteria with the lowest concentration of slag (10%) in the growth media. 100% inhibition of growth of some bacteria was observed only in slags LS4, DS3 and AS2 in concentrations 20% - 60% of slag. Antibacterial activity of slag samples was decreasing in the order: LS4 > DS3 > AS2 > GS1 > CS5. Growth of all model yeasts was 100% inhibited at as low concentration as 20% of slag GS1 and DS3, and 10% of slag LS4. Antiyeast activity of slags was decreasing in the order: LS4 > GS1 = DS3 > AS2 > CS5. Regarding that filamentous fungi were selectively sensitive to presence of slags, it is possible to determine only approximate order of inhibition effectiveness of slags to fungi: LS4 > GS1 = DS3 > AS2 = CS5.

1. Introduction

Microbially influenced concrete biocorrosion is a serious problem wherever the suitable conditions for a life of the particular microorganisms, such as temperature, pH and moisture of the environment, presence of oxygen, radiation, input of nutrients and others, have come to existence. Biodeterioration reduces the utility efficiencies of concretes, mortars and their useful life. Biocorrosion, as a specific type of chemical corrosion, is caused by various biogenic organic acids, mineral acids (sulphuric acid H₂SO₄, nitric acid HNO₃) as well as by corrosive hydrogen sulphide H₂S and ammonia NH₃, which result from metabolic activity of microorganisms [1]. These aggressive metabolites react mainly with calcerous components of concrete and mortar stone forming their non-binding calcareous salts, some of them cause sulphate degradation, resulting in extreme expansion in the concrete and leads to a complete destruction of concrete structural elements. It was found out in the previous study [2], that the fine ground granulated blastfurnace slag possesses fungistatic properties. Since metallurgical slags are utilized in concretes as artificial, manufactured aggregates, as fine ground inorganic type I addition – filler aggregates and as fine ground inorganic type II addition – latent hydraulic material, this article aims to study the antimicrobial activity of all types of metallurgical slags used in concretes, possibly mortars, plasters and to compare them mutually.



2. Materials and methods

2.1. Materials

Following kinds of metallurgical slags were tested: granulated blast-furnace slag (GS1), air cooled blast-furnace slag (AS2), demetallized steel slag (DS3), calcereous ladle slag (LS4), slag from copper refining (CS5). All of them were ground to a specific surface area of 400 m²/kg. The chemical composition of the slags was analysed by X-ray fluorescence analysis (XRF) according to EN 196-2 using apparatus SPECTRO X-LAB 2000. The semi-quantitative chemical composition of the slags is given in table 1.

Table 1. The chemical composition of metallurgical slags in wt.%.

Slag	Unit	GS1	AS2	DS3	LS4	CS5
L.O.I*	[wt.%]	0.95	0.09	6.02	5.32	+ 4.30**
SiO ₂	[wt.%]	42.17	40.57	12.81	13.97	27.26
Al ₂ O ₃	[wt.%]	6.87	8.12	1.64	17.77	7.01
Fe ₂ O ₃	[wt.%]	0.32	2.81	29.78	1.90	46.64
CaO	[wt.%]	41.92	41.73	52.30	58.97	7.48
TiO ₂	[wt.%]	0.42	0.11	0.34	0.14	0.21
MgO	[wt.%]	10.39	8.44	2.54	3.30	1.90
K ₂ O	[wt.%]	0.60	0.72	0.04	0.06	0.40
Na ₂ O	[wt.%]	0.17	0.19	0.07	0.07	1.07
SO ₃	[wt.%]	1.84	2.39	0.28	1.98	0.15
MnO	[wt.%]	0.68	2.31	3.54	0.38	0.61
P ₂ O ₅	[wt.%]	0.05	0.14	0.48	0.05	1.26
Cl	[wt.%]	0.0173	0.0112	0.0138	0.0017	0.0012

*L.O.I: Loss on ignition

**Increment on ignition (caused by e.g. oxidation of metallic particles, sulphides, disulphides, sulphites etc.)

The mineralogical composition of the samples was determined by XRD technique using BRUKER AXS D8 Advance device. The identified mineralogical composition of the slags is as follows: GS1 – melilite (solid solution of gehlenite C₂AS and akermanite C₂MS₂); AS2 – melilite, brownmillerite C₄AF, quartz SiO₂; DS3 – wüstite FeO, brownmillerite C₄AF, free lime CaO, portlandite Ca(OH)₂, β-C₂S, quartz SiO₂; LS4 – free lime CaO, β-C₂S, shanonite γ-C₂S, gehlenite C₂AS, tricalcium aluminate C₃A, gypsum CaSO₄·2H₂O, quartz SiO₂ and CS5 – fayalite 2FeO·SiO₂, anortite CaSi₂, pyroxene type CaAlAlO₆ (abbreviations in the compounds mean C = CaO, M = MgO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃).

2.2. Methods of testing

The antimicrobial activity of metallurgical slags was tested on selected representatives of bacteria, yeasts, and filamentous fungi (moulds). Following microorganisms were used: G⁺ bacteria - *Bacillus subtilis*, *Staphylococcus aureus*, *Micrococcus luteus*; G⁻ bacteria - *Escherichia coli*, *Pseudomonas aeruginosa*, *Serratia marcescens*; yeasts - *Candida albicans*, *Rhodotorula glutinis*; microscopic filamentous fungi (moulds) - *Aspergillus niger*, *Penicillium funiculosum*, *Chaetomium globosum*, *Alternaria alternata*, *Trichoderma viride*, *Cladosporium herbarum*. As growth media, meat-peptone bouillon for inoculation of bacteria, meat-peptone agar for cultivation of bacteria, Sabouraud glucose bouillon for inoculation of yeasts and malt agar for cultivation of yeasts and mycelial fungi were applied. For diluting of inoculum of bacteria and yeasts, saline was used, for preparation of spore suspension (moulds), water solution of Tween 80 was used. The tests were performed in the laboratory

incubator at temperatures 30 °C for bacteria, 28 °C for yeasts, 25 °C for filamentous fungi and at relative humidity 95%.

Antimicrobial activity was determined by dilution methods in agar growth media so that resulting concentration of tested slags in growth media was 10, 20, 40 and 60% by weight. The pH value of growth media with addition of slags was strongly basic (pH 11), thus half of samples of each slag was tested at this pH, and the second half of samples was tested at modified pH (bacteria pH 7.2, yeasts and filamentous fungi pH 6.6). The first half of samples with original pH represented real conditions for growth of microorganisms in concrete, the second half of the samples with modified pH represented optimal conditions for growth of microorganisms *in vitro*.

The microorganisms growth at slags presence was compared with the microorganisms growth in control growth media without slags in dependence on time. Inhibiting effect of slags was inspected: microbistatic (microorganisms are not growing; after transferring microorganisms into growth media without inhibitor, they are growing broader) and microbicidal - lethal (microorganisms are dead; after transferring microorganisms into growth media without inhibitor, they are not growing).

3. Results and discussion

The highest antibacterial activity was achieved at slag LS4, which intensely inhibited growth of G⁺ as well as G⁻ bacteria, what was proved also at the lowest concentration of the slag LS4 (10%) in growth media. Bacteria, except *M. luteus* did not grow at higher concentrations of slag LS4. The growth of G⁺ bacteria *S. aureus* and *B. subtilis* was inhibited by slag DS3 in growth media as early as the concentration 10% and at higher concentrations, the growth was completely (100%) inhibited. 100% inhibition of growth of some bacteria was observed only in the samples of slags LS4, DS3 and AS2 in concentration range 20% - 60% of slag. Antibacterial activity of slag samples was decreasing in the order: LS4 > DS3 > AS2 > GS1 > CS5.

The growth of all model yeasts was 100% inhibited at as low concentration as 20% of slag GS1 and DS3, and 10% of LS4, at basic as well as modified pH of growth media. Growth of model yeasts was intensively reduced at the presence of slag AS2 in concentrations 40% and 60%. Slag CS5 partially inhibited the growth of model yeasts without 100% inhibitions at the highest 60% concentration. Antiyeast activity of slags was decreasing in the order: LS4 > GS1 = DS3 > AS2 > CS5.

The tested model filamentous fungi were sensitive to presence of the slag samples in various manners. As it is apparent from the results of inhibition, all slags inhibited the growth of filamentous fungi by 100% - 40% in concentration 60% of slag. The most sensitive to presence of all slags were *A. niger* and *T. viride*, the growth of which in concentrations 20% - 60% of all slag samples at basic as well as modified pH value, was inhibited on 100% with fungistatic effect (they stopped growth of fungi), and in concentration 60% of slag LS4 with fungicide effect (killed fungi) at *T. viride*. The most resistant was *A. alternata*. Its growth was the most intensely inhibited by slag LS4, 100% inhibition was observed at 40% - 60% of slag, with mostly fungistatic effect. The most inhibiting activity for all fungi was disposed by slag LS4, which 100% inhibited growth of almost all model filamentous fungi in concentrations 20% - 60% at basic pH of growth media, with mostly fungistatic effect. Only the *T. viride* growth was inhibited on 100% with fungicide effect at basic pH of growth media in concentration 60% of slag LS4. At modified pH of growth media, the growth of model filamentous fungi was inhibited on 100% in concentration range 20% - 40% of slag LS4 with fungistatic effect and at concentration 60% of slag LS4 was inhibited on 100% with fungicide effect on *A. alternata*, *A. niger*, *T. viride*, *Ch. globosum*. Lower inhibiting effect on filamentous fungi growth was observed at slags GS1 and DS3, but they inhibited the growth of all tested filamentous fungi on 40% - 100% at concentration 40%. The lowest impact on the growth of model filamentous fungi was observed at the presence of slag CS5 in growth media, which affects only the growth of the most sensitive fungi *A. niger* and *T. viride*. The most resistant was *A. alternata*. Its growth was the most intensely inhibited by slag LS4, 100% inhibition was observed at 40% - 60% of slag, with mostly fungistatic effect.

Regarding that model filamentous fungi were selectively sensitive to the presence of tested slags, it is possible to determine only approximate order of inhibition efficiency of slags to filamentous micromycetes: LS4 > GS1 = DS3 > AS2 = CS5.

The pH values of growth media did not significantly affect the intensity of inhibition of model microorganisms growth.

4. Conclusion

According to these results, metallurgical slags possess the great potential for using as antimicrobially active agents for building materials against biodeterioration. The highest antimicrobial efficiency had calcerous ladle slag (LS4), the medium efficiency granulated blast-furnace slag (GS1) and demetallized steel slag (DS3), lower efficiency air cooled blast-furnace slag (AS2) and the lowest efficiency slag from copper refining (CS5), respectively.

References

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