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Risk assessment

MICROBIALLY-INDUCED DETERIORATION OF CONCRETE FROM HYDROELECTRIC POWER PLANTS – AN INITIAL STUDY

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Abstract. Microorganisms can grow on the surface of concrete and inside its pores and micro-cracks, producing different metabolites. Microbial metabolites, particularly acids, degrade concrete components and enhance its deterioration by abiotic factors. Deterioration of concrete is a serious problem worldwide since it affects construction functionality and requires high maintenance costs. This paper presents microbiological and chemical analyses of 12 concrete samples originating from 6 hydroelectric power plants in Serbia, investigated in order to evaluate the key chemical factors affecting microbial growth on concrete. In most of the concrete samples, microorganisms from all examined groups were present in high numbers (bacteria 8.64×10^3–3.4×10^8, fungi 9×10^2–2.08×10^6, sulphur-oxidising bacteria 16.8–2.5×10^4 CFU/g). The high number and the presence of various physiological groups of microorganisms indicate the high intensity of deterioration caused by biological sources. Values of pH of the concrete samples were in the range 8.46–11.23, Ca content 5.43–19.93%, Fe 151–61100 ppm, sulphate 37.4–623.7 ppm and chloride 96.3–914.1 ppm. Correlation analysis between microbiological and chemical factors indicated a statistically significant strong negative correlation between sulphur-oxidising bacteria and pH (–0.759, $p < 0.01$).

Keywords: concrete corrosion, sulphur-oxidising bacteria, pH, microorganisms, biodeterioration.

AIMS AND BACKGROUND

Concrete degradation can be caused by various physical and chemical changes such as corrosion cracking or load fatigue. In addition to these processes, durability of concrete can be influenced by deterioration arising from biological sources[1,2]. Organisms that contribute to this biologically induced deterioration are bacteria, archea, cyanobacteria, yeast and fungi, algae, mosses, lichens and terrestrial plants[3,4]. Deterioration can cause severe damage to concrete sewerage systems,

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wastewater treatment systems, bridges and piers, offshore platforms, etc. thus severely influencing the economy by raising maintenance costs[1,5].

The distribution and metabolic activities of microorganisms on concrete surfaces depend on various environmental and material factors such as: pH, Eh, carbon source type and concentration, water availability, concrete composition, pore structure, size and distribution[5,6]. Microorganisms affect concrete deterioration by fouling (biofilm formation), mechanical breakdown due to microbial growth or movement and chemical deterioration due to excretion of metabolites such as organic acids[4,7,8].

Various bacterial genera have been detected in deteriorating concrete: sulphate reducing bacteria (SRB) such as *Desulfovibrio*, *Desulfomaculum*, neutrophilic sulphur-oxidising bacteria (NSOB) (*Thiobacillus*, *Thiothrix*, *Thiomonas*, *Halothiobacillus*), acidophilic sulphur-oxidising bacteria (ASOB) *(Acidithiobacillus*), and heterotrophic bacteria (*Bacillus*, *Ochrobactrum*, *Mycobacterium*)[5,9,10]. The general processes of concrete deterioration have been extensively studied in the sewerage systems. At first, concrete has a very high pH (~12–13) due to the formation of calcium hydroxide ($Ca(OH)_2$) (Ref. 2). In the headspace of sewerage systems, CO_2 and H_2S are present due to the action of SRB biofilms, and these gases will, *via* gas diffusion, decrease the concrete pH abiotically through carbonation and the attack of thiosulphuric and polythionic acid formed by chemical oxidation of H_2S. Next, when the pH reaches ~9, NSOB will colonise the surface and produce acidic compounds which will further decrease the concrete pH to ~3–5. This will provide suitable conditions for the appearance of ASOB, which will continue to release acids and cause the decline of pH to 1 (Refs 2, 5 and 9). During the first stage of the process, there is no significant material loss. Later, when acids are produced, the sulphate causes the leaching of calcium hydroxide and precipitation of expansive sulphate salts such as gypsum and ettringite. These salts are responsible for large volume expansion which leads to the increase of pressure and the disruption of structural integrity of concrete[2,4,5,9,11].

Apart from the biogenic sulphur compounds, biogenic nitrogen compounds can also cause biodeterioration of concrete. These nitrogenous compounds can be oxidised by various microorganisms to nitrite and nitrate, which reacts with calcium hydroxide to form soluble calcium nitrate[12].

Since concrete deterioration in sewerage systems is the most studied type, mechanisms involved in the deterioration of other infrastructure items (bridges, piers, damns, concrete structures in water cooling systems) remain unclear. Microorganisms may not directly contribute to the deterioration of such structures, but instead, they can accelerate other damaging processes, although there is no definite understanding of all the mechanisms involved[2,7,12]. Carbonation can reduce the alkalinity of concrete, while deposits from acid rain, air and water pollution can be a source of nutrients and moisture that in turn favour the colonisation of microorganisms. However, the type and abundance of microbial species will depend on environmental factors[7,13].

The environmental factors together with the concrete characteristics vary considerably in different geographic locations and are essential for the understanding the deterioration processes[5,6,9]. Hence, the purpose of this study was to quantify the microorganisms in concrete samples taken from six hydroelectric power plants located in Serbia, and to investigate the relationship between microbial growth and different physicochemical and chemical properties of the concrete. Initial studies such as this one are important for preventing deterioration of concrete, planning remediation and monitoring the effects of concrete reparation.

EXPERIMENTAL

Sampling. Concrete samples were taken from six hydroelectric power plants built in Serbia during 1954–1982: Djerdap (river Danube; concrete samples 593, 594), Potpec (river Lim; 892, 893), Uvac (river Lim; 894, 895), Kokin Brod (river Lim; 897, 898), Brana Lazici (river Beli Rzav; 877, 878) and Ovcar Banja (river Zapadna Morava; 888, 890) (Fig. 1). Within each of the six different hydroelectric power plants, concrete samples were taken from two different locations where visible deterioration was present. Sampling was performed in March 2016 according to modified standard methods ASTM D 6051:2015 and SRPS CEN/TR 15310-1,2,3,4,8:2009.

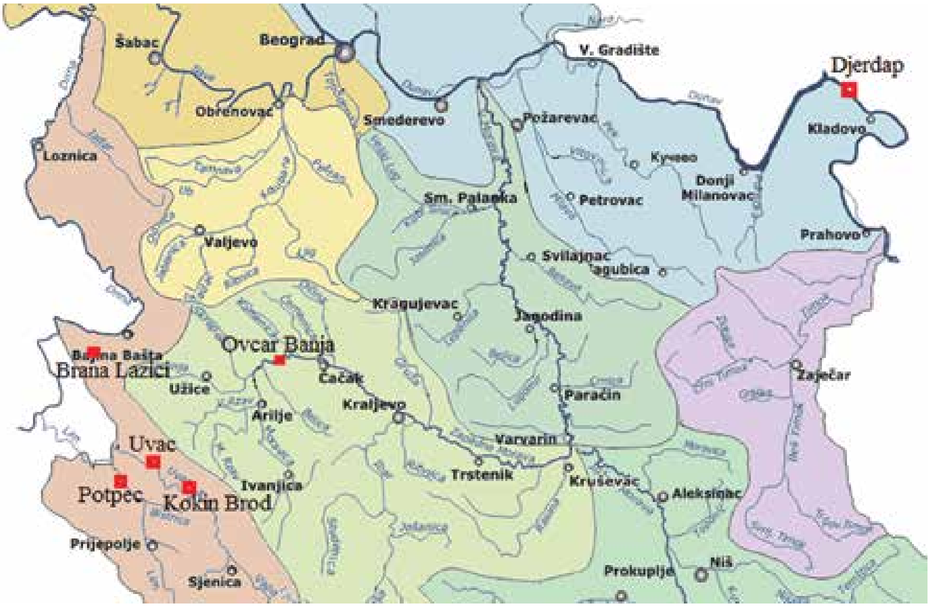

Fig. 1. Partial view of river basins in Serbia with studied site locations

Chemical analysis. Specific conductivity and pH were determined according to ASTM D 1125A:2009 and modified SRPS H.Z1.111:1987 standard methods, respectively. For NH_4^+ determination, SRPS H.Z1.184: 1974 was used. For NO_3^-, Cl^-, and SO_4^{2-} determination, modified methods from Standard methods 4110B, i.e., with sample preparation according to EPA M 300.0 method, were used.

Determination of elements was performed using a modified method based on EPA M 200.7:2001 with sample preparation according to EPA M 3050B:1996. The content of elements (Ca, Mg, Fe, Mn, Na and K) in all concrete samples was determined using inductively-coupled plasma with optical emission spectrometer (ICP-OES Spectro Blue Ti – Spectro Analytical Instruments GmbH, Germany). For calibration, a multi-element ICP standard (Roth Carl) and periodic table mix 1 ICP (Fluka) were used. The metals in soil standard reference material (ERA, Colorado, United States) were digested in triplicate and analysed to support quality assurance and control.

Microbiological analysis. Concrete samples (0.5 g) suspended in saline solution (10 ml) were used for preparation of further decimal dilutions. Total numbers of heterotrophic bacteria, SRB and fungi were determined using the plate count method on nutrient, iron-sulphite and malt agar, respectively. For the determination of *Bacillus* spp. the concrete samples suspended in saline were incubated for 45 min at 80°C and then inoculated onto nutrient agar. The number of iron-oxidising bacteria (FeB) was determined using medium with the following composition: 0.5 g/l NH_4NO_3, 0.5 g/l $NaNO_3$, 0.5 g/l K_2HPO_4, 0.5 g/l $MgSO_4$, 0.2 g/l $CaCl_2 \times 6H_2O$, 10 g/l ferric ammonium citrate, 15 g/l agar[14]. The number of NSOB was determined by a most probable number (MPN) technique using Beijerinck medium (5 g/l $Na_2S_2O_3 \times 5H_2O$, 1 g/l $NaHCO_3$, 0.2 g/l $Na_2HPO_4 \times 2H_2O$, 0.1 g/l NH_4Cl, 0.1 g/l $MgCl_2 \times 6H_2O$, 0.009 g/l $FeSO_4 \times 7H_2O$, pH 8.5) (Ref. 15).

Statistical methods. The relationships between microbial numbers (log-normalised data) and chemical data (pH, conductivity, concentrations) were studied using correlation analysis (Microsoft Excel).

RESULTS AND DISCUSSION

Chemoorganoheterotrophic bacteria, fungi, spore forming bacteria and bacteria specific for S and Fe nutrient cycles were analysed as microbiological parameters. Content of Ca, Mg, Na, K, Fe, Mn, sulphate, chloride, nitrate as well pH and conductivity were analysed as chemical parameters. The results of microbiological and chemical analyses of concrete samples from hydroelectric power plants in Serbia are shown in Tables 1 and 2.

It is noticeable that various types of microorganisms were present in almost all concrete samples, and their chemical parameters differed greatly. Total number of bacteria was in the range of 10^3–10^8, spore-forming bacteria 10^2–10^6, fungi

10^2–10^6 CFU/g, while maximum number of iron-oxidising bacteria was 6.4 × 10^6, neutrophilic sulphur-oxidising bacteria (NSOB) was 2.5 × 10^4 CFU/g and sulphate reducing bacteria (SRB) 2.2 × 10^3 CFU/g. pHs of the concrete samples were in the range 8.46–11.23, Ca content 5.43–19.93 %, Fe 151–61100 ppm, sulphate 37.4–623.7 ppm and chloride 96.3–914.1 ppm.

Concrete samples 594, 893, 877, 888 and 892 were singled out compared with all others due to exceptionally high or low values of either microbial growth or some chemical parameter. The highest numbers of aerobic sporulating bacteria (*Bacillus* spp.) and SRB were present in concrete sample 594. This concrete sample also contained an elevated number of all other tested microorganisms and it had the maximum concentrations of sodium and chloride detected, and thus, had very high conductivity. The highest counts of iron-oxidising bacteria and chemoorganotrophic bacteria were noted in concrete sample 893 (Table 1). Furthermore, this concrete sample contained the highest concentration of ammonium ions measured in this study.

Table 1. Numbers of specified groups of microorganisms in concrete samples (CFU/g concrete sample)

Sample	Bacteria	*Bacillus*	Fungi	SRB	NSOB	FeB
593 Djerdap	8.68 × 10^5	4.68 × 10^5	2.51 × 10^4	1.67 × 10^3	7.52 × 10^3	5.20 × 10^5
594 Djerdap	3.40 × 10^8	2.80 × 10^6	1.20 × 10^3	2.20 × 10^3	2.50 × 10^4	9.50 × 10^5
877 Brana Lazici	<1000	<100	<100	<10	<300	<100
878 Brana Lazici	6.00 × 10^5	2.60 × 10^5	9.00 × 10^2	<10	9.00 × 10^2	1.23 × 10^5
888 Ovcar Banja	1.57 × 10^6	1.96 × 10^2	5.32 × 10^3	21	16.8	9.52 × 10^4
890 Ovcar Banja	1.96 × 10^4	1.04 × 10^4	1.17 × 10^3	8.48 × 10^2	3.18 × 10^3	8.06 × 10^4
892 Potpec	8.64 × 10^3	8.64 × 10^2	<100	2.98 × 10^2	4.80 × 10^2	2.78 × 10^3
893 Potpec	6.24 × 10^8	1.01 × 10^5	3.12 × 10^5	3.12 × 10^2	7.80 × 10^3	6.40 × 10^6
894 Uvac	1.96 × 10^5	5.01 × 10^2	<100	27.3	4.60 × 10^3	6.64 × 10^4
895 Uvac	1.43 × 10^5	<100	<100	<10	6.80 × 10^2	1.50 × 10^2
897 Kokin Brod	2.52 × 10^5	<100	1.22 × 10^3	<10	6.48 × 10^2	5.18 × 10^3
898 Kokin Brod	3.64 × 10^6	<100	2.08 × 10^6	<10	3.12 × 10^2	1.50 × 10^5

Representatives of the analysed groups of microorganisms were not found in concrete sample 877, probably due to its high pH, which was 10.78 (Table 2). In concrete sample 888, with an even higher pH (11.23), chemoorganotrophic bacteria were numerous (1.57 × 10^6 CFU/g), but the other groups of investigated bacteria were present in low numbers only, indicating that factors other than pH affect what type of microorganisms will develop on concrete surfaces.

Concrete sample 892 had extremely high concentrations of iron and manganese, which probably exhibit a toxic effect on microorganisms, thus decreasing their numbers. Concrete sample 894 also contained high concentrations of iron and manganese, and relatively low numbers of total heterotrophic bacteria and fungi. However, this concrete also had the highest concentration of sulphate detected and relatively high numbers of NSOB and iron-oxidising bacteria. The metabolism of these bacteria likely explains their tolerance to the high levels of metals measured in this concrete. It is well known that high sulphate concentrations will cause the precipitation of gypsum and ettringite from concrete[2,16].

In relation to the other concrete samples, concrete samples 893, 898 and 593 contained relatively high numbers of fungi (Table 1).

Although there were some differences between concrete samples taken from the same power plant, based on the total number of microorganisms and their diversity, it can be concluded that the highest level of microbially induced deterioration (MID) was observed in concrete taken from Djerdap and Potpec and the lowest in concrete from Brana Lazici. The presence of different physiological and biochemical types of microbial communities in the concrete samples indicates succession and long term exposure[2,10]. This is supported by the lower pH (~8.5) of concrete from Djerdap and Potpec. The findings obtained are consistent with the generally accepted MID models, where acids produced by microorganisms are the main factor in the biological degradation of the concrete matrix.

To distinguish the chemical parameters important for the growth or activity of the groups of microorganisms studied, the relationships between microbial and chemical data were subjected to correlation analysis. A statistically significant, strong negative correlation (–0.759, $p = 0.004173$) between SOB levels and pH was found. Since sulphuric acid is the main metabolic product of NSOB, this additionally supports our previous conclusion.

Concrete is a widely used construction material, and various methods of maintenance are performed to prevent harmful structural changes and repair existing damages. Traditionally, methods such as modification of concrete composition, protective coating and treatment with biocides are applied for many years in order to minimise microbially-induced deterioration. Over the last decade, researchers have focused on the phenomenon of concrete healing, where innovative methods based on biotechnological, polymeric and chemical materials are introduced[17]. From the point of view of the present study, the (micro)-biological approach is particularly attractive, as there is a useful microbial solution for the detrimental effect induced by the activity of other microorganisms.

Table 2. Physicochemical and chemical properties of concrete samples

Sample	pH	Conductivity (μS/cm)	Ca (%)	Mg (%)	Na (%)	K (%)	Fe (ppm)	Mn (ppm)	NH_4^+ (ppm)	NO_3^- (ppm)	Cl^- (ppm)	SO_4^{2-} (ppm)
593 Djerdap	8.55	323	6.32	0.43	0.14	0.15	151	14.0	124.7	1.0	949.1	139.8
594 Djerdap	8.46	733	11.62	0.11	3.20	0.09	867	7.2	149.7	7.2	1104.2	73.2
877 Brana Lazici	10.78	361	15.01	0.03	0.03	0.01	400	19.0	141.4	13.3	375.2	165.5
878 Brana Lazici	9.89	238	13.08	0.03	0.05	0.07	200	44.3	170.6	1.0	103.7	120.1
888 Ovcar Banja	11.23	669	16.83	1.16	0.05	0.15	4000	182.5	174.8	41.3	85.2	170.3
890 Ovcar Banja	9.32	395	15.65	0.43	0.11	0.19	3700	238.2	187.3	12.2	172.3	79.0
892 Potpec	8.39	258	15.05	0.12	0.02	0.02	61100	4900.0	233.2	11.3	91.2	48.2
893 Potpec	8.89	197	13.41	1.26	0.03	0.04	2900	366.2	254.1	1.0	88.2	54.8
894 Uvac	8.85	295	5.48	0.10	0.07	0.43	16200	4700.0	216.5	1.0	914.1	623.7
895 Uvac	9.09	226	19.93	0.13	0.02	0.03	2700	270.2	37.4	1.0	111.2	37.4
897 Kokin Brod	9.19	238	18.42	0.41	0.03	0.09	5400	369.0	204.0	8.2	96.3	230.2
898 Kokin Brod	9.26	759	14.33	0.31	0.24	0.61	5900	288.2	224.9	1.0	974.2	84.4

Microbially-induced calcium carbonate precipitation (MICCP) is defined as the capability of microorganisms to form calcium carbonate extracellularly through metabolic activity[18]. In suitable conditions, many bacteria can initiate the formation of calcium carbonate by various metabolic pathways, but for engineering purposes, the most studied system is urea hydrolysis and alkaliphilic *Bacillus* spp. Bacterially generated precipitate is able to penetrate deep into the cracks, resulting in reduced permeability and increased compressive strength of concrete structure. The efficacy of MICCP for surface treatment and repair of cracks in cementitious materials has been demonstrated at laboratory scale and some promising results have been obtained at field scale. Furthermore, this principle is under study for its application to a self-healing approach, i.e. addition of healing agents into the concrete mix in order to activate repair when it is necessary.

CONCLUSIONS

In this study, concrete samples from different hydroelectric power plants in Serbia are analysed to estimate the extent of biodeterioration and the corresponding chemical parameters important for the growth and activity of microorganisms. Most of the concrete from the hydroelectric power plants contains high numbers of microorganisms, with their abundance and diversity indicating high levels of concrete deterioration and long-lasting exposure. Concrete samples from Djerdap and Potpec power plants contain the highest microbial levels, indicating the greatest deterioration of concrete, while concrete from the Brana Lazici power plant is less deteriorated. Among the microbiological and chemical parameters analysed, the SOB level and pH are the best indicators of deterioration of concrete.

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