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Hydrogen Sulphide in Industrial Enterprises Water Management Infrastructure - The Factor of Chemical and Microbiological Corrosion Concrete Degradation of Water Facilities

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Abstract. The durability of concrete, the material which is widely used for water facilities depends on accumulation in operational environments (drain water, air-gas space) of hydrogen sulfide. Now the mechanism of corrosion destruction of concrete in drainage pipelines is represented as result of biogenous sulphuric acid aggression – influence of the sulphuric acid formed by thionic bacteria. The analysis of data on H_2S concentration in drain waters of various industrial enterprises demonstrates that they create in gaseous operational media H_2S concentration, sufficient for development in aerobic conditions of thionic bacteria. As the results of urban sewer networks inspection have shown, the correlation between concentration of H_2S in aqueous phase and its concentration in air environment, between concentration of H_2S in air environment and the corrosion rate of concrete's coffering part is observed. Chemical and X-ray crystallography of this concrete showed that in corrosive concrete decreases *pH*, reaching in some examples of values 1-2, and sulfates collect. In dynamics of corrosion process the exponential growth of concentration in concrete of extremely acidophilic thionic bacteria is noted.

Introduction

One of the most significant risk factors at water drainage system operation is accumulation in operational environments of concrete pipelines (drain water, under-arch space, condensate moisture on the arch) hydrogen sulfide, its derivatives and oxidates initiating biogenous sulphuric acid corrosion of the concrete arch [1-4]. Corrosion is the reason of 70-75% of accidents on reinforced concrete drainage pipelines of urban sewer networks, reducing their durability from planned 50 to 10-15 years. And the frequency of accidents on reinforced concrete drainage pipelines (which length is 25% of slowness of all network) - 1.8-4.6 km/year - 2-4 times higher, than on ceramic and 20-40 times above, than on brick [4-7].

On objects of water management of the industrial enterprises the aggression of hydrogen sulfide is a factor of reliability and accident rate of objects, amplifies presence of other gaseous emissions [8-10]. So, at oil production the majority of the formations opened by the well contain in the structure a number of the components which are active in relation to cement stone [11]. One of the most aggressive components is hydrogen sulfide which amount can be from 3-5 to 20-25%. And aggressive influence of hydrogen sulfide in relation to hydrate phases is strengthened by oxygen and hydrocarbons. Researchers consider the corrosion reason hydrosulphuric gas corrosion therefore presence of H_2S demands the differentiated approach to the choice of composition of the tamponing mixes for increase in wellbore durability [10, 11].

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Now most of local and foreign experts show the mechanism of corrosion destruction of concrete in drainage pipelines as a result of biogenous sulphuric acid aggression - influence of the sulphuric acid formed on the arch by thionic bacteria [4, 5, 7, 12]. According to these representations the hydrogen sulfide accumulated in the atmosphere of self-flowing collector is dissolved in condensate moisture on the arch of the collector and with mandatory presence at the environment of oxygen is oxidized autotrophic and mixotrophic thionic bacteria to sulphuric acid. Thus, in the gas environment of under-arch space containing hydrogen sulfide, direct aggressive agent in relation to concrete is sulphuric acid (corrosion of the II type by V.M. Moskvin's classification). In concrete corrosion researches on objects of oil production the activating influence of oxygen on aggression of hydrogen sulfide in relation to concrete is also noted [11].

As concrete and reinforced concrete are applied as structural materials to large-scale water drainage constructions, refusals in their work and furthermore accidents, bring not only significant economic damage and violations in functioning of the enterprises, but also intensive pollution of all biosphere environment with long-term environmental impacts and threat of safe activity of the population [4-6, 10, 13].

Research Methods

The purpose of work is the analysis of physical and chemical, mineralogical and chemical concrete transformations of urban sewer networks in the course of the corrosion initiated by presence of hydrogen sulfide at air environment.

Concentration of hydrogen sulfide in water and gaseous operational environments of industrial enterprises water management infrastructure was controlled on objects of the city and industry sewerage and also objects of oil production. Corrosion of concrete and processes which initiate it, were investigated on networks of Kharkiv water drainage and also when modeling these objects in vitro. For research of the microbiocenosis developing in water disposal networks microbiological methods were used [14]. The composition of sewage and concrete was defined by standard procedure [15]. Concrete was investigated with the use of special methods of physical and chemical and structural analysis [16].

Results and Discussion

Results of own inspections of water management infrastructure objects of various industrial enterprises and also data of scientific and technical literature on the maintenance of H_2S in operational environments of water management constructions are provided to tab. 1. Apparently, H_2S concentration in aqueous mediums of the majority of objects rather high to create the increased concentration of H_2S in gaseous operational media (maximum allowable concentration of this compound in the working area of 10 mg/m^3, and on objects of oil production - 3 mg/m^3), development of thionic bacteria, sufficient for initiation, - producers of sulphuric acid, on the humidified surfaces in aerobic conditions. Genesis of H_2S in aqueous mediums of the considered industrial enterprises, possibly differs, but result of this phenomenon is the same: quite active elution of H_2S from aqueous medium in air-gas and the accumulation in it are governed by physical laws [17].

According to our researches, between H_2S concentration in aqueous phase and its concentration in air environment of collecting pipes of the same diameter certain dependence (fig. 1) is observed. And the established correlation between concentration of H_2S in air environment and the corrosion rate of concrete (fig. 2) is corresponded also to data of other authors [4].

Chemical, mineralogical, physical, chemical and microbiological analysis of the corroded concrete allows to establish type of corrosion and its nature. pH of native concrete 12.3-12.5 in the course of corrosion decreases, reaching at deep damage values below 1 that demonstrates acid aggression, whereby very strong acid. Sulfuric acid belongs to strong acid, and hydrosulphuric acid (product of dissolution of gaseous H_2S in aqueous medium) is weak acid.

Table 1. H_2S content in aqueous and gaseous medium of water management constructions of various enterprises

Industry	Water management object	H_2S Content	
		In aqueous medium (mg/dm^3)	In gaseous medium (mg/dm^3)
Oil production	oil tanks [10]	to 250	≥180
	Produced water: wellhead pump station	 0-20 0,07	
Urban sewer network	Drainage pipelines	5-25	0-200
Pulp and paper industry	Drainage pipelines	25-40	36-177
Nonferrous metallurgy enterprises	Drain waters [9].	10 - 1500	
Ferrous metallurgy enterprises	Drain waters [9].	to 30	

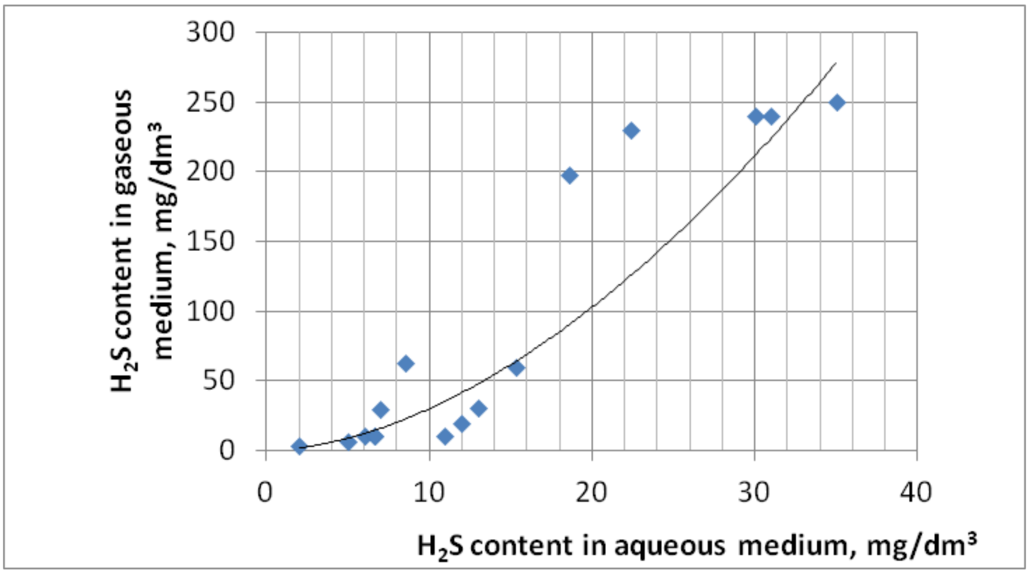

Fig. 1. The H_2S concentration influence in aqueous medium on H_2S concentration in the gas environment over water in collecting pipes

Acid concrete corrosion dynamics is objectively reflected by accumulation of acids which can be controlled by samples pH value, to which other indicators of concrete were compared. It is established that in corrosion sulfur dynamics in corrosive concrete is collected mainly in inorganic compounds, namely in sulfates (fig. 3).

Concentration of sulfur-containing organic compounds (cysteine, thioethyl alcohol) did not exceed 0.1 mg/g. As to the main mineral of corrosion - X-ray crystallography data (tab. 2) demonstrate accumulation of calcium sulfate, two-water plaster. In the course of corrosion in concrete also anhydrous sulfosilicate steadily collects.

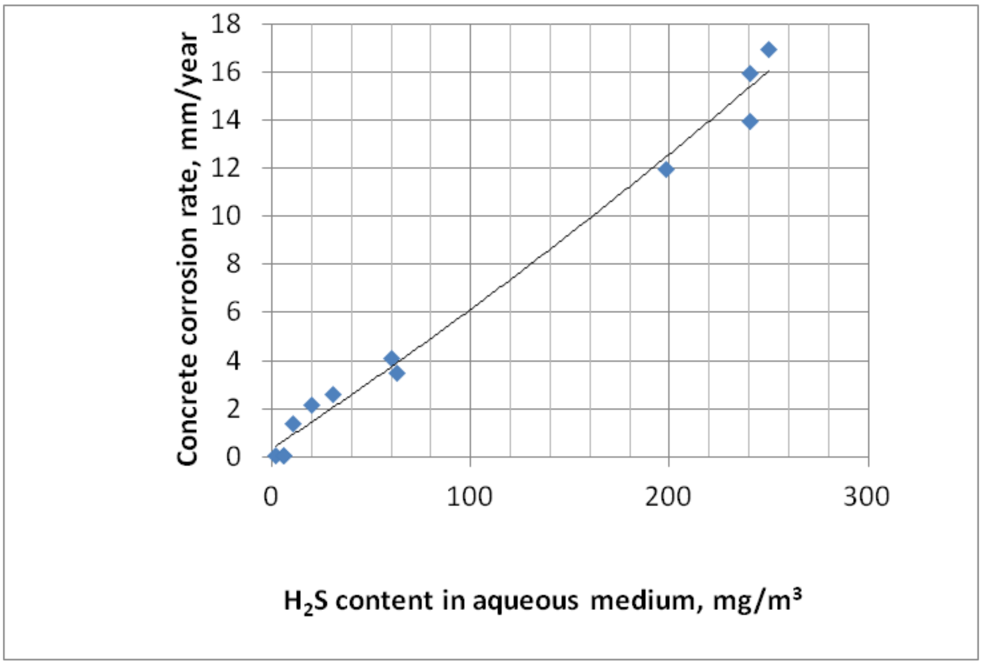

Fig. 2. The Influence of H_2S concentration in the atmosphere of collecting pipes on the corrosion rate of under-arch concrete

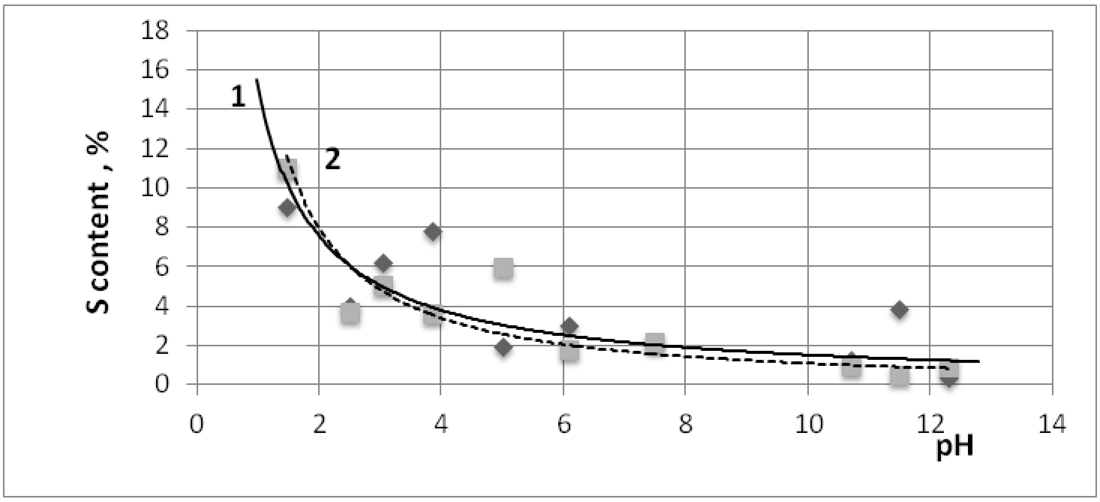

Fig. 3. Concentration of total sulfur (1) and sulfur of sulfates (2) in concrete in dynamics of corrosion process

Table 2. The abundance of sulfur-containing crystal mineral phases (points) on individual reflections (dn, nanometer)

pH concrete	Plaster dihydrate 0,760-0,750	Ettringite 0,980-0,960	Anhydrous sulfosilicate 0,280	Ammonium sulfate 0,510	Iron sulfide
2.9	9.0	0	1.6	0.2 (2.0)	0.32
3.0	9.0	0	1.0	Traces	0.3
3.5	Traces	0	0.2	Traces	0.3
4.2	5.0	0	0.6	0.3	0.3
6.1	Traces	0.5	0.2	0.3	Traces
7.8	9.0	1.0	0.4	0.4	0.2
8.6	4.0	1.0	0.3	0.4	0.2
12.2	0	0.5	0	0	0

In the process of corrosion other sulfate-containing minerals - ettringite and ammonium sulfate had more difficult dynamics. Concentration of ettringite during initial stage of corrosion was increasing, and with further corrosion process development and *pH* concrete values fall to less than 7.8 was decreasing. At pH <6.8 ettringite in concrete samples was not detected. Gross concentration of ammonium sulfate in concrete in the course of corrosion increased to concrete pH 7.8, and then decreased that is probably connected with solubility of this mineral and its active leaching in acidic environment.

In dynamics of corrosion process the exponential growth of extremely acidophilic thionic bacteria *Thiobacillus thiooxidans* concentration oxidizing H_2S to H_2SO_4 (fig. 3) is noted.

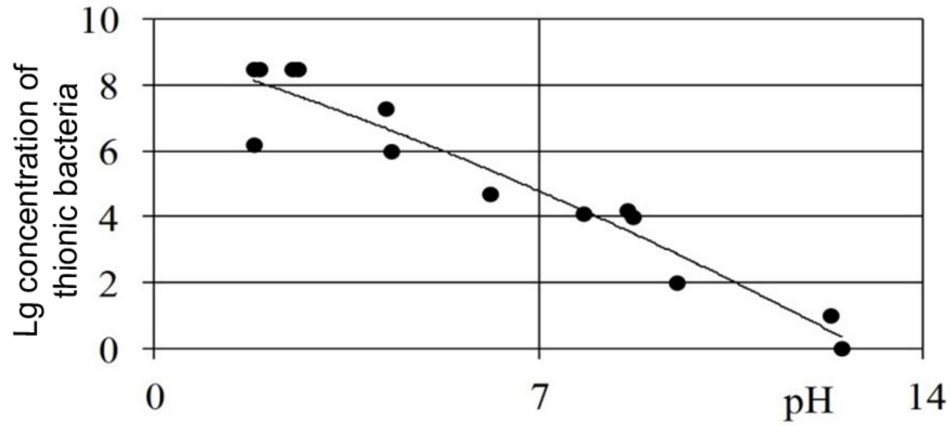

Fig. 4. The concrete corrosion depth influence (pH concrete) on concentration in it extremely acidophilic thionic bacteria *(Thiobacillus thiooxidans)*

Conclusions

The obtained data demonstrate that H_2S in enterprises water facilities belonging to various type of the industry creates corrosion aggressive environment for concrete structures.

Results of chemical, mineralogical, physical and chemical, and microbiological analysis of the corroded under-arch concrete part of Kharkiv sewer network collectors water drainage have shown that it was exposed to biogenous sulphuric acid aggression.

References

[1] V.Ya. Kofman, Serovodorod i metan v kanalizacionnyx setyax (obzor), Vodosnabzhenie i sanitarnaya texnika. 11 (2012) (in Russian).

[2] S.V. Fedorov, V.M. Vasil`ev, M.N. Klementev, Issledovanie gazovydeleniya na uchastke kanalizacionnoj seti, Vodosnabzhenie i sanitarnaya texnika. 5 (2019) (in Russian).

[3] I. Valentina, L. Elena, B. Elena, Environmental Safety of the Sewage Disposal by the Sewerage Pipelines, Transbaltica-2015. Procedia Engineering. 134 (2016) 181-186.

[4] G.Ya. Drozd, N.I. Zotov, V.N. Maslak, Kanalizacionnye truboprovody: nadezhnost, diagnostika, sanaciya, Doneczk: IEP NAN, Ukrainy, 2003. (in Russian).

[5] V.A. Yurchenko, E.V. Brigada, Kineticheskie xarakteristiki mikrobiologicheskoj korrozii betona v setyax vodootvedeniya, Voda i ekologiya. Problemy i resheniya. 1 (2014) 51-61 (in Russian).

[6] G. Dmitri, G. Alexei, B. Dmitri, Z. Gennadii, On renovation of the destroyed tunnel sewer collector in Kharkov, World journal of Tngineering. 13 (2016) 72-76.

[7] N.K. Rozental, Korroziya i zashhita betonnyx i zhelezobetonnyx konstrukcij sooruzhenij ochistki stochnyx vod, Beton i zhelezobeton. Oborudovanie, materialy, texnologiya. 1 (2011) 96-103. (in Russian).

[8] L.N. Fesenko, A.Yu. Cherkesov, S.I. Ignatenko, Metody udaleniya serovodoroda iz proizvodstvenny`x stochny`x vod i puti ix razvitiya, Voda Magazine. 2 (102) (2016) https://watermagazine.ru/nauchnye-stati2/novye-stati/24763-metody-udaleniya-serovodoroda-iz-proizvodstvennykh-stochnykh-vod-i-puti-ikh-razvitiya.html. (in Russian).

[9] A.S. Vinogradova, Yu.V. Trofimenko, Metody ochistki stochnyx vod ot serovodoroda na proizvodstvennyx uchastkax avtoservisa, Nauchnoe obozrenie. Pedagogicheskie nauki. 2-3 (2019) 19-21. (in Russian).

[10] R.Z. Saxabutdinov, Rrazrabotka texnologicheskix processov sbora, podgotovki i transportirovki uglevodorodnogo syrya s minimalnymi poteryami uglevodorodov i vybrosami vrednyx veshhestv v atmosferu. diss… doktora texn. nauk: 25.00.17. Tatarskij nauchno-issledovatelskij i proektnyj institut nefti, Bugulma, 2001. (in Russian).

[11] F.A. Agzamov, L.N. Lomakina, N.B. Hababutdinova, R.F. Davletshin, A.K. Kriga, T.V. Tokunov, Cement stone corrosion processes affected by acidulous components of bedded fluids, Геология. Геофизика. Бурение. 13(4) (2015).

[12] V.M. Vasilev, G.A. Pankova, Yu.V. Stolbixin, Razrushenie kanalizacionny`x tonnelej i sooruzhenij na nix vsledstvie mikrobiologicheskoj korrozii, Vodosnabzhenie i sanitarnaya texnika. 9 (2013) 67-76. (in Russian).

[13] A.Yu. Cherkesov, Ochistka sernisto-shchelochnykh stochnykh vod nefteorgsinteza ot serovodoroda: dis. kand. tekhn. nauk [Purification of Sulfurous-Alkaline Waste Waters of Petroleum Synthesis from Hydrogen Sulfide: Cand. Engin. Sci. Diss.], , Novocherkasskii politekhnicheskii universitet Publ. Novocherkassk. 2014. [in Russian].

[14] D.G. Zvyagintsev, *Methods of soil microbiology and biochemistry,* Ed. Moscow, Moscow State University. Moscow, 1991. (in Russian).

[15]. Unificirovanny`e metody issledovaniya kachestva vod. Metody ximicheskogo analiza vod, Moscow, 1987. 662. (in Russian)

[16]. L.N. Popov, Laboratornye ispytaniya stroitelnyx materialov i izdelij, Vysshaya shkola, Moscow, 1984. (in Russian)

[17] A.A. Usyk, I.L. Derkach, E.A. Shishkin Issledovanie processa massoperenosa serovodoroda v sisteme «gaz-zhidkost», Kommunalnoe xozyajstvo gorodov. 93 (2010) 414-421. (in Russian).