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ANALYSIS OF WATER QUALITY ZERO CONDITION IN THE AREA OF SILICON MATERIAL FACTORY

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ABSTRACT

Construction of the silica material factory named "R-S Silicon", with an annual production capacity of 15,210 ton of Si-metal, was planned in the village of Bjelajce, municipality of Mrkonjić Grad. The factory for production of Si-metal shall have direct and indirect environmental impacts, especially on waters, by washing off working areas, leachate and other waste water that must be treated due to contamination, so that their quality would be at least the quality of surface recipient into which they are discharged.

Before the construction, i.e. commissioning of subject factory, it is necessary to determine the zero condition of waters quality around the factory in order to have a realistic picture of its impact on the water quality during its operation.

Key words: *factory "R-S Silicon", water quality, zero condition*

INTRODUCTION

Basic part of factory "R-S Silicon" is its electric arc furnace, which represents a reactor in which chemical reactions are conducted at high temperatures, resulting in the production of Si-metal as the principal product and silicate dust as a by-product [1].

With the aim of determining the "zero condition" of the quality of surface waters in the area of construction site "R-S Silicon", Mrkonjić Grad, in order to follow up the mentioned plant's impact, surface waters were sampled and analysed at 3 measuring spots every month during the year 2015. Based on the established condition, water quality is monitored during later operation of "R-S Silicon", factory for the production of silicon metal. The factory is located on the bank of the Crna rijeka that represents the most significant watercourse in the area of the municipality of Mrkonjić Grad. The Crna rijeka, as well as its river system, in an area of about 111.00 km^2, represents a primary recipient of untreated waste water from many settlements in its watershed [2,3]. The quality of surface waters is to a great extent determined by natural and anthropogenic processes. During the annual hydrological cycle, the quality of surface waters depends on a number of natural and anthropogenic factors: atmospheric precipitation, deposits, i.e. soil

erosion in the watershed, number of populace and development of industry in the watershed area [4,5]. The impact of the pollutants in the rivers depends on the type of pollutants, their concentrations in the water and the length of exposure to human activities [6].

According to our preliminary researches, we can state that the most prominent polluters of the watershed and watercourse of the Crna rijeka are industrial and communal waste waters, occurrence of random waste landfills (so-called "wild landfills), traffic, agro-chemical agents etc. The impact of industrial waste waters on environmental water ecosystems, and on humans as well, is multiply inconvenient. Depending on industry type, in waste waters can be found not only increased concentrations of organic, but also inorganic substances, especially ions of toxic metals and newly synthesised organic compounds that had never occurred in natural waters.

Knowing and maintaining the watercourse quality represents a good basis from both the aspect of agriculture development and from the aspect of the environmental protection. Surface waters monitoring represents a very significant factor in the monitoring of water quality and the health of living beings.

DETERMINATION OF WATER QUALITY ZERO CONDITION IN THE AREA OF THE FUTURE FACTORY "R-S SILICON"

For a credible determination of water quality in the area of the future factory "R-S Silicon", it was necessary to perform measurements of certain parameters at several locations. All tests of water samples were done in line with accredited methods prescribed by BAS/EN, at the accredited laboratory "Euroinspekt" LLC Osječani, Doboj, and results were synthetized and presented in a the form of a diagram. Measurements were done at three locations, where surface water and groundwater were sampled in the area of construction site; it is to say its direct vicinity.

Every test cycle consisted of measurements of the following parameters of quality of surface waters and groundwater:

- temperature,
- pH,
- total suspended solids,
- precipitation solids (Imhoff),
- electrical conductivity,
- COD,
- $BOD_{5,}$
- dissolved oxygen,
- iron and
- mineral oils.

Sampling frequency was once a month; it is to say 12 times during the year 2015.

MEASURING LOCATIONS

With the aim of analysing the zero condition of water quality at the location of the future factory "R-S Silicon" Mrkonjić Grad, surface waters and groundwater were sampled and tested in the area of construction site, it is to say its direct vicinity in three positions, Figure 1:

1) the Crna rijeka watercourse, at a distance of ca 200 m downstream from the construction site plot (measuring location 1),

2) a concrete shaft in which water from the underground well is collected in the area of construction site, next to the administration building (measuring location 2),
3) the Crna rijeka watercourse, upstream from the industrial plot (measuring location 3).

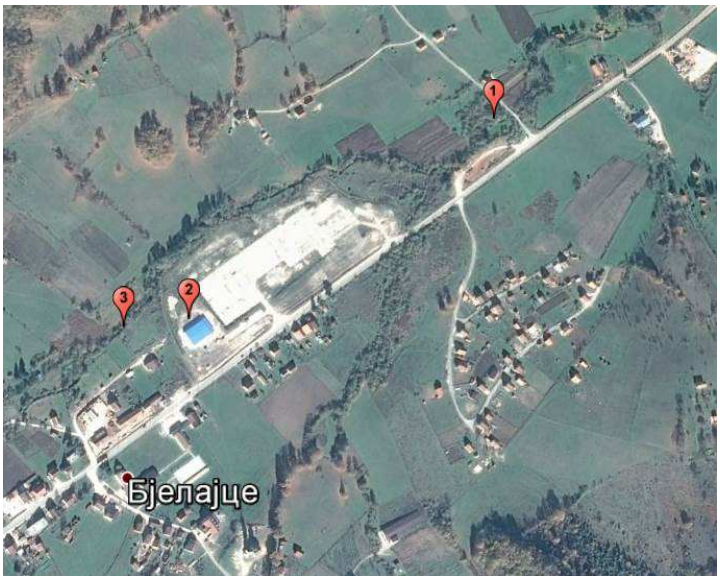

Figure 1. Water sampling positions

Surface water sampling locations coordinates (Crna rijeka), ca 200 m downstream from the construction site plot (measuring location 1.): 44° 26' 28.72" N and 17° 9' 26.56" E, Figure 2, sample 1.

Sampling spot 1.	Sampling spot 2.	Sampling spot 3.

Figure 2. Place of sampling

Water sampling positions coordinates in which water from the underground well is collected (measuring location 2.) are 44° 26' 18.46" N and 17° 9 '5.00" E, Figure 2, sample 2.

Surface water sampling locations coordinates (Crna rijeka), upstream from the industrial plot (measuring location 3.) are 44° 26' 18" N and 17° 9' 82" E Figure 2, sample 3.

TESTING METHODS

After sampling certain type of water, composite samples were formed in which some parameters (T, pH, dissolved O_2) were determined on the spot, and the remaining samples were adequately conserved and sent for laboratory analyses in line with standard methods.

Results of analysing water samples from the Crna rijeka were commented in line with the Decree of watercourses classification and categorisation (RS Official Gazette, No. 42/01) [7]. For parameters that belong to the group of general physical-chemical parameters, tested water sample quality assessment was done based on relevant values for each parameter. An overview of tested parameters and applied methods is given in table 1.

Table 1 List of parameters with testing methods

Ord. no.	Parameter	Standard testing method	Ord. no.	Parameter	Standard testing method
1.	Water temperature	BAS DIN 38404-4:2000	6.	Chemical oxygen demand – HPK (with potassium dichromate)	BAS ISO 6060:2000 Reflux distillation and titration
2.	pH value of water	BAS ISO 10523: 2010 Electro-chemical	7.	Biological oxygen demand after 5 days - BPK_5	BAS ISO 5815:2002 Determining biological oxygen demand with an electro-chemical - oxygen meter after 5 days
3.	Total suspended solids	BAS EN 872:2006 Filtration and gravimetry	8.	Dissolved O_2	BAS EN 5814:2014 electro-chemical - oxygen meter
4.	Precipitable solids after 30 minutes by Imhoff	EPA 160.5:1974	9.	Iron	BAS ISO 6332:2000 Spectrophotometric at 510 nm. (with 1,10 fenantrolin)
5.	Electrical conductivity	BAS EN 27888: 2003 electro-chemical	10.	Mineral oils	EPA 1664-R-A : 1999

According to normative definitions of the ecological status of water quality and allowed limit values for some quality parameters, all surface waters comprised by the Decree of watercourses classification and categorisation (RS Official Gazette, No. 42/01) are classified into five classes, from 1 to 5. According to the ecological quality of water, which must be maintained or achieved by introducing preventive measures and the nest economically available technologies, the Crna rijeka surface watercourse is classified in the II watercourse category.

MEASUREMENT RESULTS

Based on the results of measurement of tested quality parameters for surface waters and groundwater at subject location, results can be commented in line with the Decree of watercourses classification and categorisation (RS Official Gazette, No. 42/01) [7].

Measured pH value in taken samples of surface water at measuring location 1 (the Crna Rijeka watercourse, at a distance of ca 200 m downstream from the construction site plot) ranged between 7.04 and 8.10, and at measuring location 3 (upstream from the industrial plot) pH value ranged from 7.18 to 8.44, which is within the limits for first class surface watercourse, which amount to 6.8-8.5. At measuring location 2 (concrete shaft) pH value ranged from 6.67 to 8.26, which is within the limits for third water quality class, whose allowed limit values amount to 6.5-9.0. Minimal pH value of 6.67 was measured during the tests in the month of December, and the highest pH value of 8,26 during the tests in the month of June (at measuring location 2).

Dissolved oxygen and water temperature are very important *in situ* parameters for the monitoring of surface waters quality. Water temperature is a significant parameter from the aspect of dissolvability of oxygen and other gases from the air in the water, and any increase in temperature leads to an increase in the velocity of oxygen consumption (biochemical oxidation). The highest temperature of surface water in analysed samples of water was recorded at measuring location 1 in the month of September when it amounted to 16.1^{0}C, whereas at measuring location 2 (concrete shaft) the value of temperature ranged up to 12.,3 ^{0}C, also in the month of September.

Dissolved oxygen in the water is a significant parameter of water ecosystems because it provides life and activity of aerobic microorganisms that dissolve organic substances in order to acquire energy that is necessary for growth and procreation. At measuring location 1, the value of dissolved oxygen ranged from 5.8 mg/l to 8.9 mg/l, where 45% of samples had a value within the limits of second class, and 17% within the limits of third water quality class. The measured value of dissolved oxygen in taken samples of surface water at measuring location 3 ranged in the limits of first class in 75% of samples, 17% in the second class and 8% in the third water quality class. The lowest values of dissolved oxygen were recorded at measuring location 2 (a concrete shaft in which is collected water from the underground well in the area of construction site) with a result of only 4.0 mg/l; and out of the total number of results, 83% of values fall under the third water quality class.

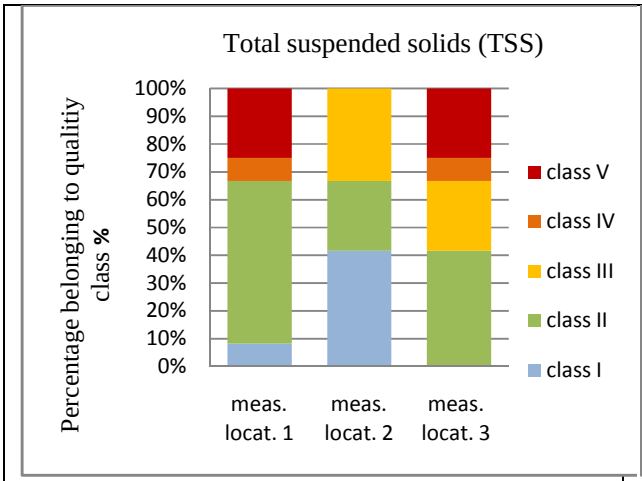

Figure 3 Percentage of water classes according to the parameter total suspended solids (TSS)

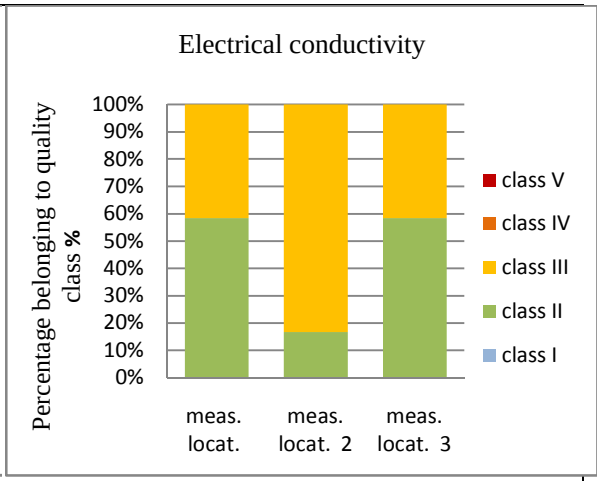

Figure 4 Percentage of water classes according to the parameter electrical conductivity

Suspended solids impact on many aspects of surface water quality. Larger amounts of suspended solids encourage the growth of algae, which affects the learning process of eutrophication [8]. Surface water (measuring location 1 and 3) sampled in the watercourse Crna rijeka downstream and upstream from the industrial plot "RS-Silicon" LLC Mrkonjić Grad, for shown values of the parameter total suspended solids in an amount of 25% of samples belongs to the values prescribed for class V, and 8.3 % of results apiece belong to water quality class IV (figure 3). The highest values of total suspended solids were recorded in the month of February, when at measuring location 3 it amounted 370 g/m^3, and at measuring location 1

as much as 408 g/m^3. At measuring location 2, out of the total number of samples, 33% of results were higher than the allowed, and belong to water quality class III.

Electrical conductivity of water depends on the salt content, a higher value of this parameter may indicate that it is polluted water. Based on the electrical conductivity of water we tested measurement of defining the limits of II and III category of water quality (figure 4).

As an indicator of organic pollution of water are used chemical and biochemical oxygen demand. Chemical oxygen demand (COD) is a quantity of oxygen that is consumed for a complete oxidation of organic substances in the water and directly represents an indicator of water pollution with organic substances. Oxidation is only performed in acid environment, with potassium-permanganate or potassium dichromate. Biochemical oxygen demand (BOD_5) represents a quantity of oxygen consumed by microorganisms for dissolution of organic substances in the water. Value of concentrations for COD (figure 5) in surface water at measuring location 1 and 3 only in one sample did not meet the prescribed values for second quality class, notably in the month of June, when the value of COD amounted to 22.5 gO_2/m^3 at measuring location 3, it is to say 23 gO_2/m^3 at measuring location 1. At measuring location 2 (concrete shaft), the results of COD of all taken samples were within the limits of values of the first water quality class in line with the Decree of watercourses classification and categorisation (RS Official Gazette, No. 42/01) [7].

Values of concentrations for BOD_5 were at the lowest level at measuring location 2, and in 58.3% of samples it corresponded to the values prescribed for the first water quality class, and only in the month of March it deviated from the prescribed second water quality class, when the value of BOD_5 amounted to 13.2 gO_2/m^3 (which corresponds to the values of VI water quality class). At measuring location 1, the value of BOD_5 exceeded allowed limit values for the prescribed second water quality class in 58.3% of samples, whereas at measuring location 2 these exceeding amounts were recorded in about 50% of samples (figure 6).

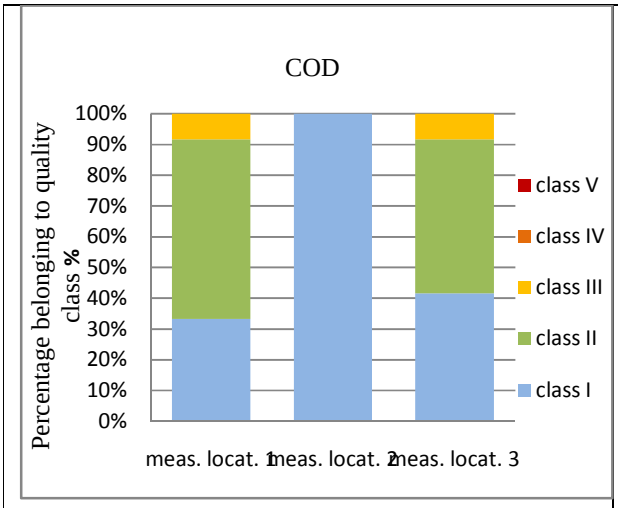

Figure 5 Percentage of water classes according to the parameter COD

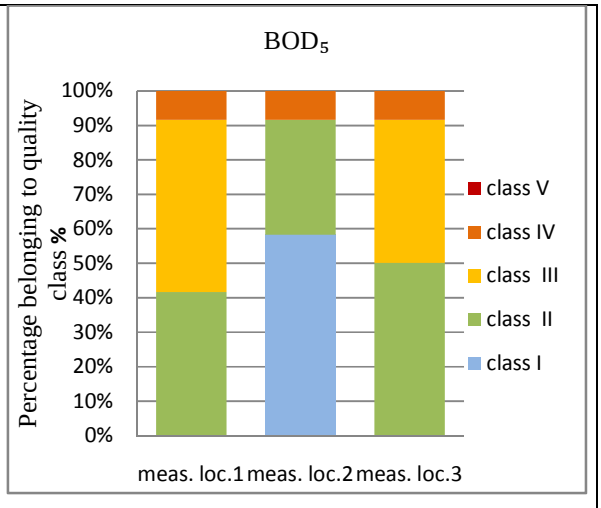

Figure 6 Percentage of water classes according to the parameter BOD_5

According to the parameter iron (figure 7), water quality at measuring location 2 was in all measurements in the I water quality class, whereas at measuring location 1 and 3 in 41.6% of samples it did not meet the allowed limit values for the prescribed second water quality class [7].

With regard to presence of mineral oils, the results of analyses of all taken samples of surface water and groundwater showed that the values of this parameter were in the limits of values for the first water quality class, it is to say that all measured values were lower than 2.5 mg/m^3.

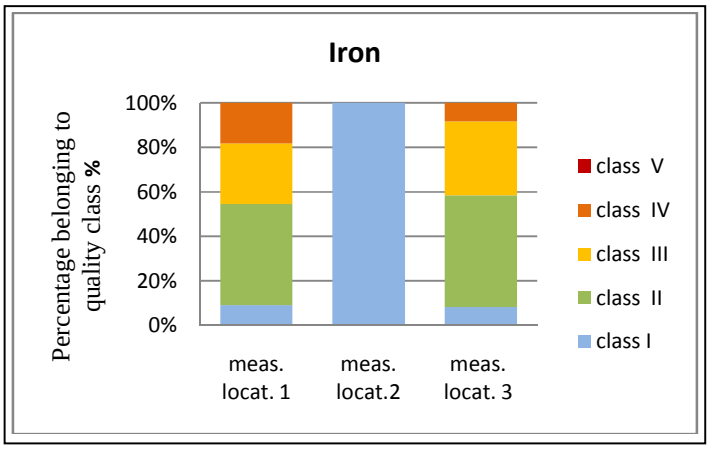

Figure 7 Percentage of water classes according to the parameter iron

With regard to presence of mineral oils, the results of analyses of all taken samples of surface water and groundwater showed that the values of this parameter were in the limits of values for the first water quality class, it is to say that all measured values were lower than 2.5 mg/m^3.

Precipitable substances by Imhoff area particles in suspension, which will be precipitated under the influence of gravity during a period of time. The results of precipitable substances (by Imhoff) showed that the values in all values mostly ranged up to 0.2 ml/l (92% in samples at measuring location 1 and 3, and as many as 100% in samples at measuring location 2). Only in the month of June, the results amounted to 0.5 ml/l and 0.4 ml/l at measuring location 1 and 3, respectively.

CONCLUSION

Results of water quality measurement at three measuring locations in the area of the future factory "R-S Silicon" lead to a conclusion that water quality for the majority of tested parameters does not meet the prescribed II water quality class, in line with the Decree of watercourses classification and categorisation (Republika Srpska Official Gazette, No. 42/01). The quality of sampled water in the surface watercourse Crna rijeka in a position upstream and downstream from the industrial plot (measuring places 1 and 3) corresponds to the allowed values for the V watercourse quality for the parameter total suspended solids, and high concentrations of BOD_5 were also recorded, which in 50% of samples exceeded the allowed limit values for the recommended second water quality class. Shown results of BOD_5 imply a high level of organic pollution, and a high level of total suspended solids implies strong turbidity of water, which is a consequence of discharging untreated communal and industrial waste water from Mrkonjić Grad and surrounding smaller settlements and surface erosion in the river drainage basin.

The values of tested parameters of groundwater quality (measuring location 2) do not exceed allowed limit concentrations prescribed for III water course quality, except in one sample when the value of BOD_5 was in the IV water quality class [7]. Still, given a fact that this is groundwater, high values of some parameters (total suspended suspended solids and electrical conductivity) are very surprising, which imply that surface waters percolate into groundwater, or polluting substances are washed off from the surrounding terrain, since it comes to an open concrete shaft.

Significance of determining a water pollution degree, it is to say zero condition of water quality, prior to the construction and commissioning of factory "R-S Silicon" is a fact that only in this way can negative impacts of the factory on water quality during its operation be assessed. Besides, determining zero condition gives an insight into a compulsory level of treatment of leachate and waste water from the factory, so that they would be at least at the level of quality of surface recipient into which they are discharged.

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