Aspects Regarding Instantaneous Corrosion of Nodular Iron in Household Wastewater

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Abstract. Waste water pumps operates under high corrosion and wear conditions due to the working environment containing sand particles, suspension particles, sulfuric acid and various dissolved salts, etc. Because of the operating conditions, the rotor and sometimes the pump stator (especially immersion ones) suffer various aggressions, such as material avulsion, corrosion, etc. This paper represents a study on the nodular cast iron samples corrosion from the rotor of a single-chamber pump, which were tested in synthetic corrosion environments that mimic the characteristics of natural environments.

1. Introduction
Nodular cast iron is a cast iron with spheroidal graphite. Due to the nodular aspect of the graphite, the rejection effect (crack propagation) is minimized and high tensile and tearing strength is obtained. Thanks to these properties, these materials have multiple uses, such as cylinder heads, engine shafts, gears, grills, parts for pumps, presses, or electric machines. In this study we have chosen a nodular cast iron used for the construction of pumps used in pumping stations for domestic wastewater transfer into the sewerage network [1-4].

The study aims to quickly assess instantaneous corrosion, corrosion that occurs on direct contact between metal and wastewater, and the pH influence on this process.

2. Materials and methods
The composition of the alloy was determined by optical emission spectrometry with a Foundry Master spectrometer and is shown in Table 1. In addition to these alloy elements, Mo, V, Co, Sn are present in less than 0.01%. The microstructure was determined using the Zeiss metallographic inverse optical microscope and is shown in Figure 1.

Considering the use of nodular cast iron in the construction of pumps used in wastewater transfer, in this study we decided to study the corrosion of the material in a series of domestic waste water simulating solutions.

To this end, we started from Boeije's studies [5] on the average composition of decanted water from municipal wastewater from municipal sewage. Choosing synthetic solutions components is based
on the expected composition of domestic water discharges. Compared to the composition proposed by Boeije, minor modifications have been made to the solution used here, especially on the ratio of the mineral components.

Table 1. Chemical composition for the nodular cast iron, [%].

| Element | Fe  | C   | Si  | Ni  | Mg  | Mn  | P   | S   | Cr  | Ti  | Al  | Cu  | Nb  |
|---------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Percent | balance | 4.50 | 2.28 | 0.12 | 0.10 | 0.09 | 0.05 | 0.04 | 0.02 | 0.02 | 0.01 | 0.01 | 0.01 |

![Figure 1](image)

**Figure 1.** Nodular cast iron microstructure with ferrite-pearlite metal base: (a) 200X; (b) 100X.

The composition of the basic synthetic residual water, abbreviated as DWW-1, is shown in Table 2. Inorganic components are responsible for the corrosive properties of the solution, while food components can function as protectors or inhibitors. The DWW-1 solution presents a pH value close to neutral: pH = 6.5.

To study the influence of pH on corrosion behavior, base solution (DWW-1) was used. The pH was modified by the addition of sodium hydroxide. Thus the following solutions were obtained:

- DWW-2: pH = 3.0 - by adding 0.1M HCl solution to the basic solution,
- DWW-3: pH = 11.0 - by the addition of 0.1M NaOH to the basic solution.

Table 2. The basic residual wastewater composition (DWW-1).

| Chemical components | mg/l | Food components | mg/l | Metallic residues | mg metal/l |
|---------------------|------|-----------------|------|-------------------|------------|
| NH₄Cl               | 15   | Powdered milk   | 118  | Cr(NO₃)₃·9H₂O     | 0.10       |
| CH₃COONa·3H₂O       | 142  | Beer yeast      | 54   | CuCl₂·2H₂O        | 0.20       |
| MgSO₄·7H₂O          | 32   | Starch          | 122  | MnCl₂             | 0.05       |
| CaHPO₄              | 20   | Soybean oil     | 15   | NiSO₄·7H₂O        | 0.08       |
| K₃HPO₄·3H₂O         | 56   |                 | 15   | PbCl₂             | 0.07       |
| FeSO₄·7H₂O          | 14   |                 |      |                   |            |
| Urea                | 98   |                 |      |                   |            |
| Peptone*            | 15   |                 |      |                   |            |

Electrochemical study methods are a quick and effective means of obtaining information about the following: the thermodynamic corrosion probability of a metal immersed in a liquid, the instantaneous corrosion rate (corrosion rate at simple metal immersion in the corrosion environment),
the corrosion type (generalized or localized) and its intensity, as well as factors that can influence the corrosion process (temperature, pH level, accelerators or corrosion inhibitors), [6-8]. Electrochemical corrosion is an oxidation-reduction process in which metal anodic oxidation occurs simultaneously with a cathodic reduction process in which the electrons generated in the anodic reaction are consumed. The two processes are coupled and carried out at the same speed, at a common potential called mixed potential, or corrosion potential \( E_{cor} \). The speed of the two processes is directly proportional to the current. The thermodynamic tendency of a metal or alloy oxidation, submerged in an electrolytic environment can be expressed by the corrosion potential \( E_{cor} \), while the corrosion rate is expressed by the anode \( \rightarrow \) cathode electrons transfer. At the corrosion potential, the anode current \( (I_a) \) is equal to the cathodic current \( (I_c) \) and the current in the outer circuit is zero. Under these conditions, the metal/solution system is at thermodynamic equilibrium, \( (I_a-I_c)E=E_{cor}=0 \), and no apparent reaction takes place on the surface of the metal. However, metal degradation takes place only in the anodic process by oxidation, so that corrosion occurs at a rate proportional to the anode current (generally equal to the cathode current): \( I_{cor}=(I_a)_{E_{cor}}=(I_c)_{E_{cor}} \) proportional with the corrosion current, \( I_{cor} \), respectively the current density, \( j_{cor}=I_{cor}/S \). The current density measured at the corrosion potential is a measure of the equilibrium oxidation process speed at the simple immersion of the metal or alloy in the solution and is called instantaneous corrosion rate.

The corrosion behavior of the alloy has been studied on the basis of the linear polarization curves obtained with a Dynamic Electrochemical System, VoltaLab 40 (PGZ 301) (Radiometer Analytical SAS - France).

The measurements were carried out in a three-electrode cell. Samples used for studies (work electrodes) are circular discs of 10 mm diameter, which are mounted in the special cell support and provide a flat surface of 6 mm in diameter. The metal surface exposed to the electrochemical treatment is circular without edges or corners and has in all cases the value of 0.283 \( cm^2 \). Prior to mounting in the electrochemical cell, each sample was polished onto SiC paper to 2500 grit, degreased in acetone and washed with water. The auxiliary electrode, which polarizes the work electrode, was platinum and is supplied by the appliance manufacturer.

The reference electrode, the one used to measure the the potential of the working electrode, was a saturated calomel electrode (ECS) that exhibits good stability over time. Usually, when the potential value of the electrode is indicated, the reference electrode used to measure it is also indicated: E mV (ECS) or E mV/ ECS. In the present paper, in order not to complicate the writing, the potentials were expressed in mV or V without indicating the type of electrode to which they were measured. The determinations were performed at 25°C.

Linear polarization measurements were performed in the potential range (+200 ... -200 mV) against the open circuit potential with a scanning potential rate of \( dE/dt=0.5 \) mV/s. The acquisition and processing of the electrochemical data was done with the VoltaMaster 4 software.

3. Results and discussions

The density of the instantaneous corrosion current can also be evaluated on the basis of the linear polarization curve using the polarization resistance method, this one representing the slope of the tangent to the potential-current density curve \( [E=f(j)] \) in the equilibrium point \( (E=E_{cor} or \eta=0) \), where \( \eta=E-E_0 \) is the overpotential), that means at the corrosion potential: \( R_p=(dE/dj)_{E_{cor}} \).

The polarization resistance, \( R_p \), is evaluated on the basis of the Butler-Volmer equation. If the electrode is corroding the metal through a single electrode controlled charge reaction can be written as [9, 10]:

\[
 j = j_{cor} \left[ \exp \left( \frac{2.303(E-E_{cor})}{b_a} \right) - \exp \left( -\frac{2.303(E-E_{cor})}{b_c} \right) \right]
\] (1)
where: $b_a$ and $b_c$ represent the slopes of the linear portions of the anode and cathode sections in the diagram $E = f(\log J)$ close to the corrosion potential, known as the Tafel slopes:

$$b_a = \left( \frac{\partial E}{\partial \log j} \right)_a = \frac{RT}{\alpha n F}$$

respectively

$$b_c = \left( \frac{\partial E}{\partial \log j} \right)_c = \frac{RT}{(1 - \alpha) n F}$$

(2)

It has been experimentally observed that $j$ variation is approximately linear according to the applied potential ($E$), starting at about $50...60$ mV with respect to the corrosion potential and only on a range of about $10...20$ mV. Stern și Geary [11, 12] have simplified the Butler-Volmer equation for the case of low overvoltages relative to $E_{cor}$, linearizing this equation by developing logarithmic terms in a series ($e^x = 1 + x + x^2/2! + x^3/3! + ...$), and neglecting the terms of superior order.

The simplified equation it may be given:

$$R_p = \left( \frac{dE}{dj} \right)_{E_{cor}} = \frac{b_a \cdot b_c}{2303. \ J_{cor} \ (b_a + b_c)} \ (\text{ohm} \cdot \text{cm}^2)$$

(3)

After re-arranging the equation we can obtain for instantaneous corrosion intensity:

$$J_{cor} = \frac{b_a \cdot b_c}{2303(b_a + b_c) \cdot R_p} \ (\text{mA} \cdot \text{cm}^2)$$

(4)

The corrosion rate, expressed as penetration velocity, can be evaluated with the [12-19] relation:

$$v_p = 3.27 \sqrt{\frac{A}{Z}} \ \frac{J_{cor}}{\rho} \ (\text{mm/an})$$

(5)

where $\sqrt{\frac{A}{Z}} = \sum g_i \frac{A_i}{z_i}$ represents the average electrochemical equivalent of the alloy; $g_i$ represents the gravimetric fractions (mass fractions) of the alloy components and $(A_i/z_i)$ the corresponding chemical equivalents.

The corrosion potential was evaluated from the linear polarization curves, using the Evans diagram, which represents the logarithm of the current density according to the potential of the electrode over a overpotential range of $\pm 50...60$ mV. In these coordinates at the intersection of the linear portions of the anodic and cathodic sections of the polarization curve, on the potential axis is obtained the corrosion potential value, $E_{cor} = E_{I=0}$.

The Evans diagram for the nodular casting behavior in the three corrosion environments and the Tafel slope evaluation module are shown in Figure 2. All measures necessary to calculate the corrosion rate, including corrosion rate, were evaluated using the features of the VoltaMaster 4 software. The results are shown in Table 3. The calculated area taken into consideration was $120$ mV ($\pm 60$ mV around the corrosion potential) and the linearity range on the Evans curves was $25$ mV.

The analysis of these data allows to highlight the following observations:
(a) The corrosion potential values indicates that from the thermodynamic point of view the most aggressive medium is the solution with almost neutral pH and the least aggressive solution is the alkaline solution.

(b) The polarization resistance has the highest value for the neutral solution, this being reflected in a low value of current density and corrosion rate. In acidic environment the very low value of the polarization resistance leads to the highest corrosion rate. In basic medium, the rate of corrosion has an average value of the solution between the one corresponding to the neutral and the acidic solution. Apparently, there is a contradiction between the conclusions that can be highlighted on the basis of the corrosion potential and those resulting from polarization resistance or current density analysis. This can be explained by the fact that the corrosion potential is a purely thermodynamic balance of the redox reactions in the system, which does not take into account the kinetic factors that influence differently the two coupled reactions, the oxidation of the metal and the reduction of hydrogen or oxygen.

(c) The fact that in all cases, \( b_a \) is lower than \( b_c \) can explain the contradiction above. If the anodic and cathodic reaction rate is equal, the two Tafel slopes are equal. When the rate of reaction is controlled by the transfer rate of the ions from the solution to the metal surface, polarization of the concentrations may occur. In addition, the pH of the solution can have a significant influence on electrode reactions;

- in acidic environment:
  - metal oxidation occurs at the anode: \( \text{M} \rightarrow \text{M}^{z+} + ze^- \)
  - hydrogen reduction occurs at the cathode: \( z\text{H}^+ + ze^- \rightarrow z/2 \text{H}_2 \)
  - the global reaction is: \( \text{M} + z\text{H}^+ \rightarrow \text{M}^{z+} + z/2 \text{H}_2 \)
- in neutral or basic environments:
  - at the anode: \( \text{M} \rightarrow \text{M}^{z+} + ze^- \)
  - at the cathode: \( z\text{H}_2\text{O} + ze^- \rightarrow z\text{OH}^- + z/2\text{H}_2 \)
  - the global reaction is: \( \text{M} + z\text{H}_2\text{O} \rightarrow \text{M}^{z+} + z\text{OH}^- + z/2 \text{H}_2 \)

Hydrogen is released in both the acidic and the basic environment at the cathode. In the case of the studied alloy, the oxidation component is iron, and the global reactions are:

- in acidic environment: \( \text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2 \)
- in neutral or basic environments: \( \text{Fe} + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{OH}^- + \text{H}_2 \)

![Evans diagram for nodular cast iron behavior for those three corrosion environments](image1)

![Evaluation of Tafel slopes and corrosion potential for the standard sample](image2)

**Figure 2.** (a) Evans diagram for nodular cast iron behavior for those three corrosion environments; (b) Evaluation of Tafel slopes and corrosion potential for the standard sample.
When the diffusion of oxygen or hydrogen through the corrosion medium is not fast enough, it can be argued that the reaction is kinetically controlled and \( b_a < | b_c | \), with the reaction rate being different from the thermodynamic predicted one. The formation of oxide on the surface of the metal, which may or may not lead to passivation, alters the surface of the studied sample, and this changes the data of the Butler-Volmer equation and thus the values of the Tafel constants. Mixed control of the corrosion process can occur when hydrogen and oxygen are simultaneously reduced in the cell, which further complicates the global corrosion reaction [13-24].

| Corrosion Agent | pH | \( E(I=0) \), mV | \( R_p \), ohm.cm\(^2\) | \( j_{cor} \), mA/cm\(^2\) | \( v_{cor} \), mm/an | \( b_a \), mV/dec. | \( b_c \), mV/dec. |
|-----------------|----|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| DWW-1           | 6.5 | -689            | 2410            | 0.0150          | 0.176           | 194             | -311            |
| DWW-2           | 3.0 | -484            | 467             | 0.0660          | 0.773           | 135             | -252            |
| DWW-3           | 11.0| -352            | 1310            | 0.0301          | 0.351           | 238             | -250            |

4. Conclusions
Using the method of polarization resistance, was analyzed the instantaneous corrosion of a nodular cast iron used in the construction of pumps used in the circulation of waste water in simulated domestic waters, and the influence of pH on the corrosion rate was also studied. The studies showed that the corrosion rate is about 4.5 times higher in acidic environment and only twice as high in the alkaline environment than in neutral wastewaters.

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