METHODOLOGY FOR DETERMINING THE EFFICIENCY OF OXYGEN REDUCING AGENTS IN AQUEOUS COOLANT

Serhii Kontsevoi[1]

[1]National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", Ukraine

serkon157@ukr.net

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In heat exchange systems where water is isolated from air, preventing oxygen corrosion primarily involves removing dissolved oxygen. For circulating water systems, chemical reduction of oxygen is the preferred method, with reducing agent effectiveness traditionally evaluated through various physical and chemical methods in industrial and laboratory settings. The article also presents the rationale for the need to dose oxygen reducing agents in heat supply systems where damage to heat exchangers for consumers' hot water supply is possible. We present a widely accessible technique for chemical laboratories to determine reducing agent effectiveness by measuring its concentration before and after heating water to a specified temperature in the isolated reactor with a sample material from the heat exchange system. The presence or absence of corrosion products in the water sample after heating without air contact serves as a qualitative indicator. Using an autoclave reactor at 70°C, we observed reduction efficiencies of 75% without catalyst and 98% with catalyst (Co^{2+}, 0.01 mg/dm³) for Steel 3 samples. For Steel 40 samples, efficiencies were 85% and 99%, respectively. Corrosion products were detected in water after heating without catalyst but were absent when catalyst was present. While catalyst concentration was selected based on literature data, our proposed method allows determination of minimum effective concentrations for known catalysts and facilitates investigation of novel oxygen reducing agents and their catalysts at water temperatures up to 190°C and beyond. This approach builds upon a previously developed method using the same laboratory equipment, which determines safe water composition to prevent calcium carbonate formation during heating. The methodology presented here will require adaptation to evaluate the effectiveness of corrosion inhibitors based on film-forming substances.

Keywords: *effectiveness of reducing, heat exchange systems, oxygen reduction catalysts, preventing oxygen corrosion, reducer's thermal stability, sodium sulfite*

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1. Introduction

The use of sodium sulfite as a widely available reducing agent (a by-product of flue gas purification from SO_2) has been well established since the early work of Carpenter (1939), and research into reduction kinetics and catalysts for this process continues in modern aqueous systems (Gomelya, 2023). Currently, sodium sulfite's applications in water treatment extend beyond its reducing properties (Wu, 2021), though equipment corrosion protection remains its primary use, often in combination with film-forming corrosion inhibitors, predominantly amine-based reagents (Chauhan, 2020), which are also used independently (Jero, 2024).

Oxygen reducers and film-forming inhibitors based on organic substances (Vorobyova, 2023) are likewise widely utilized, with their efficiency primarily evaluated through electrochemical methods. These substances can simultaneously inhibit scale formation processes (Vasyliev, 2020), making them particularly promising for power engineering applications.

A reliable method for determining the effectiveness of oxygen reducing agents under laboratory conditions is essential for preventing oxygen corrosion in various water treatment and power equipment. In our assessment, a significant limitation of electrochemical methods for evaluating anticorrosion measures is the lack of guaranteed correlation between laboratory results and actual corrosion rates observed in real systems. For instance, the author's observations during analyses conducted in thermal systems in Kyiv (1994–1999) revealed good correlation in hot water supply systems (characterized by high oxygen concentrations in heated water, 2000–8000 µg/L) but overestimated corrosion rates for thermal networks (with low oxygen concentrations, 20–40 µg/L).

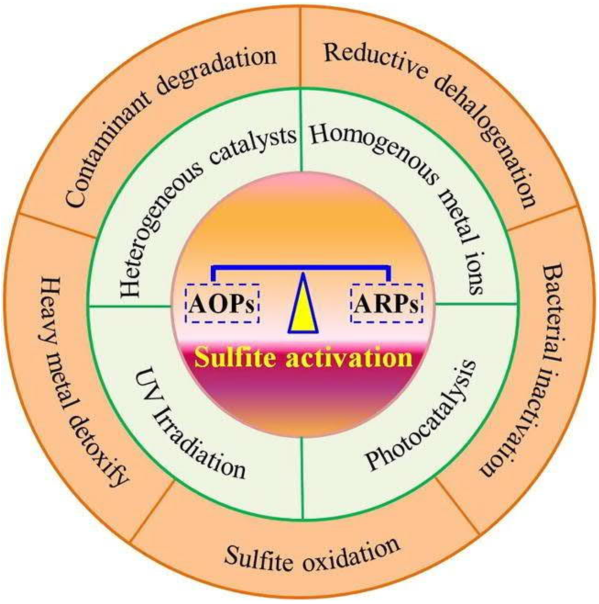

Fig. 1. *Sulfite-based advanced oxidation and reduction processes for water treatment (Wu, 2021)*

Laboratory methods for process evaluation are typically most effective when they accurately simulate conditions occurring in industrial facilities. Developing such a method is the primary objective of this work.

The water treatment system for heating network make-up water at power plants and district boilers typically includes vacuum or atmospheric deaeration, which, under normal operation, maintains oxygen concentration below 50 µg/L. Sodium sulfite dosing serves as an additional method when deaerator operation is disturbed. However, we have previously established the necessity of sulfiting even for systems operating without deaeration disturbances (Kontsevoi, 2006).

Figure 2 illustrates a scheme where a heat exchanger ("hot water tank") heats tap water. If the heat exchanger surface becomes damaged, water of different compositions can mix in a direction determined by the pressure difference between flows:

- Treated "network" water enters the tap water, increasing water consumption at the heat source treatment facility;
- Tap water enters the "network" (circulation) water, increasing its hardness and oxygen concentration.

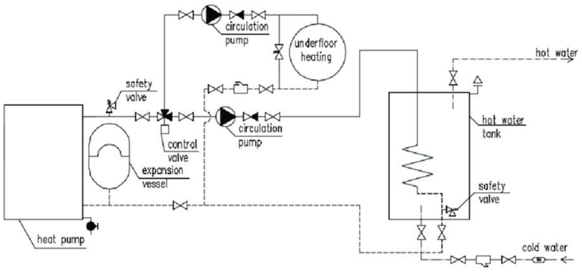

Fig. 2. *Scheme of the heat distribution system (Skoneczny, 2018)*

In systems common throughout Ukraine, shell-and-tube boilers with brass heat-exchange surfaces (regularly damaged) are widely used, leading to significant suction of untreated water. This results in oxygen corrosion and increased water hardness from

50 µmol/L in make-up water to 200–300 µmol/L or higher in network water (Kontsevoi, 2006).

These parameters are typical for systems where regular work is conducted to detect and disconnect damaged boilers for repair (for example, in "Kyivenergo"). From a chemical perspective, network water represents a mixture of water treated at the heat source (make-up water) and untreated water from damaged boilers.

To estimate the actual average oxygen concentration in the heat network, the proportion of untreated water suction (d) must first be determined:

$$d = G_{untr} / G_{tr} = \qquad (1)$$
$$= (WH_{net} - WH_{tr}) / (WH_{untr} - WH_{net}),$$

where G_{untr} – “untreated” tap water flow rate; G_{tr} – treated water flow rate; WH_{net} – hardness of network water; WH_{tr} – hardness of treated water; WH_{untr} – hardness of untreated water. G in m^3/hour, WH in µmol/L.

Average oxygen concentration in the actual makeup (mixture of treated and untreated water), µg/L:

$$C(O_2)_{act} = (C(O_2)_{tr} + d \cdot C(O2)_{untr})/(1+d) \quad (2)$$

WH_{net} values in the range (285–500) µmole/dm^3 corresponds to the value of d in the range (0.05–0.10) and $C(O_2)$ actual in the range (400–800) µg/L at $C(O_2)_{tr}$ and $C(O_2)_{untr}$ 50 and 8000 µg/L, respectively.

Thus, the actual concentration of oxygen in network water (400–800 µg/L) is dozens of times higher than that observed in return network water ($C(O_2)_{net}$ = 20 µg/L), because most of the oxygen is spent on corrosion of the steel pipelines surfaces.

The degree of oxygen reduction (X_{red}) by iron in steel is in the range (95–97.5)% according to the formula (Kontsevoi, 2006):

$$X_{red} = (C(O_2)_{act} - C(O_2)_{net}) / C(O_2)_{act} \cdot 100 \quad (3)$$

The actual efficiency of “protective” carbonate and iron oxide film (EPF) is (5–2.5)%:

$$EPF = 100 - X_{\mathrm{red}} \quad (4)$$

Therefore, constant dosing of oxygen reducing agent is mandatory for systems where damage to consumers' hot water boilers is observed. This necessitates a methodology to determine oxygen reducing agent effectiveness based on its concentration (excess), water temperature, and system equipment material.

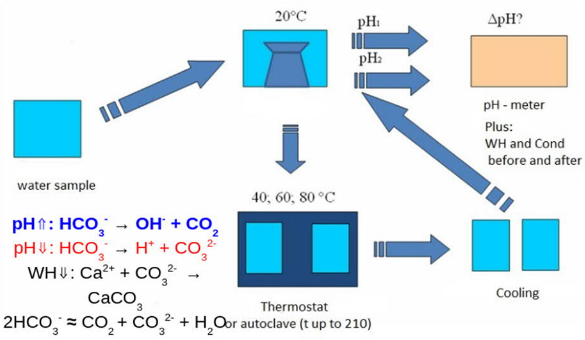

Fig. 3. *Complex method for determining the possibility of scale formation (Kontsevoi, 2022)*

Such a technique is developed based on previous work (Kontsevoi, 2022). It enables determination not only of calcium carbonate formation potential by monitoring pH value changes before and after heating the water sample without air contact (see Figure 3), but also assesses scale formation intensity through hardness reduction after heating. pH decrease can result from decomposition via the H-mechanism, rather than the OH-mechanism:

$$HCO_3^- \rightarrow H^+ + CO_3^{2-}, \qquad (5)$$
$$HCO_3^- \rightarrow OH^- + CO_2 . \qquad (6)$$

Scale formation intensity is further determined by the reduction in hardness after heating the water sample, resulting from the reaction:

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3 \qquad (7)$$

3. Materials and Methods

Standard solutions and techniques for determination of water hardness (WH) with EDTA and Alkalinity (Alk), tap water (Kyiv) in the Igor Sikorsky KPI laboratory, pH meter (Jenway, UK, accuracy 0.01 pH units), Na_2SO_3 as oxygen reducer, $CoSO_4 \cdot 7H_2O$ as oxygen reduction catalist, Steel 3 and Steal 40 samples, iodine solution (0.05 N) to determine the concentration of reducing agent.

The method involves thermostatting an aqueous solution sample without air contact at temperatures ranging from 30–190°C, followed by chemical analysis (sodium sulfite concentration determined by iodometric method) of water samples before and after thermostatting at 20°C. Steel samples with previously calculated specific surface areas were placed in the reactor volume (Thermostat in Figure 3), and the oxygen reducing agent concentration was determined.

The specific surface area of the steel samples (ratio of pipe surface area to unit water volume, cm²/cm³) for pipes with diameters ranging from 100–1000 mm is 400–40 cm⁻¹. With an autoclave volume of 2 L, the plates (Steel 3) and pipe (Steel 40) had a surface area of approximately 800 cm².

The proposed method was implemented as follows: a water sample of specified composition was supplemented with a known amount (with or without stoichiometric excess) of oxygen reducing agent (Na_2SO_3) with or without catalyst (copper or cobalt salts). The sample was transferred to a non-corrosive reactor (steel autoclave or plastic reactor with reliable seal) containing cleaned steel samples and heated to a temperature corresponding to industrial conditions (approximately 70°C for heating networks – the temperature of return circulation water). The sealed reactors were thermostated for 60 minutes (corresponding to the average duration of water heating in heat exchange equipment) at temperatures between 30–190°C. The reactors were cooled in a closed state to 20°C, after which the reducing agent (sodium sulfite) concentration was determined by the iodometric method.

To obtain more accurate reduction efficiency values, a "blank" control experiment was performed without steel samples, allowing experimental determination of the maximum possible change in reducing agent concentration. Without such a control, this value would be calculated from known initial oxygen concentration.

The actual oxygen reduction efficiency (ORE_t) was defined as, %:

$$ORE_t = \Delta C(RA)_{\text{sample}} / \Delta C(RA)_{\text{blank}} \cdot 100, \qquad (8)$$

where t – represents the set thermostatting temperature; $\Delta C(RA)_{\text{sample}}$ – the change in reducing agent (RA) concentration in the presence of steel samples; $\Delta C(RA)_{\text{blank}}$ – the change in reducing agent concentration in the experiment without steel samples.

4. Results and Discussion

The tap water used as a heat transfer fluid model was characterized by a hardness of 5.1 mmol/L, an alkalinity of 3.6 mmol/L, and a pH of 7.6.

A 5% sodium sulfite solution (98% purity) was used to prepare a working solution using tap water. The initial oxygen concentration, determined by the Winkler method, was 6.2 mg/L. Considering a 10%

excess of sodium sulfite and its stoichiometric ratio (7.875 mg sodium sulfite per 1 mg O_2), the required concentration of sodium sulfite was calculated to be 53.71 mg/L (6.2 × 7.875 × 1.1). The actual initial concentration was 55 mg/L – 1.1 mL of 5% (50 mg per 1 mL) sulfite solution per 1 L of tap water.

In the "blank" experiment, the concentration of sulfite after temperature equilibration was 4.46 mg/L, resulting in a change in sulfite concentration ($\Delta C(RA)_{\text{blank}}$) of 50.54 mg/L. When converting this change to equivalent oxygen concentration (50.54/7.875), we obtained 6.416 mg/L – closely matching the result from the Winkler method. This demonstrates an alternative approach for determining oxygen concentration in water.

The results of sulfite concentration measurements after thermostatting in the presence of corrosive material samples ($C(RA)_2$) and the calculated reducing agent efficiency (ORE_{70}) are presented in the Table 1.

Table 1. *Effectiveness of sodium sulfite as an oxygen reducing agent at 70 °C*

Material /catalist	**C(RA)*2***	**ΔC(RA)**	**ORE**
Steel 3/no	17.05	37.95	75.08
Steel 3/yes	5.45	49.55	98.03
Steel 40/no	12.06	42.94	84.95
Steel 40/yes	4.98	50.02	98.96

In our autoclave reactor experiments with Steel 3, the oxygen reduction efficiency at 70°C (ORE_{70}) was 75% without catalyst and increased to 98% with catalyst (Co^{2+}, 0.01 mg/L). For Steel 40, the ORE_{70} values were 85% and 99%, respectively. In experiments without catalyst, corrosion products were visible in the water after thermostatting, whereas no such products were observed in the presence of a catalyst.

The actual oxygen reduction efficiency represents the degree of oxidation of the reducing agent by oxygen in competition with the iron in the steel.

It is noteworthy that iron in steel reacts so actively with dissolved oxygen even in the presence of dissolved sodium sulfite. Historical context supports this observation; in the mid-20th century, power plants in the Soviet Union employed filters made of steel shavings installed downstream of deaerators, treating water containing oxygen without sodium sulfite.

The measurement results in our method may be influenced by the sample preparation procedure for the corroding materials. The steel samples underwent initial acid cleaning followed by alkali passivation. After each experiment, the surfaces were carefully cleaned mechanically using an eraser.

5. Conclusions

Dosing of oxygen reducing agents is necessary to prevent oxygen corrosion in heat supply systems due to the ingress of untreated tap water from damaged hot water supply heat exchangers into the circulating network water. This process increases the hardness of network water by 5–10 times compared to makeup water and leads to oxygen corrosion of heat supply system equipment, primarily affecting return network water pipelines operating at temperatures up to 70°C. Paradoxically, better pipeline protection corresponds to higher oxygen concentration in the network water, which at temperatures up to 150°C in hot water boilers or high-speed boilers of thermal power plants can lead to corrosion of this equipment.

The catalyst concentration in this study was selected based on literature values, but our proposed method enables both the determination of minimum effective concentrations for known catalysts and the investigation of novel catalysts.

Our method for determining the actual efficiency of oxygen reduction in water allows for measurement of both the reduction degree under conditions corresponding to industrial settings and the required concentration of reducing agent and reduction catalyst to ensure acceptable values.

Thermal instability of sodium sulfite, the most widely available reducing agent, occurs at temperatures above 250°C (as established in the 20th century). We have developed a verification method to confirm this phenomenon and to evaluate the thermal stability of alternative reducing agents under experimental conditions without corroding material samples.

We previously developed a method using the same accessible laboratory equipment to determine the safe composition of water at which calcium carbonate does not form when heated to a specified temperature. The method presented in this study will require adaptation to determine the effectiveness of corrosion inhibitors based on film-forming substances.

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МЕТОДИКА ВИЗНАЧЕННЯ ЕФЕКТИВНОСТІ ВІДНОВНИКІВ КИСНЮ У ВОДНОМУ ТЕПЛОНОСІЇ

Концевой С.А.[1]

[1]Національний технічний університет України
«Київський політехнічний інститут імені Ігоря Сікорського», Україна
serkon157@ukr.net

У системах теплообміну, де вода ізольована від повітря, запобігання кисневій корозії передусім передбачає видалення розчиненого кисню. Для циркуляційних водних систем хімічне відновлення кисню є кращим методом, а ефективність відновника традиційно оцінюється за допомогою різних фізичних і хімічних методів у промислових і лабораторних умовах. Також представлено обґрунтування необхідності дозування відновників кисню у системах теплопостачання, в яких можливо ушкодження теплообмінників гарячого водопостачання споживачів. Ми представляємо широкодоступну для хімічних лабораторій методику визначення ефективності відновника шляхом вимірювання його концентрації до та після нагрівання води до заданої температури в ізольованому реакторі зі зразком матеріалу із системи теплообміну. Якісним показником є наявність або відсутність продуктів корозії в пробі води після нагрівання без контакту повітря. Використовуючи реактор-автоклав при 70°C, ми спостерігали ефективність зниження 75% без каталізатора та 98% з каталізатором (Co^{2+}, 0,01 мг/дм^3) для зразків сталі 3. Для зразків сталі 40 ефективність становила 85% і 99% відповідно. Продукти корозії були виявлені у воді після нагрівання без каталізатора, але були відсутні при наявності каталізатора. Хоча концентрація каталізатора була обрана на основі літературних даних, запропонований нами метод дозволяє визначити мінімальні ефективні концентрації для відомих каталізаторів і полегшує дослідження нових відновників кисню та їх каталізаторів при температурах води до 190°C і вище. Цей підхід базується на раніше розробленому методі з використанням того самого лабораторного обладнання, який визначає безпечний склад води для запобігання утворенню карбонату кальцію під час нагрівання. Представлена тут методологія вимагатиме адаптації для оцінки ефективності інгібіторів корозії на основі плівкоутворюючих речовин.

Ключові слова: *ефективність відновлення, запобігання кисневій корозії, каталізатори кисневого відновлення, натрій сульфіт, системи теплообміну, термостабільність відновника*