Comparison of ferrate production methods and assessment of its possible applications for water treatment

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Abstract. This article discusses modern alternative methods of water purification based on sodium ferrate, describes the technology and apparatus for its production and the possibility of its adaptation to existing technologies for water and wastewater treatment.

1. Introduction

Through the mankind growth problems of water treatment have always been an important part of social life. Forehanded and optimal usage of water treatment methods allows to protractedly maintain maximum concentration limits (MCL) of hazardous substances at acceptable levels.

The world most common method of water treatment is chlorination, and it is still in-demand since its first usage in the 19th century [1]; only in Russian Federation (RF), where yearly production of chlorine is about 1 000 000 tons [2], at least 60 000 tons is consumed for water treatment, which covers waters up to 99% of all water types [3]. Along with other methods, such as ozonation an UV treatment, chlorination is the simplest and cheapest way to disinfect water, which can guarantee stable water quality for a long time at any point of water supply network.

Despite its widespread use, this method has a list of significant disadvantages, such as formation of carcinogenic compounds with residual chlorine in prepared water during its processing and danger of direct contact with liquid or gaseous chlorine. In order to support ideas of best available technologies (BAT) [4], usage of hypochlorite – more stable and safe chlorine compounds - is widely spread.

In strong conditions of the Far North, chlorination meets additional requirements for usage, such as non-stable quality of raw water due to difficult weather conditions, and special requirements for water treatment on ships and offshore facilities in accordance with the requirements of The International convention for the Prevention of Pollution from ships [5].

There can be mentioned several alternative water treatment technologies, such as ozonation, UV treatment, Iodation, electrochemical methods, etc. [6]. Herewith it should be stated that only chlorination has a feature of prolonged action of disinfectant; none of alternative technologies is able to maintain prolonged disinfection as for tap water in current conditions of consumer culture in RF. Several EU countries, such as Sweden [7], use ozonation as a regular technology, but it is incorrectly comparing its consume culture along with industrial giants, such as RF, China or USA.

Ferrates of alkali metals are ones of the strongest oxidizers and are capable of decomposing a variety of compounds. Decomposition of ferrates proceeds gradually, changing the oxidation state step by step from 6+ to 3+, while ferrate-ion systematically collects all kinds of radicals around itself, and the strength if the ion is strong enough to create even big complexes, what makes ferrate-ion as a coagulant, flocculant and disinfectant at once [8], [9], [10], [11]. Ferrates can oxidize lots of organic
compounds, such as organic matter, sulfur and nitrogen compounds, phenol, endocrinogen compounds (EDC). Ferrate destroys nitrosamines, which in turn are strong carcinogens, decomposes methyl tertiary butyl ether (MTBE) – a gasoline additive, which is present in in soil and groundwater [12]. Ferrates are able to remove organic pollutants from soil and aquatic environments, resulting from industrial disasters (for example, petroleum products spill and their derivatives). Also it is possible to purify associated waters during hydrocarbon production process, extraction of aqueous media in the nuclear industry. In case of increased toxicity and saturation of associated waters with organic matter ferrates can on the contrary affect the environment [12].

2. Methods of ferrate production
Several methods are known for the synthesis of ferrates: chemical, thermal and electrochemical [12].

2.1. Chemical method
Chemical (also known as low-temperature oxidation) method consists in oxidation of iron (III) hydroxide in the alkali solution. The disadvantages of chemical methods are low output of ferrates in the solution (liquid or solid-state), use of oxidizing agents that require subsequent separation, complex technological design and high energy consumption, rapid decomposition of Na- and Li-ions in the both processes of synthesis and purification, use of chemical exchange reactions for more stable production processes, high cost of ferrate’s production in the industrial scale. Despite these disadvantages there is one commercially successful company which produces apparatus for the chemical ferrate production – Ferrate Treatment Technologies LLC, which widely uses this method in its practice..

2.2. High temperature oxidation method
Method of high temperature oxidation (Thermal method) consists in the reaction of sodium peroxide with iron oxide in the air. Practically speaking this method is more preferrable then the previous one because the key element of the process is an oven with working temperature starting at 200 °C. Disadvantages of the method are contamination of crystalline ferrate with reaction by-products and unreacted primary products, additional energy and material costs for heating, high cost of stabilization, packaging and transportation of dry ferrates, high cost of production of dry ferrates on an industrial scale.

2.3. Electrochemical method
This method consists of electrolytic decomposition of iron anode in an alkali solution. Comparing with uppermentioned methods, this method is the most pragmatic because its realization requires alkali solution, iron anode and a source of current – with no in advance requirement for the purity of the process, as it does not require significant heating as a catalyst. Electrochemical method differs from chemical and thermal ones by simple design, low comparatively low energy consumption and low cost of reagent production.

The advantages of ferrate production in situ is absence of necessity in any storage, transportation, purification or stabilization of the product; the process also provides cost reduction by increasing the reaction output, also as less requirements for initial materials for production of the same amount of ferrate.

Among methods of electrolysis of iron (in a reactor without a membrane, with a diaphragm, and with an ion-exchange membrane), membrane electrolysis with a cation-exchange membrane is distinguished by the highest productivity and economy, which ensures high productivity of the apparatus and allows controlling the energy consumption of the process depending on the given target output [13], [14], [15], [16].

Electrolizers according to the connection (wire) type are divided into monopolar and bipolar; in monopolar ones the power is applied to electrodes of each separate cell, when in bipolar – only to marginal anode and cathode. Monopolar electrolyzers can be characterized by high currents (hundreds
of kA) and low voltage (up to 4 V), for bipolar currents of up to 10-20 kA and a voltage of several hundred volts. For an electrolyzer with a sacrificial anode, a monopolar design with replaceable anodes is safer and not so complicated.

3. Adaptation of ferrates to currently used water treatment practice

There are several issues that define the actuality of ferrate application. First issue is prohibition of chlorine content in treated effluents, which go to rivers and nature basins, second is necessity of chlorine content reduction in drinking water, what finally creates organochlorine compounds, which have toxic, mutagenic and carcinogenic effects.

There are proposed new design approaches and technologies for the combined production of anolyte and ferrate, which in mutual action increase the efficiency of disinfection and purification of water and wastewater.

Anolyte is a water solution of chlorine in water (gaseous Cl₂, ClO₂, etc.), which has a long disinfecting effect, obtained by membrane electrolysis at the place of consumption from a saturated water solution of sodium chloride. Anolyte is currently the most economical, safe and effective reagent for disinfecting water. Disinfection with ozone and ultraviolet does not provide a long-term disinfecting effect.

Sodium ferrate (Na₂FeO₄) is currently the strongest oxidizing agent with a disinfecting and coagulating effect, and can be also obtained at the place of consumption by alkaline membrane electrolysis with a concentration of 20 % or more. This compound is not toxic when being decomposed, but does not have a prolonged effect, therefore it is promising for the disinfection of effluents or water in combination with anolyte.

The selected method of complex chemical water treatment using a chlorine-containing anolyte and sodium ferrate provides a synergistic effect, determined by the complementary properties of these two reagents.

Anolyte and ferrate are obtained at the place of consumption by membrane electrolysis (Figure 1). According to foreign literature, generation of ferrates at the place of consumption is cheaper than the production of hypochlorite in situ, ultraviolet and ozone disinfection comparing by capital, operating and maintenance costs per 1 nominal liter of reagent [17]. The use in the technological process of electrolysis of 20 % alkali solution (a by-product of the anolyte production) reduces its cost in terms of dry matter by more than 10 times, comparing to analogues working on 40 – 45 % alkali with comparable energy costs [18], [19].

Figure 1. Technological process scheme for combined production of anolyte and sodium ferrate, patent RU169435 [20]

4. Automated apparatus for the combined production of anolyte and ferrate

The apparatus for the combined production of anolyte and ferrate is shown in Figure 2. It includes independently functioning separate electrolysis modules for the production of anolyte and sodium.
ferrate, equipped with individual automatic control system (ACS). Chlorine modules produce anolyte in saturated saline (mainly in gaseous state) to chlorinate water and alkali with a concentration of ~ 20% as a by-product of electrolysis. Ferrate modules produce a solution of sodium ferrate from a sacrificial anode in an alkaline solution.

The prototype allows producing up to 25 kg of chlorine per day with energy consumption for its production up to 3 kWh·kg⁻¹ and producing up to 10 kg of ferrate per day with energy consumption up to 6 kWh·kg⁻¹. The amount of output reagents is sufficient for disinfection of drinking water (up to 300 m³ per hour – estimation based on the required dose of chlorine of 3.5 mg·L⁻¹) and disinfection of wastewater (up to 800 m³ per hour – estimation based on the required dose of sodium ferrate up to 0.5 mg·L⁻¹ for tertiary treatment of domestic wastewater). The dosages of chlorine and ferrate depends significantly on the contamination of the target water, therefore the average value of dosage of these reagents are indicated.

![Chlorine unit (left) and ferrator (right)](image1)

![Chlorine units (backside)](image2)

![Operator’s panel of chlorine unit](image3)

![Ferrator (front and back side)](image4)

![Flow photometric sensor of ferrate’s concentration](image5)

![Operator’s panel of ferrator unit](image6)

**Figure 2.** Test equipment for study of complex anolyte and ferrate production

Modules for the production of anolyte and ferrate can be located at various sites, while chlorine modules, which operate on water treatment stations, produce anolyte for disinfection of drinking water and an alkali with a concentration of about 20% as a by-product of electrolysis. Ferrate modules can be integrated into existing technological processes of disinfecting and treating water and effluents instead of existing modules, or as modules of new complex devices for on-site industrial production and use.

The results of testing of the equipment and technology for producing a solution of sodium ferrate and the usage for the disinfection of drinking water and the treatment and post-treatment of domestic wastewater in industrial condition are presented in tables 1 and 2.

**Table 1. Results of drinking water samples’ disinfection by ferrate**

| Sample | Doze of | Doze of | Application | Control parameters for drinking water [21] |
|--------|---------|---------|-------------|--------------------------------------------|
|        |         |         |             |                                            |

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Based on the data of the required doses of anolyte, ferrate and hypochlorite, the comparative cost and cleaning efficiency were calculated and presented in table 3; options for the implementation of disinfection and purification of various waters with sodium ferrate were substantiated.

### Table 2. Results of storm water disinfection by ferrate

| Sample № | Doze of Na$_2$FeO$_4$, mg·L$^{-1}$ | pH (after 15 min) | Coliform organisms, CFU in 100 ml | E. Coli, CFU in 100 ml | Coliphages, PFU in 100 ml | Enterococcus, CFU in 100 ml | Staphylococcus, CFU in 100 ml |
|----------|-----------------------------------|-------------------|-----------------------------------|------------------------|--------------------------|----------------------------|-------------------------------|
| 1        | 0,5                               | 7,8               | 400000                            | 1000                   | -                        | -                          | -                             |
| 2        | 1,0                               | 8,25…8,15        | < 50                              | < 50                   | 0                        | 0                          | 8                             |
| 3        | 1,5                               | 8,35…8,25        | < 50                              | < 50                   | 0                        | 0                          | 0                             |
| 4        | 2,0                               | 8,49…8,39        | 230                               | < 50                   | 0                        | 0                          | 0                             |
| 5        | 2,5                               | 9,20…9,09        | 230                               | 60                     | 0                        | 0                          | 0                             |
| 6        | 4,5                               | 9,49…9,38        | < 10                              | 0                      | 0                        | 0                          | 0                             |

### Table 3. Estimation of the comparative cost and cleaning efficiency

| Reagent, sorbent                              | Reagent cost, ₽·g$^{-1}$ | Reagent doze, g·m$^{-3}$ | Treatment cost, ₽·m$^{-3}$ |
|----------------------------------------------|---------------------------|--------------------------|-----------------------------|
| 1. Disinfection of drinking water after reagent treatment (water treatment station at Dzerzhinsk) |
| Sodium ferrate                               | 0,58                      | 0,5                      | 0,29                        |
| Chlorine in anolyte                          | 0,04                      | 4,5                      | 0,18                        |
| 2. Disinfection of drinking water after reagentizing (water treatment station at Nizhniy Novgorod) |
| Sodium ferrate                               | 0,58                      | 0,2                      | 0,11                        |
| Chlorine in anolyte                          | 0,04                      | 2,0                      | 0,08                        |
| 3. Disinfection of sewage waters (water treatment station at Nizhniy Novgorod) |
| Sodium ferrate                               | 0,58                      | 0,1                      | 0,06                        |
| Hypochlorite (electrolytic)                   | 0,05                      | 2,5                      | 0,13                        |
| 4. Reagentizing + disinfection                |                           |                          |                             |
| Reagent, sorbent                          | Reagent cost, ₽·g⁻¹ | Reagent doze, g·m⁻³ | Treatment cost, ₽·m⁻³ |
|------------------------------------------|---------------------|---------------------|----------------------|
| (water treatment station at Nizhniy Novgorod) |                     |                     |                      |
| 4.1 Sodium ferrate                       | 0.58                | 1                   | 0.58                 |
| 4.2 Chlorine (electrolytic) + coagulant of aluminum oxychloride + flocculent “Praestol 650” | | | 3.98 |
| Chlorine in anolyte                      | 0.04                | 2                   | 0.08                 |
| Aluminum oxychloride                     | 0.30                | 12                  | 3.60                 |
| “Praestol 650”                           | 0.30                | 1                   | 0.30                 |

Equipment and technologies for the production of sodium electrolysis ferrate are perspective for use in the following areas:
- at water treatment stations for disinfection of drinking water instead of primary chlorination;
- at water utilities for additional treatment of wastewater (after aeration and biological treatment) instead of hypochlorite;
- at industrial enterprises and landfills of liquid toxic wastes for detoxification of industrial effluents, municipal solid waste (MSW), storm drains;
- for disinfection and cleaning of reservoirs, pools, water bodies.

5. Efficacy estimation of complex wastewater treatment technology application

Testing of sodium ferrate effectiveness was carried out on the waters of three maps of the waste landfill of liquid toxic waste “Krasny Bor”, St. Petersburg (maps № 59, 66 and 67) and stormwaters of the waste landfill.

After oxidation of storm drains with sodium ferrate with doses of 10…20 mg·L⁻¹ and water samples from three acid maps of the landfill (cards № 59, 66 and 67) with doses of 50…60 mg·L⁻¹, quality of purified water met MCL requirements for sewage. For example, after oxidation with ferrate, the following values of controlled parameters were obtained on the map of landfill № 59:
- nitrogen content decreased from 480 to 48 mg·L⁻¹,
- oil products content decreased from 0.43 to 0.05 mg·L⁻¹,
- chlorides decreased from 1500 to 52 mg·L⁻¹,
- the pH increased from 4 to 9,
what meets the requirements of MCL for sewage for domestic purposes. The content of heavy metals in the water of maps of landfill № 64 and 68 after oxidation with a solution of ferrate was reduced by a factor of 2000 in terms of Cadmium and by a factor of 100 in terms of Lead, what satisfied the requirements of the MCL. The obtained results confirmed the high efficiency of the ferrate solution in case of detoxification of toxic industrial effluents (Figure 3). Figure 3 shows the results of the integrated treatment of the waters of the landfill maps (№ 59, 66 and 67) after oxidation with ferrate (Figure 3b), filtering the precipitate (Figure 3c) and filtering through the Baltek sorbent for additional treatment and pH correction (Figure 3d).
Figure 3. Results of water detoxification from maps of the waste landfill “Krasniy Bor” with use of sodium ferrate

Technological (flow) scheme of toxic wastewater treatment for the apparatus is presented in Figure 4a. In order to reduce the duration of oxidation, precipitate sedimentation and filtration speed up, as well as the possibility of treatment with ferrate in several stages with pH adjustment, the proposed scheme for processing toxic wastes is implemented on the model shown in Figure 4b.
Figure 4. Flow scheme and apparatus for testing of water treatment technology with sodium ferrate

This technological scheme can be used for effluents of any chemical field, where there can be selected the flow rate of the purified water, the rate of dosing of ferrate and coagulants (if necessary) and sorption loading, the number of oxidation and separation cycles of the sediment with subsequent pH adjustment to the final sorption treatment. Water comes to the first reaction chamber (the necessary dose of ferrate and coagulant is also injected here) and the process of formation of pollutant flakes (oxidized organic matter, toxic compounds) starts. By next step the water enters the second sedimentation chamber, where flocculent contaminants are precipitated. At this stage, the pH of the treated water and the consumption of ferrate are controlled by the amperometric method. If necessary, the pH of the treated water is adjusted and sedimentation is reprocessed to achieve the MCL requirements for all controlled parameters. Henceforth water is filtered through a sorbent (if necessary, a multilayer sorbent load is selected) to remove colloidal impurities and finally adjust the pH. Such processing parameters as the dose of ferrate and coagulants, the type of sorbent (or multilayer load), are determined experimentally for each processed water sample. Test of the apparatus was performed on the stormwaters of the waste landfill “Krasny Bor”, St. Petersburg; application of the proposed technology is recommended for the industrial effluents treatment processing of the contents of landfills of liquid toxic and municipal waste landfills.

The technology may find its application in the treatment of filtration effluents from the solid waste landfill “Noviy Svet”, in the city of Gatchina, Russia. Preliminary obtained treatment results satisfy the MCL requirements. The cleaning result is shown in Figure 5.

Figure 5. Result of treatment of filtered sewage at the solid waste landfill “Noviy Svet” with use of the complex wastewater treatment technology

6. Conclusion
Ferrate ions over its two-century research history have now become a serious competitor in the field of water treatment; the great potential of this reagent, of course, lies in acidic environments (domestic, waste, industrial effluents of enterprises) due to its relatively high redox potential.

The topic of using green chemistry reagents and ferrates in particular in the Far North is a separate area of research with the prospect of introducing environmentally friendly technologies for water disinfection and the processing of toxic industrial wastewater. An obvious advantage is the ability to store ferrate at low temperatures.

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