Mössbauer spectroscopy and quality control in ferrate technology

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Abstract This paper describes some prospective reactants for the ferrate technology of water treatment, the ways of their industrial production and the application of the Mössbauer spectroscopy for their quality control.

1 Introduction

The usage of the tetraoxoferrate(VI) anion (ferrate(VI)-ion, FeO_4^{2-}) for oxidation of the undesired substances and/or their removal from water is now seriously considered as a prospective branch of future water treatment technology. A huge number of publications devoted to the usage of the ferrate(VI)-ion for cleaning of water from numerous contaminants has been published since 1974, when Murmann and Robinson applied FeO_4^{2-}-solutions for the removal of a variety of metallic cations, suspended particles, odour and bacteria from water [1]. Two international meetings (Prague, 2004 [2] and San Francisco, 2006 [3]) devoted to this subject were organized during recent years.

The FeO_4^{2-}-ion exists in solid compounds—tetraoxoferrates(VI), frequently called "ferrates(VI)" or even simply "ferrates". These commonly used names are acceptable in many cases. But it must be understood that in more general circumstances the name "ferrate" is assigned to diverse iron compounds with different oxidation states, coordination polyhedra and elemental surroundings of iron. In particular, tetraoxoferrates(V) and (IV) comprising ions FeO_4^{3-} and FeO_4^{4-} respectively are

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also known and can be used for water treatment. At the present time information about various ferrates and other ferrate-containing reactants as well as devices for their production can be easily found by an internet search. Production of the reactants and their application for water cleaning is now conventionally called "ferrate technology".

FeO_4^{2-}-ions are used for water treatment in dissolved form, their common target concentration being less than 10^{-3} M. This concentration corresponds to an iron concentration < 0.006 mass % which is below the sensitivity of absorption Mössbauer spectroscopy. Thus, Mössbauer spectroscopy cannot be applied for routine analysis of industrial solutions of FeO_4^{2-}-ions. But Mössbauer spectroscopy seems the most important technique for quality control of the solid reactants used to prepare the solutions.

This paper describes some prospective reactants for the ferrate technology of water treatment, the ways of their industrial production and the application of the Mössbauer spectroscopy for their quality control.

2 Experimental

The synthesis of ferrates and their Mössbauer study have been conducted in the Laboratory of Nuclear Chemical Methods of the Moscow University for many years. The Laboratory has now the necessary equipment for pilot-scale production of different individual ferrates and mixed reactants. We use conventional synthetic approaches modified according to our "know-how" information.

Potassium and potassium-sodium ferrates(VI) were synthesized by precipitation from solutions. The solutions are obtained by anodic dissolution of metallic iron in strong alkalis or by dissolution of raw ferrates.

Ferrates(IV) and (V) as well as mixed-valence reactants were obtained by solid-state synthesis using different sodium and potassium oxides and metallic iron powder or iron oxides and hydroxides. Some information about our approaches in solid-state synthesis was published earlier [4, 5].

Barium ferrate was obtained by mixing two solutions containing FeO_4^{2-}-anions and Ba^{2+}-cations respectively.

Mössbauer spectra were recorded using Mössbauer spectrometers "Perseus" (modified design of the Research Institute of Instrument Making, Moscow, Russia [6]) working in a constant velocity mode and MS1101E (Mostec Co., Rostov-on-Don, Russia) working in a constant acceleration mode. Mössbauer sources of Co-57 in chromium and rhodium matrices produced by Cyclotron JSC. (Obninsk, Russia) were used previously. Recently we have used the sources of Co-57 in rhodium matrices produced by Ritverc JSC (Saint-Petersburg, Russia).

The isomer shifts in this paper are presented relative to α-iron.

3 Results and discussion

There are several known ways for the preparation of FeO_4^{2-}-solutions:

a)   dissolution of soluble ferrates(VI) in water;
b)   interaction of ferrates(IV) and (V) with water;

c) exchange reaction with insoluble ferrates(VI);
d) electrochemical oxidation of metallic iron or iron compounds in alkaline solutions;
e) chemical oxidation of iron(II) and iron(III) in alkaline solutions;
f) dissolution of solid Fe(VI)-containing products in water.

The huge disadvantage of the last three approaches is an inevitability of high alkalinity of the target solutions, or their enrichment by cations and anions contained in accompanying substances, or contamination by undesired ions composing initial reactants, or appearing as by-products (see e.g. procedures described in [7–9]). The first three approaches use solid substances which can be synthesized in almost pure form; some of them can be produced in industrial scale. Only comprising ferrates cations pass into water in the respective quantities.

Chemical reaction of the decomposition of ferrate-anions, FeO_4^{n-}, can be written by the following extended equation:

$$FeO_4^{n-} + (3/2 + z + n/2 - x)\, H_2O = FeO_x\, (OH)_y\; zH_2O \downarrow + n\, OH^- + (5-n)/2\, [O],$$
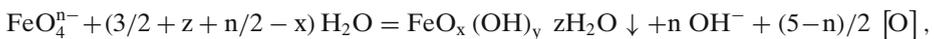
where $n = 2 \div 4$ and $2x + y = 3$. The equation shows that decomposition of a ferrate-ion leads to the formation of several OH^--ions. But the respective alkalescency can be easily adjusted by the addition of acidic reagents, for example iron(III) salts, which are commonly used as coagulants in water treatment technology. The equation demonstrates also the important fact that the quantities of OH^--ions as well as the quantities of oxidizer (symbolized as [O] in the equation) depend on the oxidation state of iron in the initial substance only and are independent of the composition of the iron(III) sediment.

Among known soluble ferrates(VI) only K_2FeO_4 and $K_3Na(FeO_4)_2$ [10, 11] can be used for water treatment [12]. The other ferrates(VI) are insoluble, contain toxic cations or are currently too complicated for synthesis in industrial quantities. These two salts are synthesized by precipitation from alkaline solutions followed by washing and drying.

K_2FeO_4 has been known for a very long time. Its Mössbauer spectra were studied in detail in 1960s–1980s (see e.g. [13–20]). Its room-temperature spectrum is a single line with isomer shift -0.90 mm s^{-1} [21]. This salt is an antiferromagnet with a Neel temperature of about 4 K [19, 20].

The formation of $K_3Na(FeO_4)_2$ was detected in the beginning of the XXI century outright thanks to Mössbauer spectroscopy. For the first time this salt was detected as an impurity in K_2FeO_4, precipitated by KOH from concentrated solution of sodium ferrate(VI). The isomer shift of $K_3Na(FeO_4)_2$ (-0.89 mm s^{-1}) is very close to one of potassium ferrate(VI), but the noticeable quadrupole splitting (0.21 mm s^{-1}) allows one to unerringly distinguish one salt from the other and to evaluate their relative contents in the mixture [10, 21].

The salts are stable for a long time. But they decompose in case of improper storage conditions. The decomposition is particularly fast if the substance is underdried or is in contact with environmental air. The decomposition is characterized by a change of the colour from black-purple to sorrel. Unfortunately a swapped colour substance is not usable anymore.

An alternative mechanism of decomposition of $K_3Na(FeO_4)_2$ was also described [22]. With time and perhaps under the influence of temperature fluctuations during
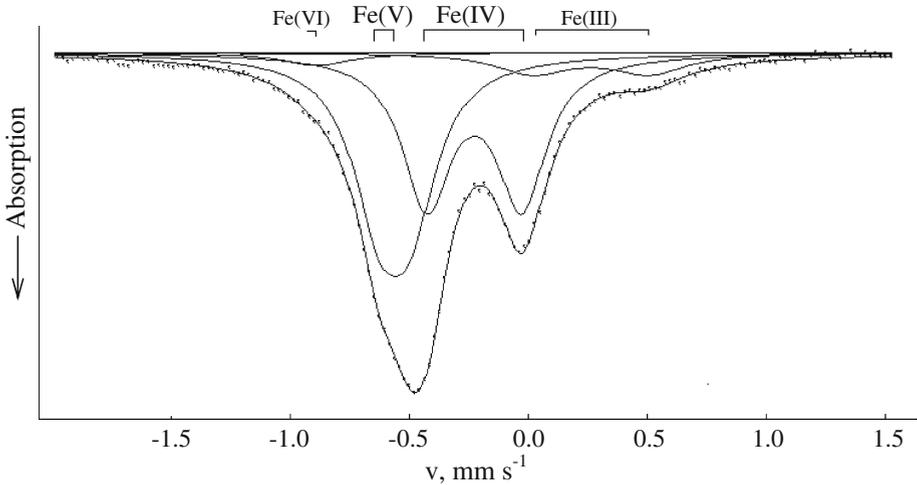
Fig. 1 Room-temperature Mössbauer spectrum of the reactant for water treatment, containing ferrates(IV) and (V)

storage the crystal lattice of the salts transforms into a more stable one, half of the iron(VI) being reduced to iron(III) [22]:

$$K_3Na\,(FeO_4)_2 \rightarrow K_2FeO_4 + \left[KNaFe^{3+}O_{2.5}\right] + 0.75\ O_2 \uparrow$$
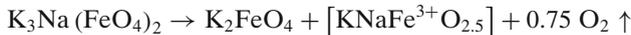
No colour change during the decomposition process is observed. The decomposition product is stable for a long time and further reduction of iron(VI) is not observed. And although only 50 % of the iron is in a hexavalent state in the decomposed substance, it can be still used for water treatment.

It is extremely important for industrial production to know the content of iron(III) in the freshly produced reactants and to control its accumulation in stored products. It can be simply performed with the help of the Mössbauer spectroscopy because the absorption lines of ferrates(VI) and iron(III) are in completely different velocity ranges. This makes it possible to detect even small impurities of iron(III) (see Fig. 1 in [22] and Fig. 2 in this paper).

Electrochemical generation of FeO_4^{2-} in alkaline mother liquor with continuous crystallization of the salts [23] is, in our opinion, the best way to obtain ferrates(VI) in large quantities.[1] But large-scale production by this way needs very high electric currents.[2] Therefore the electrochemical technology needs solid capital investments [12]. The alternative way for industrial synthesis of ferrates is an interaction of

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[1]Total capacity of Moscow water supplier "Mosvodokanal" is $6.7 \cdot 10^6$ m^{3}per day [24]. If target concentration of FeO_4^{2-} is 0.1 mol/m^3, the day ferrate production should more than 130 ton.

[2]For synthesis of 1 mol of FeO_4^{2-} by electrochemical oxidation of metallic iron:

$$Fe + 8OH^- \rightarrow FeO_4^{2-} + 4H_2O + 6e$$

electric charge 6 F$\approx$5.8$\cdot$10^5 C is necessary (F—Faraday constant). If production capacity of water station is $6.7 \cdot 10^6$ m^3 per day, the ferrate plant should be able to produce current of approx. $4.5 \cdot 10^6$ A under 100 % current yield.
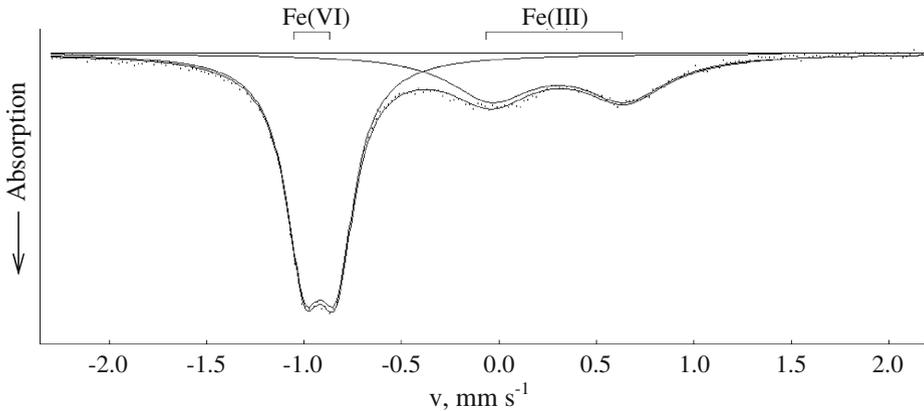
Fig. 2 Room-temperature Mössbauer spectrum of $BaFeO_4$ sample containing iron(III) as by-product

metallic iron, its oxides and hydroxides with oxides of sodium and potassium in solid-state. For example [25, 26]:

$$Fe_2O_3 + 4\,Na_2O_2 \rightarrow 2\,Na_4FeO_4 + 3/2\,O_2 \uparrow$$
$$KFeO_2 + K_2O_2 \rightarrow K_3FeO_4$$
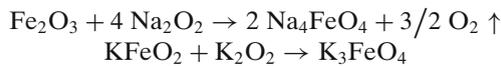
This way is fast and flexible. Changing the synthesis conditions, initial reactants and their ratio we can obtain pure ferrates as well as the mixed reactants with the desired content of iron(VI), (V) and (VI). Using different sodium and potassium oxidants it is also possible to vary the Na/K ratio.

Ferrates(IV) and (V) intensively interact with water by a disproportionation mechanism:

$$3\,Na_4FeO_4 + 8\,H_2O \rightarrow 12Na^+ + FeO_4^{2-} + 2\,Fe\,(OH)_3 \downarrow +10\,OH^-$$
$$3\,K_3FeO_4 + 4\,H_2O \rightarrow 9\,K^+ + 2\,FeO_4^{2-} + Fe(OH)_3 \downarrow +5\,OH^-$$
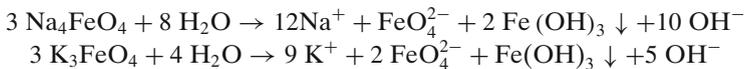
The usage of a mixture of reactants with different iron oxidation state allows us to choose the necessary ratio oxidant/coagulant. In this case a part of the coagulant ($Fe(OH)_3$ or other iron(III) species) is formed at the time of dissolution. And an additional quantity of the coagulant is formed later during slower decomposition of FeO_4^{2-}-ions. This peculiarity could be considered as additional advantage, because the formation of coagulator at the initial stage of water treatment allows one to remove suspended particulate matter and other impurities, which can be removed by adsorption. Then remaining FeO_4^{2-}-ions oxidize the other impurities forming ultra-small particles of the coagulator which adsorbs the products of the oxidation.

The solid-state approach is a simple way to produce very large quantities of the reactant using relatively inexpensive movable equipment and small space. The main disadvantage of the solid-state approach is the price of the raw substances which is noticeably higher.

Solid-state synthesis of ferrates is a sophisticated multi-step process. It is very sensitive to many conditions such as the nature of the reactants, temperature and time of synthesis as well as the program of temperature treatment. Moreover

some reactants (alkali metal oxides and hydroxides) and the reaction products are usually hygroscopic. Therefore it is mandatory to create conditions excluding the possibility of an influence of environment moisture. The synthesis could also lead to the formation of by-products, some of them frequently being unknown. This is an additional difficulty for characterisation of the reaction products.

Mössbauer spectroscopy allows us to see all iron derivatives and to compare their relative contents. It makes it also possible to identify them determining the iron oxidation state and coordination polyhedron as well as the magnetic properties of each iron compound. Therefore it is considered to be an essential technique for quality control in solid-state ferrate production.

A Mössbauer spectrum of a typical reactant for water treatment is shown in Fig. 1. The spectrum contains two doublets which are related to ferrates(IV) and (V), the content of each form being almost 50 %. Small quantities of iron(VI) and iron (III) are also observed. These are the products of disproportionation of iron(V) and iron(IV). No magnetic splittings are observed which means that the synthesized reactant contains neither impurities of initial iron reagent (Fe_2O_3) nor overheated products.

To prepare a sample for Mössbauer measurement the substance should be ground into powder. Due to the hygroscopicity of the products of the solid-state syntheses the sample preparation procedure must be performed in dry atmosphere. A glove-box dried with P_2O_5 is a suitable device for this operation. Moreover it was found [4, 5] that grinding can accelerate the decomposition of ferrates. That is why it is important to collect the Mössbauer spectrum within a short time and immediately after the sample is prepared.

To obtain a FeO_4^{2-}-solution with different counter cations, the exchange reaction between $BaFeO_4$ and the respective carbonate can be used:

$$BaFeO_4 \downarrow + CO_3^{2-} \rightarrow BaCO_3 \downarrow + FeO_4^{2-}$$
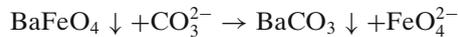
Very low solubilities of barium ferrate(VI) and barium carbonate make this reaction applicable for water treatment. This reaction can be also used for ferrate recycling.

Barium ferrate(VI) can be synthesized in a pure form by precipitation of FeO_4^{2-} by Ba^{2+}:

$$Ba^{2+} + FeO_4^{2-} \rightarrow BaFeO_4 \downarrow$$
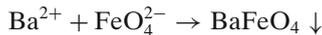
This maroon fine-crystalline compound is easy to handle. It is stable if kept in dry conditions, but wet samples slowly decompose.

The room-temperature Mössbauer spectrum of $BaFeO_4$ is a doublet ($\delta = -0.90$ mm s^{-1}, $\Delta = 0.16$ mm s^{-1} [21]). Iron(III) impurities, which can be formed during precipitation, washing and drying of the substance can be easily detected (Fig. 2). Due to noticeable mass-absorption of 14.4 keV γ-radiation a very thin absorber is obligatory for Mössbauer analysis.

4 Conclusion

We have considered three prospective ways for the industrial production of FeO_4^{2-}-ion solutions for water cleaning: dissolution of K_2FeO_4 and $K_3Na(FeO_4)_2$ in water, interaction of ferrates(IV) and (V) with water, and treatment of $BaFeO_4$ by water

solutions of CO_3^{2-}-ion. The other known ways are noticeably less attractive from ecological point of view. The use of solid ferrates or their mixtures as reactants for water treatment is a combining peculiarity of the considered approaches.

Our study shows that Mössbauer spectroscopy is a powerful technique for the control of composition and stability of the solid ferrates. It allows one to identify ferrates, evaluate their purity and keep track of their decomposition upon storage.

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