

Title: SODIUM FERRATE CONTINUOUS PRODUCTION METHOD

Authors: Federico Rivalta, Ph.D. – Isa Cicchi Ph.D.

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Throughout the years several experimental works about the Sodium and Potassium Ferrate laboratory and pilot production process and their application have been published.

This family of products showed a very high oxidant capacity, for the state of oxidation of the iron (VI) which sparked a remarkable interest in its applications both for disinfection and for especially complicated water treatments (landfill leachate, arsenic removal, ammonia, surfactant removal etc)

Furthermore, a lot of research has been conducted on the by-products of this reaction and especially on the formation of Iron Hydroxides, and their absolute absence of residual toxicity.

The limitations of the ferrate application are connected to the instability of its solutions and the poor production yield. This work, reports experimental evidences of an innovative process that allows the use of Sodium Ferrate in quantities appropriate for industrial use.

State of the art

Industrial applications tend to reduce the use of chlorine to disinfection, because of the possible formation of harmful chlorinated organic mixtures (Halo compounds) especially in presence of organic substance . Historically this spurred an effort to find alternative techniques (ozone, hydrogen peroxide, chlorine dioxide, per-acetic acid).

However the research to this day has produced results not always successful due to high costs or poor performance.

At the same time, systems based on the use of UV radiations for the purpose of disinfection did not completely achieve the desired results, because of their inability to significantly reduce the number of pathogenic bacteria.

Another alternative suggested by prevalent literature is the use of ferrate (FeO_4^{2-}), where the iron +6 oxidation state gives the final product an excellent oxidative capacity.

Iron, as it's commonly known, has the state of (II) oxidation and (III), however, being a transition metal, it could have in its most common form much higher oxidation states as (IV) (V) and (VI).

The highest and most stable oxidation state is Fe (VI) or (FeO_4^{2-}).

The ferrate (VI) is maybe the most powerful oxidative component which can be used in oxidative applications , by showing an oxidation potential of 2.2 volts in acid environment.

The table below shows the Potential REDOX of the most common oxidizers.

<i>Oxidant</i>	<i>E° , V (Basic)</i>	<i>E° , V (Acidic)</i>
Chlorine	1.358	-
Hypochlorite	1.482	0.841
Chlorine Dioxide	0.954	-
Perchlorate	1.389	-
Ozone	2.076	1.240
Hydrogen peroxide	1.776	0.880
Dissolved Oxygen	1.229	0.400
Permanganate	1.679	0.588
Ferrate(VI)	0.70	2.20

In aqueous solutions, the ion (FeO_4^{2-}) reduces itself and produces oxygen according to the reaction formula:



Another advantage of using ferrate for disinfection or oxidation processes is the formation of $\text{Fe}(\text{OH})_3$ as a by-product in water treatment.

In summary the ferrate is at the same time an oxidative as well as a coagulation agent and furthermore it does not produce anions (as chlorides or sulphates), so its use is particularly recommended for those applications where water recycle is required to close the cycle of consumption.

Several publications are available to explain in detail the following processes:

- Disinfection
- Bio-fouling control
- Water treatment of landfill leachate and ballast water
- Cyanide removal; Sulphides, surface-active agents and ammonia removal
- Antibiotic removal
- Arsenic removal
- Removal of smells from waters and mud

The newest and most interesting application developed through recent research is the possibility of using Barium Ferrate (of which ferrates of sodium and potassium are starting materials) in manufacturing of batteries that are defined as Super-iron Batteries, but this goes beyond the scope of this document.

Production methods

The production and the use of ferrates is attracting a remarkable interest and that is shown by the wide number of patents, including but not limited to the ones listed below.

US PATENT NO. 2,455,696 describes the reaction between $\text{Fe}(\text{OH})_3$ with an alkaline metal hydroxide and an oxidant agent to form ferrate.

US PATENT No. 2,536,703 describes the ferrate formation in a strong caustic solution with chlorine gas , US PATENT n. 2,758,090 describes the process utilized to stabilize ferrates with polyphosphates

The production of potassium ferrate is covered by US PATENT n. 2,835,553, an alkaline metal carbonate is made to react with ferric oxide to produce (IV) ferrate and (VI).

The use of ferrates is described in US PATENT No. 4,246,910 as added additives to cigarette filters to remove the cyanide and the hydrogen ammonia.

US PATENT No. 4,405,573, covers how to manufacture potassium ferrate starting from potassium hydroxide chlorine and a ferric salt

In US PATENTS 4,435,256 and 4,435,257 Potassium ferrate is produced through electrochemistry.

Others patents such as US PATENTS 4,535,974 , 4,551,326 . 4,385,045. 4,500,499, 4,606,843, 4,983,306, 5,202,108 5,217,584, 5,746,994 describe various aspects connected with the preparation and use of ferrates

The two most common processes for ferrate production are:

a) Wet Method through a Reaction between iron salts and hypochlorite. This method has some undesirable effects:

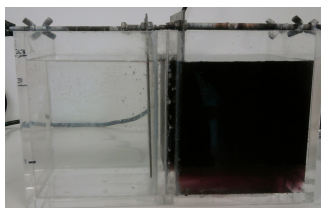
The use of hypochlorite does not produce a "chlorine free" product.

The reaction is not quantitative, so the results is a mixture of reagents and reaction products.

b) Electrochemical method in electro-cells, either not separated or separated from membranes. The most difficult aspect of this method in the ferrate production is the passivation of the anode, caused by the formation of a ferric oxide film on the iron anode. Also, the electrolysis yield is relatively modest.

The process described in this document, allows the production of sodium ferrate, using an electrolytic cell which has one sector (anolyte) containing an anode, and a second sector (catholyte) containing a cathode. Sectors are separated from a conductive membrane.

The electrolytic cell is hit with a low voltage and high intensity electric current, which produces a modest polarization on the anode. Sodium Ferrate is produced at a rate suitable for an industrial application (Picture below: The laboratory electrolytic cell)



1. ELECTROLYTIC CELL MANUFACTURE

The electrolytic cell is built out of an alkali resistant plastic material (polypropylene) divided in three (or more) sectors opened in the superior part divided by a conductive membrane.

A soft rubber gasket seals the cell to avoid any chance of leaking the anolyte into the catholyte. The membrane inside the gasket is closed. The conductive solution (sodium hydroxide) flows through the sectors, and the sodium ferrate is collected by overflow.



2. MEMBRANE MANUFACTURE

The separating membrane between the anolyte and catholyte sectors must be made of a material that is physically and chemically stable both to caustic solutions of sodium hydroxide, as well as to the oxidative action of the sodium ferrate produced during the electrolysis.

There are several materials suitable for this purpose and they are described both in scientific literature and by patents such as US 4,036,714, 4,085,071, 4,030,988, 4,065,366, 4,036,714, 4,085,071, 4,036,714, 4,085,071, 4,030,988, 4,065,366. These patents describe various polymeric formulations substantially referable to fluorinated polymers with lateral sulphonic groups.

The membrane that is used for the purpose of this research is an original formulation of a steel composite and conductive material. The thickness is about 100 microns.

3. ANODE MANUFACTURING

To achieve the maximum exposure of the surface in electrolysis, the face of every electrode must be parallel to the membrane area. The anode used for this research paper for testing purposes was manufactured in different forms including plate, sintered form, net, or porous material.

The reactive surface must be the widest possible so that the electrolysis reaction can take place quickly. The best option is a net with dimension of $2-4 \text{ mm}^2$ with thickness of the thread between 0,5 and 1 mm. The anode iron content is over 99%.

4. CATHODE MANUFACTURING

For the cathode manufacturing it is possible to use materials such as titanium, stainless steel, nickel or alloys nickel-nickel-vanadium - molybdenum .

5. ANOLYTE PARAMETERS

The Anolyte is composed of a solution of sodium hydroxide and a modest amount of chlorides which have an effect on the polarization layer. A break on the anode can be expected. The chlorides concentration is 0,2 -0,5 %. The electrolysis reaction takes place even without the ion presence. The concentration of the Hydrous Sodium Hydroxide is in the range of 10 to 15 M..

6. CATHOLYTE PARAMETERS

The Catholyte is composed by concentrated Sodium Hydroxide (10-15 M). The solution is continuously circulated in the cathode zone by a metering pump to keep it homogeneous .

7. OPERATING ELECTROLYSIS PARAMETERS

The electric current flows through the cell by connecting two electrodes to a generator which provides direct current.

The volts values are between 1 and 10 Amperes based on the Ohm Law. Considering that the conductivity is about 70.000 microSiemens, the absorbed amperes are about 30 -- 40.

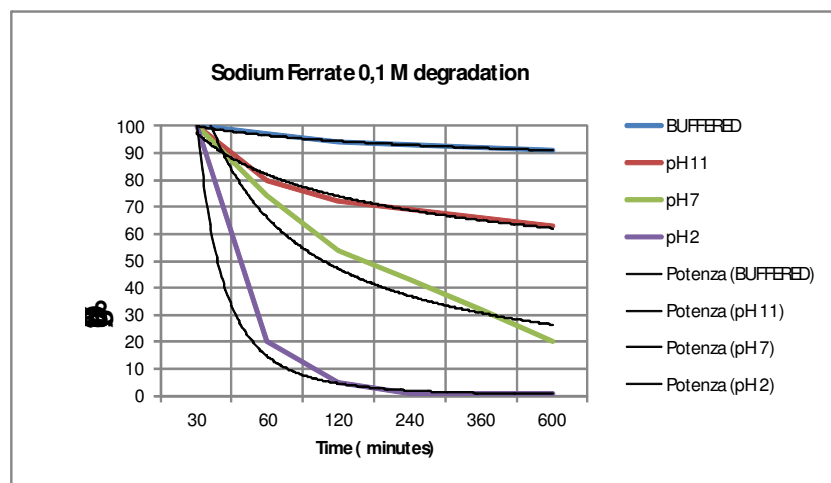
The electrode dimension is such as to ensure a charge density between 250 and 450 Amperes/sqm.

The electrolysis reaction yields on average between 45 and 60% of Sodium Ferrate based on the Faraday law.

The product is analyzed through the iron determination and the technique of UV Absorption -- visible at a length of 505 nano meter wave, which is the maximum absorption point in the visible zone of the sodium ferrate.

Methodology of use of the Sodium Ferrate

The technique we optimized does not address the isolation of the product, which has a stability as limited as evidenced in the graphic below:



Our method allows a continuous use of the Sodium Ferrate as it is produced in the electrolytic cell, through a generator which can be installed in the addition point.

The Skid is made of a steel structure which include the production cell, the feeding and re-circulating pumps, an electrical panel where the software is installed and a scrubber column for absorption of droplets of Sodium Hydroxide, which are produced during the electrolysis.

Production yields

The software provided (shown below is an example) allows to select the operating parameters, both during batch production, or in continuous working condition.

This allows the user to insert the production parameters in the input cells and immediately calculate the ferrate value. The user can then modify the parameters based on the desired output.

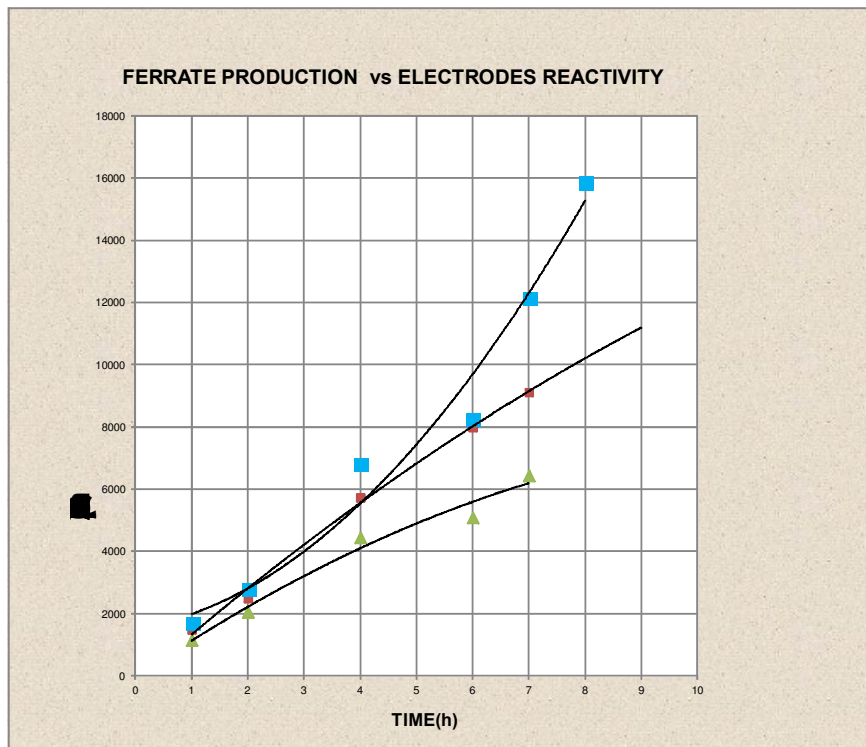
ELECTROCELL BATCH FERRATE PRODUCTION		
INPUTS		
Volume of electrocell in litre	7	
Residence time (hour)	2	
Residence time in second	7.200,00	
AMPERES READING	60	
Theoric iron dissolved (Faraday) per hour	20,86	grams/hour
Total iron produced (grams)	41,71	grams
Equivalent in ppm	5959	
Found ppm	2800	
Yield of reaction	47,0	
Sodium Ferrate produced (grams)	57,6	

ELECTROCELL CONTINUOUS FERRATE PRODUCTION		
INPUTS		
Volume of electrocell in litre	7	
FLOWRATE (litre/hour)	3,5	
Residence time (hour)	2,00	
Residence time in second	7.200	
AMPERES READING	60	
Iron dissolved (grams/hour)	41,71	grams/hour
In concentration (gr/litre)	11,92	
In concentration (ppm)	11.918,20	
Found ppm	2800	
Yield of reaction	23,5	
Sodium Ferrate produced(grams/hour)	28,82	

In our equipment pilots, ferrate production depends on several factors such as the distance between electrodes, the electrode composition, the reactivity of its surface, and the density of applied current. All these parameters can be selected through preliminary tests in which the user can choose how to lead the electrolytic cell.

The graphic below shows the correlation between reaction time and ppm of Sodium Ferrate.

Using a prototype, we were able to achieve a Sodium Ferrate production of 60 % , which is considered a very satisfactory output.



CONCLUSIONS AND INNOVATIVE ASPECTS

The research conducted helps identify new cell manufacturing aspects and operating processes which results in the designing of a generator for ferrate production in an industrial setting.

The use of the ferrate contextually to its production also allows the user to keep production costs very low thanks to the small size of the generator. In addition to these advantages, this process makes it possible to remove the inconveniences of storage of a product that is not stable and therefore would not ensure that the results could be reproduced.

In conclusion, the generation of Sodium Ferrate involves only the use of especially designed iron electrodes, the manufacturing and the use of a special membrane and the generator feeding with high purity sodium hydroxide. Thanks to this technology, the start up, production and treatment costs are acceptable.

The process described in this document is undergoing further testing to continue improving all aspects of this technology, and the experimental data will be updated as appropriate.

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