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**SODIUM FERRATE
CONTINUOUS OR BATCH PRODUCTION METHOD
INDUSTRIAL APPLICATIONS**

**Patent 2013 A 001804
Assigned to INTECNA srl**

INTRODUCTION

Throughout the last ten 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, phosphorus 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.

This work, reports experimental evidences of an innovative process that allows the use of Sodium Ferrate in quantities appropriate for industrial use and introduce the main known and consolidated applications, with a specific focus on Fisheries process requirements.

CHEMICAL NATURE AND GENERAL PROPERTIES

OXIDISING CAPACITY

Fe (VI) is a strong oxidant agent. The redox potential of ferrate is higher than ozone under acidic conditions and is the highest of all the oxidant disinfectants used for water and wastewater treatment.

Several halogen and oxygen-based oxidants are widely used, but each one of them has limitations with respect to the production of by products. During oxidation, ferrate also generates a base (OH⁻) in aqueous solution, removing metal ions present as a result of hydroxide precipitation. Studies demonstrated that ferrate has the ability to oxidize hydroxyl groups to carbonyl groups as well as *nitrosamines* in solution. Studies in the use of ferrate as an oxidant have shown that it can remove organic pollutants and effectively treat nitrogen and sulfur-containing contaminants in water and wastewater effluents by oxidizing them into harmless products. The extent of organic compounds oxidation strongly depends on the ferrate dose. Organic matter present in domestic secondary effluent was oxidized with ferrate at a dose of less than 10 mg/L (as Fe). Total Organic Carbon (TOC) and Biodegradable Oxygen Demand (BOD) from a secondary effluent were removed by 95% and 93%, respectively, by ferrate treatment.

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°</i> , <i>V (Basic)</i>	<i>E°</i> , <i>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

All studies carried on about the use of Ferrate, demonstrate that Iron(VI) and iron(V) are powerful oxidants and their reactions with pollutants are typically fast with the formation of non-toxic by-products. Oxidations performed by Fe(VI) show pH dependence; faster rates are observed at lower pH.

Fe(VI) shows excellent disinfectant properties and can inactivate a wide variety of microorganisms at low Fe(VI) doses.

Fe(VI) also possesses efficient coagulation properties and enhanced coagulation

The final product of Fe(VI) reduction is Fe(III), a non-toxic compound.

Moreover, treatments by Fe(VI) do not give any mutagenic/carcinogenic by-products, which make ferrates environmentally friendly ions.

During oxidation of organic matter and microorganisms in water, ferrate (VI) will be reduced to ferric (III), generating a coagulant that has proven to reduce turbidity of water and decrease the concentration of natural organic matter. ***One of the benefits of the use of ferrate for water and wastewater treatment is that lower doses of ferrate are needed when compared with other coagulant agents and thus the sludge generation is reduced.*** Another advantage of ferrate is that it can destabilize colloidal particles within 1 minute.

In wastewater treatment, ferrate (VI) can remove 50% more colour and 30% more chemical oxygen demand (COD) in comparison with commonly used coagulants, ferric sulphate and aluminium sulphate at the same or smaller doses.

DISINFECTING CAPACITY

Since the discovery of chlorinated by-products (CBP) and their negative health effects, great efforts have been made to minimize the CBP formation after disinfection with chlorine or other halogens. Ferrate in addition to its oxidant and coagulant powers, acts as disinfectant that does not react with organic matter to form carcinogenic trihalomethanes (THM). Since the first observation of the abilities of the ferrate to kill and inactivate bacteria and viruses, many studies have also proven that it can retard the growth of biofilms, and serves as an anti-fouling agent. Researchers have shown that for a low dose of ferrate (10 mg/L as Fe), approximately two logs of inactivation of total bacteria were observed.

Iron compounds in the oxidation state (VI) have the advantage of being powerful antioxidants and bactericides, which explains their particular interest in water treatment.

In many technical papers are reported the biocidal capacities against *Escherichia coli*, *Salmonella*, *Staphylococcus aureus*, *Bacillus sp.*, *Pseudomonas sp.*, *Enterococcus faecalis* by ferrates.

Another important aspect has been remarked:

In drinking water treatment, studies have shown that ferrate (VI) can remove 10-20% more UV254-abs and DOC than ferric sulfate for an equivalent dose over a pH range of 6 and 8. The majority of natural organic matter in surface and groundwater are humic substances, which can react with chlorine to produce DBPs. Another study demonstrated that ferrate (VI) performed better than ferric sulphate at lower doses when treating water containing humic and fulvic acids as measured by UV254 absorbance, DOC, THMFP, and ferrate (VI) achieved lower iron residual concentrations

SPECIFIC APPLICATION IN AQUACULTURE

The impact of chemistry and disinfection in aquaculture has been widely studied.

Especially, it is available a documentation related to a project carried out in UK and Scottish aquaculture sector regarding the impact of control methods on the main diffuse fish diseases.

The purpose of this project was:

- 1) to identify the key diseases that affect freshwater aquaculture operations in Scotland, particularly the trout sector, and determine their relative impact;
- 2) to identify the main methods used to control these diseases;
- 3) to identify the potential consequences if any of the main control methods were to be withdrawn; and finally,
- 4) to identify any new potential treatments that could be used instead, if any of the main treatments were to be withdrawn.

Producers, vets and health professionals surveyed confirmed that production was constrained by a limited group of common diseases that affected rainbow trout producers in England and Scotland. These included rainbow trout fry syndrome (RTFS) caused by the bacterium *Flavobacterium psychrophilum*, white spot disease caused by the endoparasite *Ichthyophonus multifiliis*, enteric red mouth disease (ERM) caused by the bacterium *Yersinia ruckeri*, proliferative kidney disease caused by the myxozoan parasite *Tetracapsulodesa bryosalmonae*, red mark syndrome (RMS) and bacterial gill disease (BGD).

Possible alternatives to the use of formalin products purchased for biocidal applications were reviewed in the event of their withdrawal from sale.

Review of the literature suggested that **FERRATES** may all have some promise as alternative treatments.

Potassium and Sodium Ferrate (Me_2FeO_4) has been identified as a potentially effective white spot treatment in a recent review (Picón-Camacho *et al.*, 2012). It is a strong oxidising agent which has non toxic break down products (FeIII and oxygen). Recent work has shown that 4.8 mg/l potassium ferrate (VI) for 2 hours was very effective *in vitro* in killing theronts and, when applied continuously over 3 days *in vivo*, caused an 80% measured reduction in the numbers of

trophonts on the test fish. A dose of 19.2 mg/l for 3 days resulted in complete clearance of infection in treated gold fish. It has been identified as a chemical for use in waste water treatment applications, due to its reported high stability, strong oxidising power and limited environmental impact. However, to this author's knowledge, no potassium ferrate product is marketed for use as a biocide in the EU now and it is not listed as EU Regulation No 37/2010 Table 1.

This depends on the fact that Ferrates are not BIOCIDES but they have a strong biocidal efficiency without generation of toxic by-products.

That will avoid to the user to carry out a complex analysis plan of residual Biocide determination into the marketed product

The pollutants generated by aquaculture are mainly nitrogen and phosphorus and causing serious environmental problems. Therefore, treating these pollutants is very much essential for successful aquaculture. Therefore, it is important in aquaculture using water reuse systems due to the toxicity of ammonia and nitrite and the chance of hypertrophication of the environment by nitrate. Moreover, the superior performance of ferrate (VI) as an oxidant/disinfectant and coagulant in water and wastewater treatment has been reported. Therefore, ferrate based treatment for aquaculture wastewater treatment will be a milestone in terms of economics, technical feasibility and social acceptability.

The ferrate treatment system has certain advantages such as precipitation of phosphorus, removes heavy metals, kills spores, bacteria, viruses and protozoa, produces no aquatic toxicity, deactivates residual drugs & pesticides, reduces organic load in the water body which reduces biochemical oxygen demand, and removes color & odors.

The final product of $\text{Fe}(\text{OH})_3$ or $\text{Fe}(\text{OH})_6$ is nontoxic and environmentally acceptable and can be easily filtered or settled without creating any toxicity to the surroundings. Moreover, there are certain challenges associated with the use of ferrate treatment strategy.

The challenges associated with the use of the proposed technology includes, Fe (VI) solutions are generally unstable; It decomposed by reduction to Fe(III) rapidly at room temperature. The instability may be retarded at low temperature. Therefore, without refrigeration the Fe (VI) solutions can not be practically stored for long time.

This problem can be minimized to generate ferrate in situ and apply the generated ferrate (VI) directly for wastewater treatment.

This is the INTECNA's proposal about a Ferrate generator installed on site.

PHOSPHORUS REMOVAL

Current phosphorus removal practice employs biological, chemical, or combined biological and chemical processes. Biological phosphorus removal relies on the function of a specific group of polyphosphate-accumulating microorganisms that are capable of taking up excessive phosphorus as intracellular storage, and the phosphorus is removed from the liquid by sludge wasting.

Chemical phosphorus removal is achieved by the addition of salts of multivalent metal ions (e.g. FeCl_3 , $\text{Fe}_2(\text{SO}_4)_3$, $\text{Al}_2(\text{SO}_4)_3$, or $\text{Ca}(\text{OH})_2$) to form precipitates of sparingly soluble metal phosphate complexes. Both of these processes target at eliminating only soluble orthophosphates or those forms in the influent that can convert into ortho-P during the treatment process, by transforming it into solids phase followed by subsequent solid and liquid separations. Since most permit limits are based on total phosphorus (TP), the effluent P level is affected by both the effectiveness of chemical and/or biological P treatment processes as well as the final solid and liquid separation efficiencies.

Many technical studies are reporting that Ferrate(VI) was applied to treat secondary wastewater and its performance as both a disinfectant and a coagulant was investigated.

In order to compare oxidation potential of the ferrate(VI) with that of chlorine, the different condition of doses and contact times were applied to the experiment for the same coliform. The disinfection rate of ferrate(IV) was faster than that of chlorine at the same concentration. The effect of ferrate(VI) supplementation on coagulation of phosphorus was examined and compared with other common coagulants.

Ferrate(VI) reduced more than 80% of total phosphorous in the range of doses between 5. and 25 mg-Fe/L. The removal efficiencies of the ferrate(VI) appeared to be similar to those of alum but higher than other iron coagulants.

Example of continuous Ferrate generators are available for sewage treatment, from pilot to full-scale trials at Hailsham North Wastewater Treatment Plant of Southern Water Ltd of UK. The work presented in the paper has significant impact on the use of ferrate (VI) in water and wastewater treatment practice; the online production and application of ferrate (VI) resolves problems of the instability and needs no transportation.

For achieving the same phosphorus removal target from the crude sewage, the ferrate dose required was in a very lower range, 0.01 - 0.2 mg Fe^{6+} /L in comparison with high doses of ferric sulphate; these will reduce the chemical demand and sludge production and therefore result in a low operating cost and generate substantial cost saving in treating sewage.

As final consideration, it is useful to remark that in Switzerland, Ferrates represent a novel technology for enhanced municipal wastewater treatment based on the dual functions of $\text{Fe}(\text{VI})$ to oxidize micropollutants and remove phosphate by formation of ferric phosphates. Second-order rate constants (k) for the reactions of selected pharmaceuticals, endocrine disruptors, and organic model compounds with $\text{Fe}(\text{VI})$ were in the range of 1 (trimethylamine) to $9000 \text{ M}^{-1} \text{ s}^{-1}$ (aniline) in the pH-range 7–8. The selected compounds contained electron-rich moieties (ERM) such as phenols, anilines, amines, and olefins. Oxidation experiments in wastewater spiked with micropollutants at concentrations in the low μM range at pH 7 and 8 showed that $\text{Fe}(\text{VI})$ doses higher than 5 mg Fe L^{-1} are capable of eliminating various ERM-containing micropollutants by more than 85%. In comparison to ozone, $\text{Fe}(\text{VI})$ was as effective or slightly less effective in terms of micropollutants oxidation, with $\text{Fe}(\text{VI})$ having the benefit of phosphate removal. To lower phosphate from 3.5 to $0.8 \text{ mg PO}_4\text{-P L}^{-1}$ (regulatory limit for wastewater discharge in Switzerland), a $\text{Fe}(\text{VI})$ dose of 7.5 mg Fe L^{-1} was needed. Overall, this study demonstrates $\text{Fe}(\text{VI})$ as a promising tool for an enhanced wastewater treatment to remove micropollutants as well as to control phosphate in a single treatment step.

Obviously, for Aquaculture sector, that represent ad added value and can represent a winning factor in the product marketing.

BASIC PRINCIPLES IN 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 produces 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:

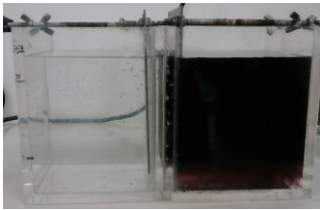
The use of hypochlorite does not produce a "chlorine free" product.

The reaction is not quantitative, so the resulting flow 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.

INTECNA's process described in this document protected by PATENT **2013 A 001804** , 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 MANUFACTURING

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. The membrane installed in INTECNA's process is an original formulation of a composite and conductive material.

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 that provides direct current.

The **VOLTS** values are in the range of 3 – 4 and resulting required **AMPERES** are based on the Ohm Law, considering that the conductivity is about 70.000 microSiemens

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

In conclusion in a ELECTROCELL of an average production capacity of 2 – 3 Kg/day of Sodium Ferrate the consumption is approximately of 1,5 – 1,8 KW

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.

INTECNA's SODIUM FERRATE PRODUCTION PLANT MACHINERY AND PROCESS

For the application in AQUACULTURE, Intecna proposes a plant for the Sodium Ferrate production to be installed on site.

Sodium ferrate will be generated in the plant by electrochemical oxidation of Iron specific electrodes in a proprietary electro-cell design accordingly to the Patent mentioned in this technical paper.

Plant is composed by the following parts:

STAINLESS STEEL CARPENTRY STRUCTURE suitable to be installed without preliminary civil works

ELECTRO-CELL: this is the core equipment and it is composed by modular cells (depending on required production quantity) to avoid the stop of the plant in case of bad working of a single cell and to allow a maintenance program on electrodes or cleaning or shut down operations.

ELECTRODES: ANODES are manufactured by specific Iron alloy in form of net and protected by a frame (approximately 1 square meter) to give to electrodes rigidity and o allow an easy insertion and extraction for cleaning, maintenance or substitution. CATHODES are manufactured in Titanium or Stainless steel (material shall be defined on preliminary water analysis Laboratory confirm)

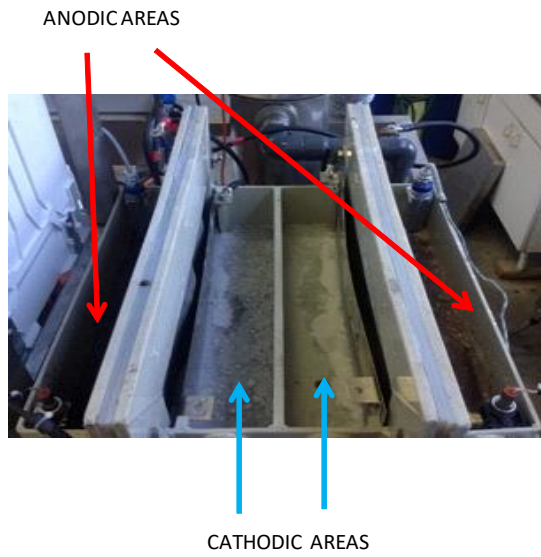
PUMPS and PIPING: every cell is equipped with recirculating pump to allow a good mixing condition

PRODUCT RECOVERY: every cell is equipped with separate valve to recovery of the produced Ferrate.

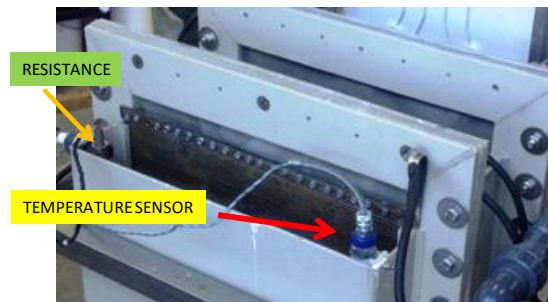
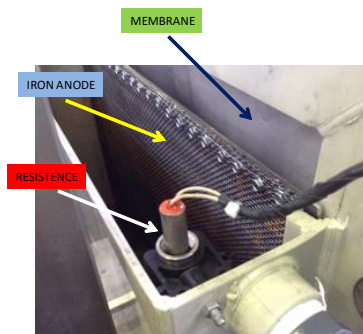
ELECTRICAL PANEL and OPERATION CONTROL: electrical panel will be separated from the plant for safety reason and to avoid aggressive humidity conditions.

For better information some photos are reported below

Single pilot cell scheme:



Cell and electrode detailed scheme



Junction between ANOLITE and CATHOLITE detail



SCHEME OF PROCESS DESCRIPTION

Operation 1: to insert the electrodes in ANODIC and CATHODIC sectors and connect the electrodes with the Alimentators clumps

Operation 2: to fill the electro-cell with Sodium Hydroxide solution 16 M till it has been reached the same level in all sectors

Operation 3: switch on the resistance for solution heating in the electrical panel

Operation 4: set the temperature value (40 – 42 °C) and check the temperature of the panel . In the panel are installed two temperature regulation connected with two anodic areas

Operation 5: when temperature will be stabilised, tension can be applied to electrodes by operating the regulation on the alimentators

By suitable analytical program, it will be possible to control the Ferrate formation in the time and to take the adequate measures to optimise the production yield.

Depending on the required daily production , we designed the Ferrate machinery to proceed in form of Batches by applying a small safety over dimensioning to face possible maintenance or shut down stops.

That to avoid big automaton costs, complex instrumentation and heavy maintenance duty.

COST OF PRODUCTION – PRELIMINARY EVALUATION FOR A BATCH PRODUCTION
5 Kg Sodium Ferrate (every 10 hours)

On the basis of average experimental calculated consumptions (for Phosphorus removal or disinfection), this quantity is enough to treat approximately 1000 cubic meter

ENERGY:

Energy calculation is as follows:

$$(3,5 \quad * \quad 800 \quad * \quad 10) * 0.18 \text{ Euro/KW} = 5 \text{ EURO/day}$$

Tension (Volt)* Current (Ampere)*time (hour) *Cost /KW = Energy daily cost

Or, referred to the Sodium Ferrate produced quantity = approximately 1 EURO/Kg

SODIUM HYDROXIDE 48% w/w

With the assumption the daily consumption is approximately
0,16 ton * 150 EURO/ton = **24 EURO /day**

Other costs (maintenance, labour...) can be evaluated as lump sum in **5 EURO/day**

In total, a realist cost is in the range of 34 – 36 EURO/day

This calculation could be applied for a pilot scale machinery.

In case of bigger installation costs, reduction is expected for the process optimization and scale economy in machinery and materials.

CONCLUSIONS AND INNOVATIVE ASPECTS

The developed process allowed to optimize the 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 fast reactive product.

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, an excellent compromise between costs and performances and complete no toxic effect on fish is achieved.

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