

## VALORIZATION OF THE PYRITE IN VIEW OF THE SYNTHESIS OF FERRATE OF POTASSIUM AND SULPHATE FERRIC WALL LAMPS IN THE TREATMENT OF THE DRINKING WATERS

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### ABSTRACT:

Pyrite  $\text{FeS}_2$  chemical formula is part of iron ore abundantly found in Madagascar. It also presents many application that a few of them are the goal of this work. The synthesis of ferric sulfate from pyrite is a simple and convenient method (cost, time, etc.) while that of ferric oxide, to serve the completion of the synthesis of ferrate, is a bit complicated. The synthesis of ferrate alkaline VI is an easy process, but requires a lot of control. It shows positive results only in a temperature above  $800\text{ }^\circ\text{C}$  over 3 hours time. Below this temperature we got another product with low oxidative we named ferrate IV or V. The application of these reagents in water treatment reveals the advantage of ferrate which is at the same time coagulant and disinfectant and ferric sulfate is cationic coagulant and a flocculent proven by its power to form large flocks.

**KEYWORDS:** *ores of iron, pyrites, ferric sulphate, ferric oxide, ferrate, treatment of waters,*

### 1. INTRODUCTION

Madagascar possesses a variety of mineral substance. The exploitation of these latter's can serve wealth and strength that will be able to play a major role in the reduction of poverty and the economic growth of the country. The majority of the exploitations focuses on the extraction of the noble ores as the nickel, the cobalt, the illmenite, etc. which is already an advantage for the country. However it can be also advantageous to find another way of valorization of these ores. So, we found an application that has not been popular yet Madagascar but we think that it cannot only serve an advantage on the economic plan but also in the domain of human health.

The growth of pollution and the needs in water increase with the economic and industrial development of a country. The deterioration of the physic, chemical and biologic quality of water (lakes, rivers, underground water, sea, etc.) generate numerous illnesses (as cholera, diarrheas, etc.).

Thus, one of the preoccupations of the leaders of a country to preserve the health of their population is to have the methods that permit to reach a maximal quality of water. So, the activity of treatment of waters is and will always be of an immense importance.

These are the reasons that pushed us to do some research on the synthesis of the ferrate of potassium and the ferric sulphate in order to study their application in the treatment of the drinking waters.

To one time where the pollution of waters grows and where the standards of drinkability harden, the powerful chemical reagents are necessary as the coagulant/flocculants to answer the demand of a treatment of waters destined to the human consumption.

The ferrate (VI) is a potential chemical reagent, to destroy the micro-organisms, to oxidize and to damage the organic impurities partly and to permit to extract the colloids in suspension and the heavy metals. (Aubertin 1996)

The ferric sulphate is a chemical reagent as capable to reach a minimal turbidity thanks to its power to form some big plops. It is about a coagulant cationic progress and a flocculating agent adapted to usages of treatment of drinking waters. (Cabana 2011)

### **Targets:**

- To determine the optimal parameters of the synthesis of the ferric sulphate and the ferrate of potassium from the pyrites in the laboratory ;
- To compare the performance of these two products for the treatment of drinking waters.

## **2. MATERIALS AND METHODS**

### **2.1. Materials**

Different scientific and technological, national and international documents have been used for the realization of this work.

Considering the multidisciplinary character of the survey, the method was the one of the compilation of the different above mentioned documents, as well as the works of research achieved in the laboratories for the mastery of the process of synthesis of the ferrate of potassium and the ferric sulphate as well as the tests of treatment of the drinking waters and the analysis of the parameters of the quality of waters.

#### *2.1.1. Synthesis of the alkali ferrate and the ferric sulphate*

It has been achieved in the laboratory of the Polytechnic Higher school of Antananarivo and the National Center of Industrial and Technology Research located at Antananarivo.

Also, the various materials used for the realization of this work are :

- the laboratory glasswares such as breaker, filters, vial, test glass, funnel,...
- an oven that resists the basis attack, steady and adjustable and that one can use to a temperature until 1000 °C or more.



**Figure 1:** photo of the outside and the interior of the oven

- crucibles in stainless steel resists to the actions of the bases to high temperature ;

The characterization of ore has been achieved in the mineral laboratory of the OMNIS [Office of the National Mines and Strategic Industries] located at Antananarivo.

#### 2.1.2. *Application in the treatment of the drinking waters*

The tests of flocculation and the analyses of waters have been achieved in the laboratory of analysis of the waters of the JIRAMA located in Antananarivo. The materials used are thus:

- adjustable Jar-Test speed between 0 and 150tr/mn ;
- glassware ;
- siphon ;
- chronometer ;
- material of measure of the pH, iron and M.O. ;
- turbidity-meter ;
- agitator.



**Figure 2 :** Photo of a Jar-Test of the JIRAMA laboratory

## 2.2. Methods

### 2.2.1. Synthesis of the alkali ferrate and the ferric sulphate

Ore used in the setting of this work has been collected in the District of Mampikony, region of Sofia (to see card below), whose geographical coordinates are the following:

- latitude 16°05 ' south,
- longitude 47°38 'S East

Ore has been extracted by hand with the shovel and the spade.



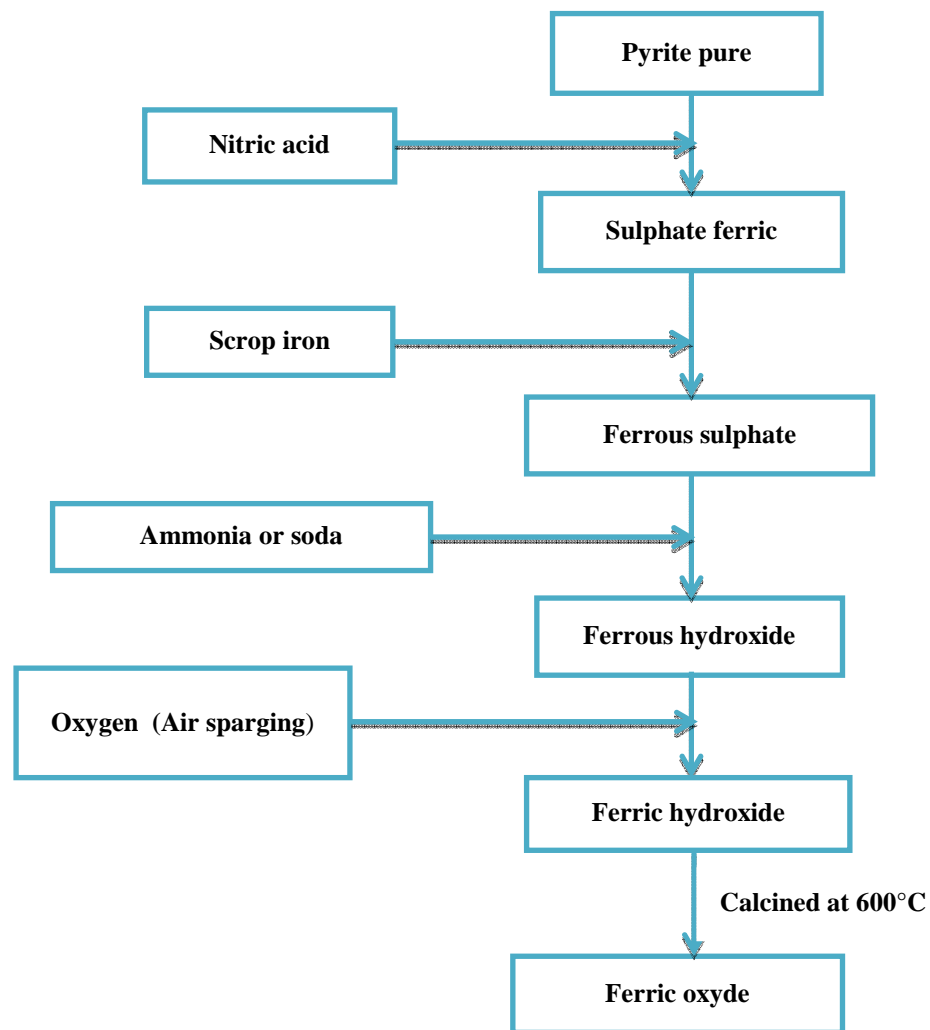
Source : map of Madagascar, [www.routard.com]

**Figure 3:** Localization of the place of collection of the iron ore,

After extraction, ore has been analyzed to determine its composition. Then, we proceeded to the preparation that consists of the sifting and the washing of the ore.

The synthesis of the ferrate has been achieved by the dry way that permits to produce a solid ferrate with a good output and stable hermetically. (Delaude 1996 ; Ostrosi 2007 ; Maghraoui 2012 ; Abdellah 2012)

We started the synthesis of the ferrate with the making of the iron oxide. The diagram of the process of synthesis of the iron oxide from the pyrites is the following one (André 1931) :



**Figure 4 :** Diagram of the process of synthesis of the iron oxide

**Note:** One notices on this diagram that the ferric sulphate is an intermediate product for the manufacture of the iron oxide.

Then, we carried to high temperature the mixture ferric oxide/potassium hydroxide/nitrate of potassium.

The ferric sulphate and the ferrate of potassium thus gotten have been analyzed and have been used for the tests of treatment of drinking waters (Aubertin and al 1996 ; Sharma 2002).

Then, we compared the performance of these two products in relation to the one of the sulphate of alumina in physic and chemical, bacteriological features point of view then and to the level of the optimum dose.

### 3. RESULTS AND DISCUSSIONS

#### 3.1. Characteristics

The result of complete chemical analysis of the raw ore is summarized below in the next table.

**Table 1** : Result of complete chemical analysis of our raw sample :

Constitue	Content [%]
Humidity	6.62
Ignition loss	1.50
SiO <sub>2</sub>	9.38
Fe <sub>2</sub> O <sub>3</sub>	27.84
TiO <sub>2</sub>	0.12
CaO	0.28
MgO	1,22
Al <sub>2</sub> O <sub>3</sub>	6.39
OH sum	34.35

One notices that the content made of iron of the sample is the order of 28%. One also notes the non negligible presence of impurities as the silica (9%) and alumina (6%).

That is why we did the purification of ore before the synthesis.

**Figure 5** : photo of the raw iron ore

### 3.2. Synthesis of the potassium ferrate

Nine (9) tests have been achieved for the synthesis of the potassium ferrate. We varied during these tests the temperature, the length (the time) and the iron oxides proportion/potassium hydroxide/nitrate of potassium.

#### 3.2.1. *Effects of the temperature variation*

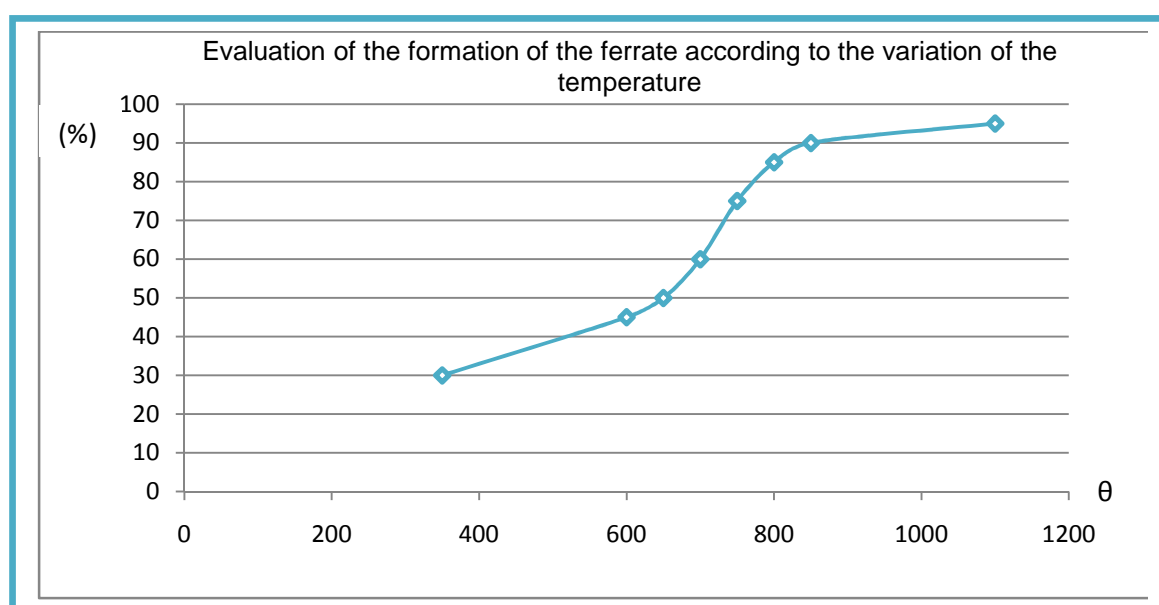
The gotten products were darker and darker while increasing the temperature. From turquoise color at to the temperature of 600 °C, they turn to the black-purplish at temperature of 850 °C. (Tsapin and al 2000)

The results of the tests are summarized below on the next table:

**Table 2 :** Result of the effect of the variation of the temperature

Temperature (°C)	600	650	700	750	800	850
Name of the product gotten	Ferrate IV or V	Ferrate IV or V	Ferrate IV or V	Ferrate IV or V	Ferrate	Ferrate
Color of the product gotten	Green olive	Green dark	Green dark green the black	Green darker toward the black	Black-purplish	Black-purplish

The table below shows more or less the evolution of the oxidization of the ferric iron below to VI ferrate in relation to the variation of the temperature, after visual and qualitative analysis.



**Figure 6:** evolution of the oxidization of the ferric iron into VI ferrate in relation to the variation of the temperature

The result of the tests shows that the temperature is essential in the synthesis of the ferrate. After several tests of production, we could note that the more the temperature is raised the more we evolve toward the formation of ferrate. It is explained by the fact that, the temperature makes the products a melt that thereafter increased the surface of contacts between the used raw materials and the reaction velocity. That is the reason of the obtaining of the ferrate in the state of IV or V oxidization when the needed temperature is not yet reached. We didn't get the ferrate in the state of VI oxidization except only from 800°C, a temperature already very elevated.

### 3.2.2. Effects of the variation of the time

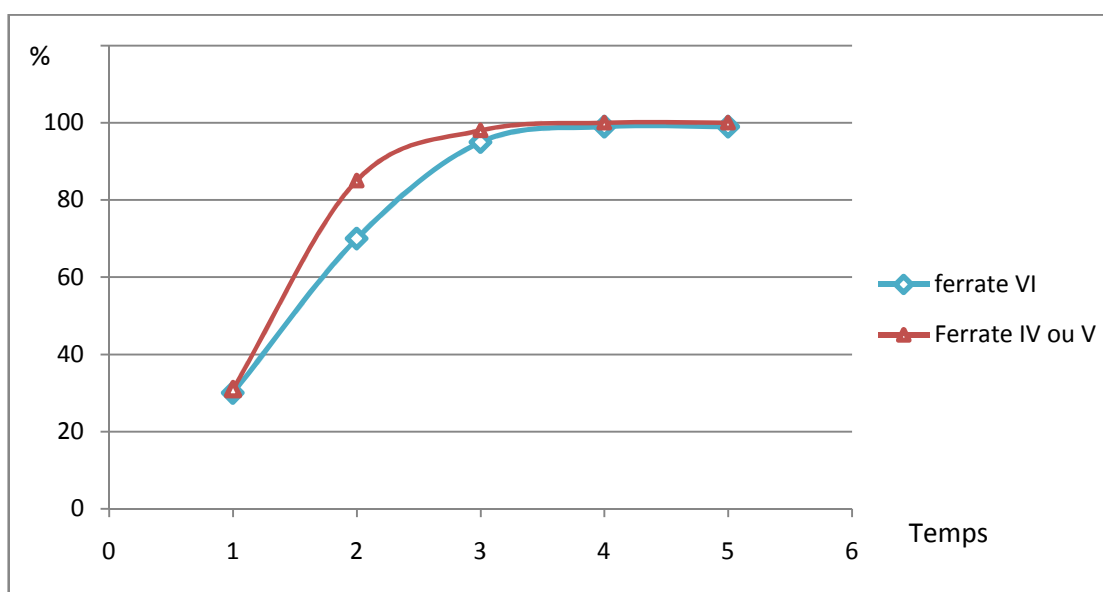
Like the temperature, we noted the effects of the variation of the time in the synthesis of the potassium ferrate. They are summarized in the next table :

(+) indicates positivity (or the success) of the gotten product, and their number presents its efficiency in relation to the time.

**Table 3 :** Result of the effect of the variation of the time

Time	2 hours	3 hours	4 hours
Ferrate IV or V	++	+++	+++
Ferrate VI	++	+++	+++

The curve below us makes the table clear : the abscissa is the time and the ordinate is the proportion estimated in relation to the time of reaction. This graph is marked approximately, after a visual and qualitative analysis.



**Figure 7 :** Effect of the variation of the time in the synthesis of the ferrate

The graph shows us that when the ideal time is reached, that means the point when the reaction is total, it is not necessary anymore to waste the time for lengthen the reaction, it also minimizes the energy waste. In our tests, the outcome of the IV iron or V is achieved in 2 hours while the VI iron is gotten only after 3 hours.

### 3.2.3. Effect of the variation of the molar ration

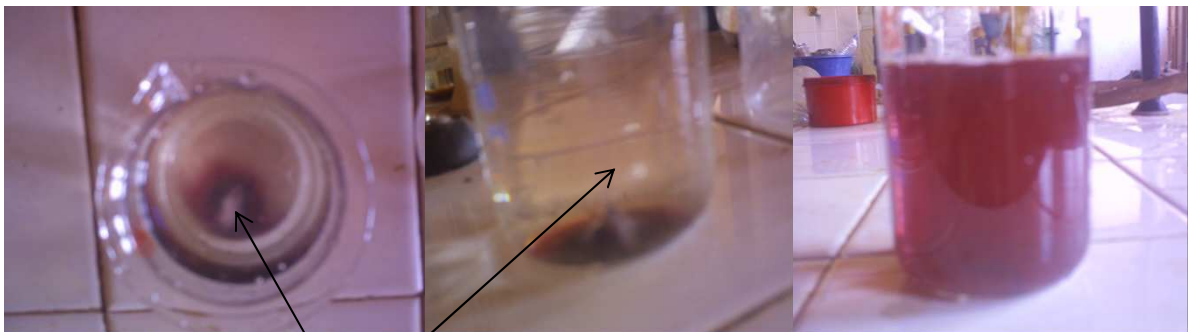
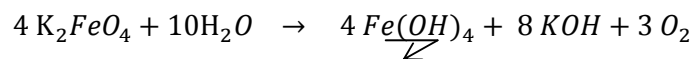
On the three ratios namely 1 :4, 1 :5 and 1 :6 that we used during the tests, we didn't find a big difference on the gotten result, only the ratio 1:4 sometimes showed a small difference but this is not in a big interval in relation to the others.



### 3.2.4. Stability of the potassium ferrate (Sharma and al 1999 ; Tsapin and al 2000 ; Ostrosi 2007)

- **Stabilization of the ferrate**

The survey of the stability of the ferrate already took several decades. The ferrate is an unstable product, especially in acidic environment, that is why, and we always keep it in greatly basic environment (until a pH of 13 to 14). When ferrate salts VI dissolve themselves in water, some oxygen is produced and some ferric hydroxide precipitates as the next reaction indicates:



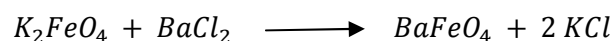
The emission of O<sub>2</sub>

**Figure 8:** Photo showing the emission of the O<sub>2</sub> at the time of the dissolution of the VI ferrate (in the left and on the middle) and photo of the less concentrated solution of ferrate (in the right)

In the liquid state, the ferrate is unstable, but when one puts it in a greatly basic environment, the solution can keep its stability until 9 hours. In a solid state, to keep tightly and safe from the sun and the humidity, the ferrate can last until several months (the literature told us until 9 months).

- **Ferrate of barium**

The ferrate can also be kept for a long time while transforming it into ferrate of barium according to the next reaction :

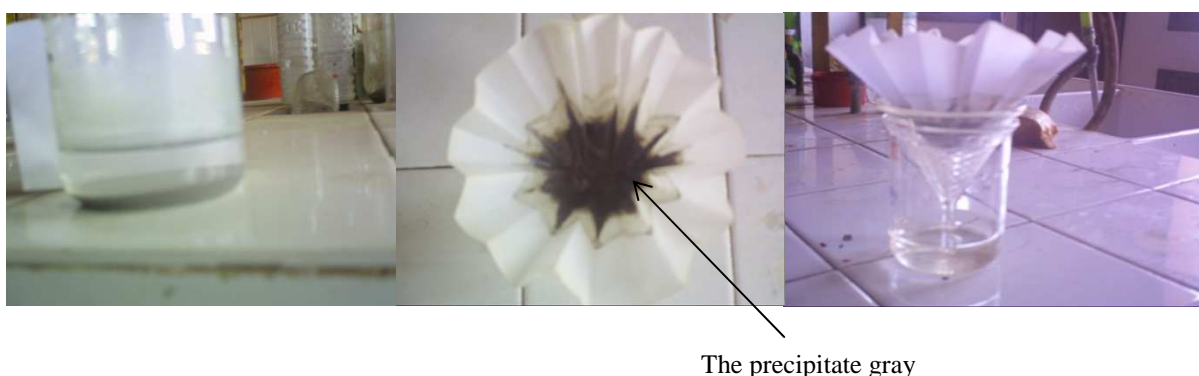


Transforming it in ferrate of barium not only helps us on its stability but also to determine the output of the ferrate gotten and the detection of its presence.

**Table 4 :** Output of the ferrate

Type of product	Outgoing mass (g)	Mass of the BaCl <sub>2</sub> (g)	Color of the precipitate gotten	Mass of the precipitate (g)	Output (%)
<b>Ferrate VI</b>	7	3.5	Precipitate gray	1.5	21.43
<b>Ferrate IV or V</b>	7	3.5	Precipitate gray	1.3	18.57

The output is about 21.43% for the VI ferrate and 18.57% for the IV ferrate or V.

**Figure 9 :** Transformation of the potassium ferrate into sulphate of barium

### 3.3. Synthesis of the ferric sulphate

#### 3.3.1. Process synthesis

The pyrites finely powdered are mixed gradually in a breaker of 1.000 ml with nitric acid. For 40g pyrites, we had added 200 ml of nitric acid. This report is gotten after the addition of the nitric acid until the total disappearance of the pyrites in the middle. After several tests, we noted that the reaction is total at the end of some minutes (15 to 30mn according to the report of the outgoing raw materials).

The nitric acid must be poured carefully 4 or 6 times distributing it to avoid any risk of accident. The reaction takes place a temperature of 80°C. The manipulation must be done with precaution because during the reaction, a big boiling point occurs and some red smokes are strongly emitted. The mixture must be agitated from time to time.

After some minutes, the emission of red smoke is entirely extinct; it tells us that the reaction is complete. At the end the reaction, we had added some drops of sulfuric acid to eliminate all traces of nitric acid fully.

At the end the reaction, we had gotten products of pale, pasty yellow color, of pungent odor.

If the reaction is successful, we must get pure ferric sulphate up to 90 to 100%. After weighing, the gotten product is soluble until 50 to 60% with distilled water, it is then filtered. At the end of manipulation, we got a ferric sulphate solution around of 50%, colored in red-brown.




**Figure 10:** ferric Sulphate before the solubilizations (on the left) and after solubilizations and filtration (on the right)

3.3.2. *Qualitative analysis*

The analysis is made qualitatively in order to verify the efficiency of the reaction while identifying the presence of the III iron and the ion  $SO_4^{2-}$  sulphate - in the final environment. The protocol and the result are summarized in the next table :

**Table 5 :** qualitative Analysis of ferric sulphate

Element to identify	Reactive of analysis	Protocol	Result	Photo of identification
$Fe^{3+}$	Solution 0,1M of thiocyanate of $NH_4SCN$ ammonium	In a tests tube containing 1 ml of the ferric solution, add some drop of 0.1 M of ammonium thiocyanate,	Red coloration by complexation	

$\text{SO}_4^{2-}$	Nitrate of $\text{Ba}(\text{NO}_3)_2$ barium Acidic HCl 6M	Add 1ml of acid HCl 6M in 1ml sulphated solution. Then add 10 drops of $\text{Ba}(\text{NO}_3)_2$ .	white precipitate of $\text{BaSO}_4$	
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### 3.4. Application of the products gotten for the treatment of drinking waters

#### 3.4.1. Origin and characteristics of raw water

The raw water used for the test of the products gotten has been taken from the river of Andromba, situated in the township of Fenoarivo Alakamisy, district of South Antananarivo.

The geographical coordinates of the point of sampling are the following :

- $18^{\circ}58$  (South latitude);
- $47^{\circ}24$  (East longitude);
- altitude 1318 m.



**Illustration 11:** satellite Picture of the part of the place of water sampling: (Google Earth), consulted on 23/10/2014, [[http://www.gosur.com/map /](http://www.gosur.com/map/)]

The samplings have been done during the month of September (September 2 and 26, 2014).

The physic and chemical characteristic of the raw water are summarized below in the next table. The analysis has been achieved by the control quality laboratory of the water of the JIRAMA located in Antananarivo.

**Table 6 :** physic and chemical characteristics of the water of the river of Andromba, collected on 2 and September 26, 2014.

Parameters	Units	Water collected September 2	Water collected September 26	Norm of drinkability
<b>Temperature</b>	°C	24.6	23.9	/
<b>Turbidity</b>	NTU	<b>266</b>	<b>236</b>	<b>&lt;5</b>
<b>pH</b>	/	7.34	7.19	6.5-9.0
<b>Conductivity</b>	(S/cm	57.3	37.5	<3000
<b>Mineral matters</b>	mg/l	40	35	-
<b>TH toughness</b>	mg/l	3.2	2.7	50
<b>Calcic toughness THca</b>	mg/l in CaCO <sub>2</sub>	1.9	1.5	-
<b>TA/TAC</b>	mg/l	0/2.2	0/1.6	200
<b>M.O</b>	mg/l	<b>2.6</b>	<b>2.44</b>	2.0
<b>NH<sub>4</sub><sup>+</sup></b>	mg/l	0.443	0.235	0.500
<b>Iron</b>	mg/l	<b>1.00</b>	<b>1.00</b>	0.50
<b>Cl<sup>-</sup></b>	mg/l	8.52	8.52	250
<b>SO<sub>4</sub><sup>2-</sup></b>	mg/l	3.89	31.39	250
<b>NO<sub>2</sub><sup>-</sup></b>	mg/l	0.036	<b>0.296</b>	0.100
<b>NO<sub>3</sub><sup>-</sup></b>	mg/l	0.571	5.050	50

We noted that only, the turbidity passes widely the norm of drinkability for the two samples.

### 3.4.2. The Jar-Test

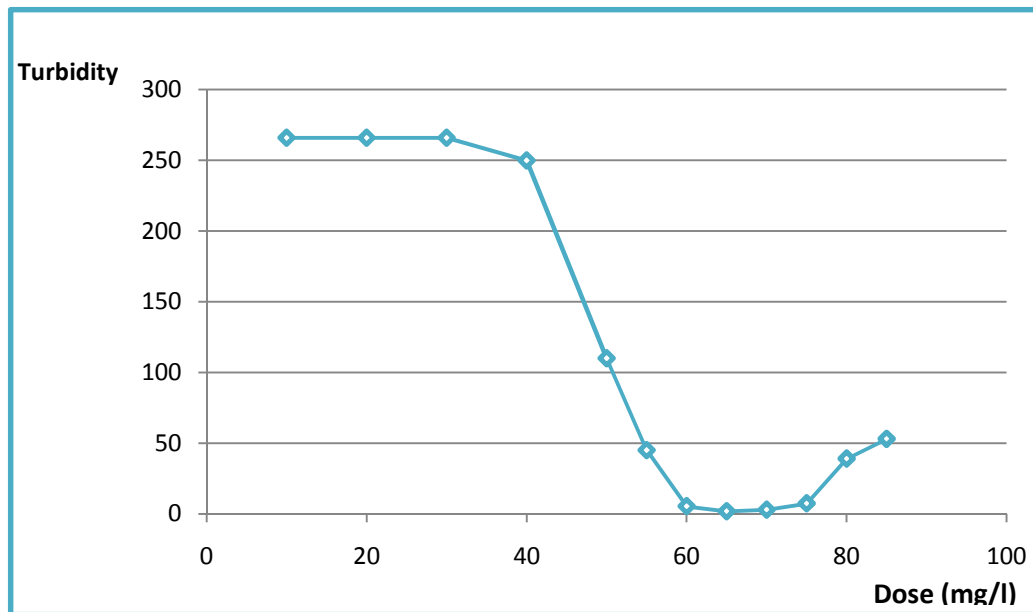
The principle consists in appreciating the quality or the size of the plops formed during the flocculation/coagulation as well as the minimal turbidity after the addition of some quantities of coagulating/flocculating agents on a certain volume of water sample.

We first compared the results of the performance of the products synthesized during this work in relation to the sulphate of alumina, classic product used by the JIRAMA society for the treatment of drinking waters in Madagascar. Indeed, the ferric sulphate (III iron), the green color ferrate (IV iron or V) and the purple color ferrate (VI iron) are all the products that have not been met usually yet at the JIRAMA according to the staff of the laboratory.

All treatments have been achieved according to the usual method of the laboratory.

The results of the Jar-Test of every product are represented in the following graphic :

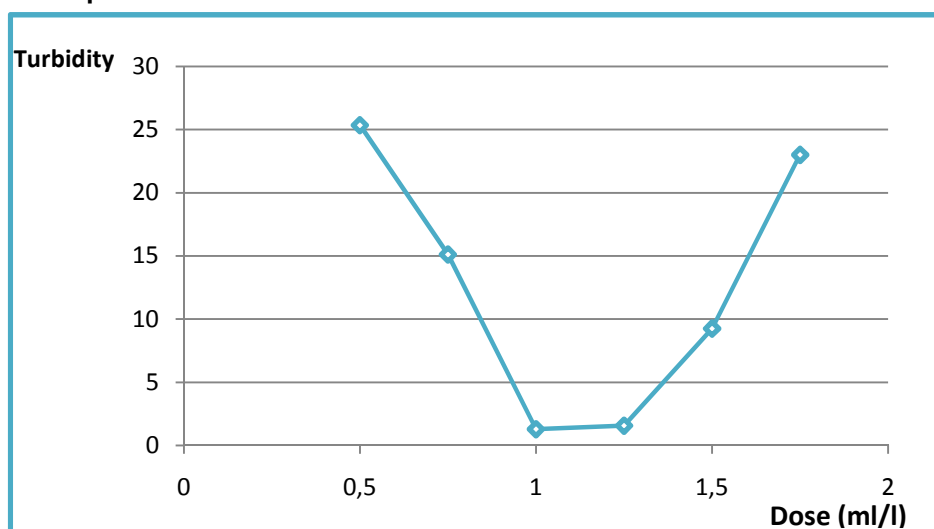
- **Sulphate of alumina**



**Figure 12 :** Curve of determination of the optimum dose of the alumina sulphate

Therefore, the optimum dose of alumina sulphate is localized at 65mg/l.

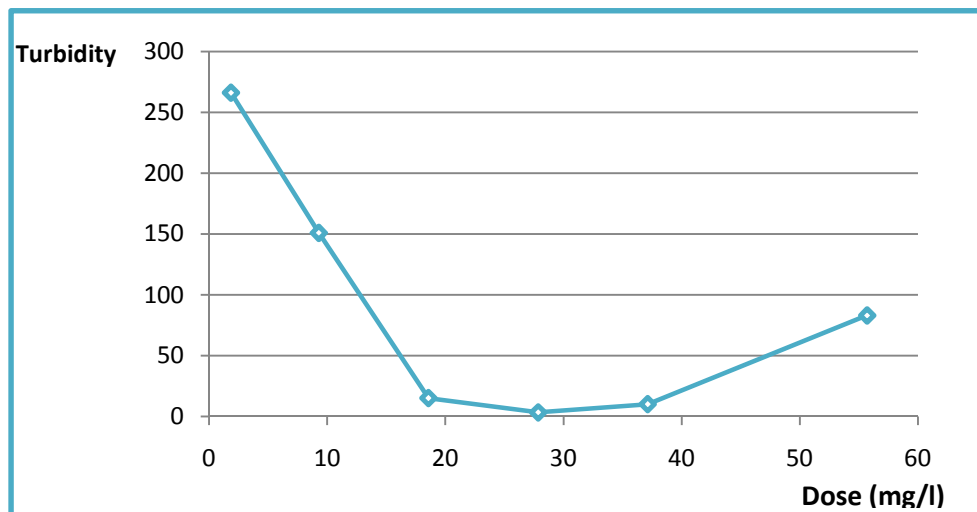
- **Ferric sulphate**



**Figure 13 :** Curve of determination of the optimum dose of the ferric sulphate

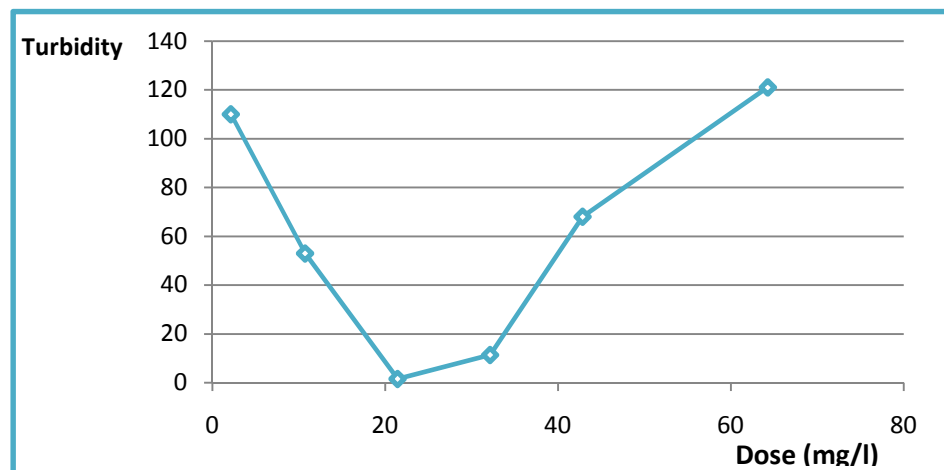
The optimum dose of the ferric sulphate is localized to 1ml for 1 L of water.

- **Ferrate IV or V**



**Figure 14 :** Curve of determination of the optimum dose of the IV ferrate or V

- **Ferrate VI**



**Figure 15 :** Curve of determination of the optimum dose of the VI ferrate

The optimal doses of ferrate IV or V and ferrate VI are respectively 27.86 mg/l and 21.43mg/l.

### 3.4.3. Physic and -chemical characteristics of the treated water

After the tests of clarifications, we did the water analysis that presents the optimal turbidity. The results are reported in the next table:

**Table 7:** Result of physic and chemical analysis of the treated, water taken away on September 02, 2014

Parameters	Units	Norm to respect	Alumina sulphate	Sulphate Ferric	Ferrate IV or V	Ferrate VI
Temperature	°C	/	24.4	24.2	23.8	24.3
Turbidity	NTU	<5	1.80	1.28	3.50	1.57
pH	-	6.5-9.0	8.31	8.33	8.51	8.30
Conductivity	(S/cm	<3000	1366	2860	2860	1400
M.M	mg/l	/	1155	2648	2120	945
TH toughness	mg/l	50	3.8	2.0	3.5	3.2
Calcic toughness THca	mg/l in CaCO <sub>2</sub>	-	1.7	1.4	0.6	1.8
TA/TAC	mg/l	200	29.4/47	12/14.0	22.4/34.6	3.0/10.3
M.O	mg/l	2.0	2.5	2.0	2.3	1.9
NH <sub>4</sub> <sup>+</sup>	mg/l	0.50	2.534	2.529	2.524	0.00
Iron	mg/l	0.50	0.60	0.60	0.40	0.36
Cl -	mg/l	250	55.38	28,4	121.41	18.10
SO <sub>4</sub> <sup>2-</sup>	mg/l	250	459.12	897.45	305.40	146.89
NO <sub>2</sub> <sup>-</sup>	mg/l	0.10	0.131	0.447	2.360	0.135
NO <sub>3</sub> <sup>-</sup>	mg/l	50	27.271	141.70	63.690	14.230



The gotten results show that the ferric sulphate is the most performing; we got the lowest turbidity with this product. During the tests of treatment, it is with this product that we got the biggest plop. Visually, waters are all limpid except the one treated with the IV ferrate or V that have a yellow color trace.

We also saw in the result of the flocculation tests, the strong presence of ammonia, nitrite, nitrate and sulphate in water. These values pass the widely of the authorized norm especially for the sulphate of alumina, the ferric sulphate and the IV ferrate or V. We noted that the value of these parameters increased during the treatment. The contribution is due to the use of ammonia as agent of rectification of the pH, for the sulphate of alumina and the ferric sulphate. The rectification of the pH is necessary because the plops only form themselves from the pH = 7 to 8.

For the one of the IV ferrate or V, the contribution is due to the insufficiency of the temperature during the synthesis of the product, the  $KNO_3$  decomposed itself in  $KNO_2$  instead of  $K_2O$ .

It is for these reasons that we did the second test of treatment. The taking of sample has been made on September 26 2014. We used lime for the correction of the pH. The optimum dose determined to have optimal plops size is the following :

**Table 8:** Dose of the lime and pH of flocculation

Type of product	Ferric sulphate	Sulphate of alumina
Rate of lime (g/l)	10	2
pH	11 à 12	8 à 9

The result of the analysis of the treated water is represented below in the next table:

**Table 9:** Result of physic and chemical analysis of the treated water, taken away on September 26, 2014,

Parameters	Units	Norm to respect	Sulphate of alumina	Ferric sulphate.	Ferrate IV or V (with lime)	Ferrate IV or V (without Lime)	Ferrate VI
Temperature	°C	/	23.6	23.9	23.6	23.5	23.7
Turbidity	NTU	<5	1.92	1.30	2.15	2.57	1.61
pH	/	6.5-9.0	7.19	7.05	8.12	8.54	8.17
Conductivity	(S/cm	<3000	848	1009	541	728	567.3
Mineral materials	mg/l	/	728	953	486	656	449.2
TH toughness	mg/l	50	45	27	19	5.0	3.7
THca toughness	mg/l in CaCO <sub>2</sub>	/	4.5	9.1	5.7	1.5	1.7
TA/TAC	mg/l	200	0/2.6	0/1.7	0/6.1	3/15.7	0/1.8
M.O	mg/l	2.0	2.0	1.3	2.6	1.9	0.9
NH <sub>4</sub> <sup>+</sup>	mg/l	0.50	0.020	0.013	0.038	0.021	0.016
Iron	mg/l	0.50	0.10	0.05	0.12	0.12	0.023
Cl <sup>-</sup>	mg/l	250	125.1	9.23	5.68	6.39	5.68
SO <sub>4</sub> <sup>2-</sup>	mg/l	250	159.36	169.05	14.6	9.35	7.18
NO <sub>2</sub> <sup>-</sup>	mg/l	0.10	0.026	0.049	2.332	2.350	0.039
NO <sub>3</sub> <sup>-</sup>	mg/l	50	3.552	15.05	78.14	97.854	2.235

After replacement of the ammonia water by the lime, the nitrite and nitrate parameters of the water treated by the IV ferrate or V persists again. It is difficult to eliminate them because it is the reagent coagulant used itself that brings these elements in the treated water. Its presences in water have never been accepted; they can provoke serious consequences on the human health. In addition, visually the water treated by the IV ferrate or V presents a yellow color trace that is not at all pleasant to see. Therefore, the IV or V iron is not appropriate for the treatment of the drinking waters.

For the other products, the parameter has improved in relation to the first test of treatment. Water treated with the sulphate of alumina and the ferric sulphate presents a pretty big value in  $\text{SO}_4^{2-}$ . However, they are still substandard; it can be explained by the presence of sulphate in the outgoing reagent.

Some parameters (as the conductivity, the mineral matters, etc.) increased in relation to the outgoing content by the effect of the reagent added during the treatment. But these values always respect the norm; thus they not cause any risk for the human health.

From a physic and chemical viewpoint, the ferrate and the ferric sulphate gave good results that can compete the sulphate of alumina, classic product used currently by the JIRAMA society for the treatment of drinking waters.

The dose of the reagents used during the treatment is given in the next table :

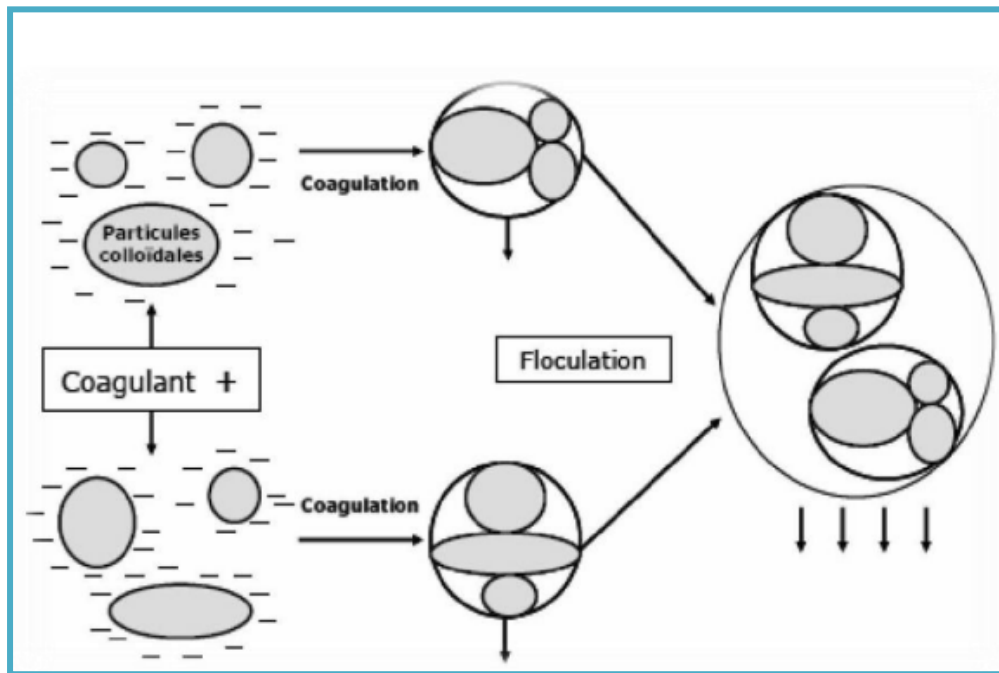
**Table 10:** Summary of the dose of the reagents at the time of the treatment of waters

Type of product	Sulphate of alumina.	Ferric sulphate	Ferrate of potassium
<b>Dose</b>	60 mg/l	1 ml/l	21.43mg/l
<b>Accompanied lime dose</b>	5ml (2g/l)	2ml (10g/l)	without

According to this picture, 1 ml of ferric sulphate was sufficient to clarify 1 liter of water, against 60 mg/l for the sulphate of alumina, even though the ferric sulphate needs dose of lime milk a lot more concentrated than the one of the alumina sulphate.

It is identical for the ferrate, the dose added to clarify 1 liter of water is lower to the one of the alumina sulphate. In addition, lime is useless for the ferrate except if the rate of iron in water is very high. Thus, it is used to decrease the rate of iron in water.

We saw previously in the physic and chemical analysis result that the ferrate and the ferric sulphate can compete the sulphate of alumina in the treatment of waters. They even show some asset on the level of some parameters, especially on the level of the organic matters; it is explained by the fact that these two products are capable to produce bigger plops than the sulphate of alumina. It is also marked on turbidity level. The system of formation of the plops happens as the next diagram shows:



Source : (Cabana 2011)

**Figure 16:** System of coagulation/flocculation

Therefore according to this diagram, it is the ferric sulphate that manages to more cohead the colloidal particles in water, then the ferrate in relation to the sulphate of alumina.

#### 3.4.4. Result of the bacteriological analysis of the treated water

For the bacteriological treatment of waters, we did 4 types of treatments:

- treated water with the sulphate of alumina without hypochlorite ;
- treated water with the sulphate of alumina added of hypochlorite ;
- treated water with the ferric sulphate without hypochlorite ;
- water treated with only ferrate.

The results of the analyses are given in the next table :

**Table 11:** Result of the bacteriological analysis of the treated waters

Type of product	Norm	Raw water	Sulphate of alumina		Ferric sulphate	Ferrate
			without hypochlorite	with hypochlorite		
<b>Total coliformes at 37°C/100ml</b>	0/100ml	1.5.10 <sup>2</sup>	1.10 <sup>1</sup>	<1	8	4
<b>Escherichia coli at 44°C/20 ml</b>	0/100ml	2.10 <sup>2</sup>	1.10 <sup>1</sup>	<1	<1	<1
<b>Streptococci fecal /100mls</b>	0/100ml	2.10 <sup>2</sup>	1.10 <sup>2</sup>	<1	6	<1
<b>Anaerobe sulfite-réducteur/20ml</b>	< 2/20ml	in	in	<1	<1	<1

According to the result presented above in the table, the sulphate of alumina permits to eliminate nearly 40% of the vestigial germs in water, the ferric sulphate manages to eliminate into 70% of the germs but the ferrate nearly eliminated all, up to 99% of the germs. Thus, this result proved the advantage of the ferrate in the treatment of the drinking waters that doesn't require hypochlorite to disinfect water.

Concerning the ferric sulphate, the result is well interesting because it doesn't need a lot of hypochlorite to disinfect water. It can be explained by the fact of its very acidic state compared with the sulphate of alumina that can kill a part of the pathogenic germs at the time of its addition in water to treat and by its power to form big plops in relation to the two other reagents that allows it to eliminate by adsorption most pathogenic germs with matters in suspension.

The reaction of the ferrate (VI) with the treated water shows that:

- the ferric hydroxide formation generates an episode of trapping and coagulation/flocculation,
- the reaction generates a clearing of oxygen that confers oxidizing properties,
- the decomposition of the ion ferrate produces an auspicious basic environment to the precipitation of the heavy metals.

## CONCLUSION

While referring on the bibliographic data that we collected, the results of the works that we did in the laboratory allowed us to deduct that the ferrate and the ferric sulphate synthesized from the ore of iron as the pyrites can be used in the treatment of waters.

The synthesis of the ferric sulphate from the ore of iron (pyrites) found in the district of Mampikony, region of Sofia is a simple process but demands a lot of precautions. A quarter of an hour is sufficient to get the ferric sulphate. The application of this latter in the treatment of waters (water of the river of Andromba) is very practicable because it nearly reduces 99% of the water turbidity while eliminating

the totality of the organic matters and matters in suspension in water by the precipitation of big flocs. It also manages to eliminate about 70 to 80% of the pathogenic germs in water.

During the synthesis of the potassium ferrate, we got a type of product (colored in turquoise blue) that we have named IV ferrate or V, because after qualitative analysis, we could note that its state of oxidization increased but not until the VI state, it is due the insufficiency of the temperature ( $<800^{\circ}\text{C}$ ) and of the reaction time. Otherwise, this product can be accompanied by nitrite like by-product by the insufficiency of the decomposition of the  $\text{KNO}_3$  in  $\text{K}_2\text{O}$ . Its application in the treatment of waters is then non acceptable because the presence of the nitrite in water has ominous effects on the human health.

After several tests to the laboratory, we succeeded in synthesizing the VI ferrate of potassium to a temperature superior or equal to  $800^{\circ}\text{C}$ . The reaction of synthesis is total after three hours. The VI ferrate of potassium is colored in black-purplish; its stability is weak because in contact with air, it decomposes itself very quickly. Its application on the treatment of waters is satisfactory to the norms of drinkability. Not only it plays the powerful coagulant role while hurling down matters in suspension but it also plays the powerful disinfectant role while destroying the totality of the pathogenic micro-organisms in water.

The comparison done on the three products (ferrate of potassium, ferric sulphate and sulphate of alumina,) showed the advantage and the efficiency of the ferrate in the treatment of waters in relation to the ferric sulphate and the sulphate of alumina. These last two products need the accompaniment of other products (the hypochlorite and the lime) to return the drinking water while the ferrate reacts only to manage to fill the conditions of physic, chemical and bacteriological drinkability by itself demanded by the norm. In addition, the quantity of added ferrate to treat 1 liter of raw water is lower to the one of the alumina sulphate. But, it is not necessary to deny that ferrates showed problems related to their stability and difficulties related to the methods of preparation, to the output and to the reduction of the production cost.

However, the ferric sulfate brings more advantage concerning the dejection of the colloidal materials in the water by cohering them to form big flocs. In addition, it presents the particular advantages on the production cost because its preparation is simple, do require neither an elevated temperature nor reagents difficult to find.

Thus, our project to propose two types of reagents, of which each presents these particular advantages, can be well placed to replace the sulphate of alumina, that already took several decades of place in the treatment of waters in Madagascar. This project can then as served a continuation of possible application on an industrial scale.

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