

ADVANCE BOND

THE PRODUCTION OF FERRATE
SOLUTIONS AND SALTS

by

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THE PRODUCTION OF FERRATE
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INTRODUCTION

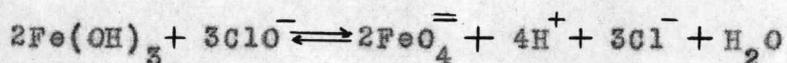
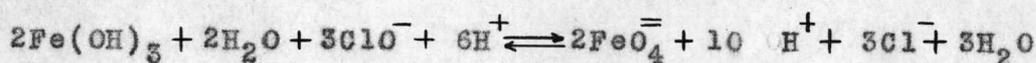
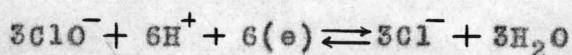
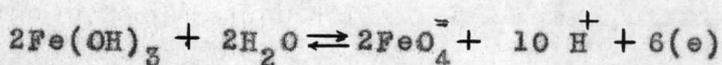
Iron occurs commonly with a valence of two or three, but under certain conditions it may exhibit a higher valence. In the form of the ferrate ion it exhibits a valence of plus six.

While a comprehensive summary of the present published knowledge on ferrate chemistry will be found in the thesis of J. M. Schreyer (15), some of the information pertinent to this investigation of sodium and potassium ferrate follows. The ferrates belong to the same group of compounds as the chromates, molybdates, selenates, sulfates, and tungstates (14). Ferrate solutions are highly colored, having an intense purple coloration similar to the permanganates. The ferrate ion, $\text{FeO}_4^{=}$, is a good oxidizing agent in basic solution and comparative with hypochlorite in oxidation potential. The ferrates are credited with being better oxidizing agents than permanganates (15). The reduction of the ferrate ion gives a hydrated ferric oxide product which is easily removed from solution.

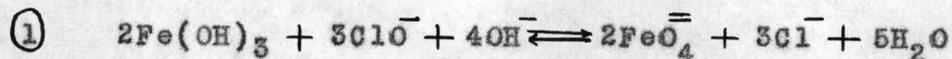
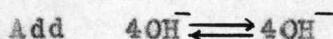
Ferrates in acid solution decompose spontaneously but show reasonable stability in alkaline solution. The sodium ferrate is known only in solution while

the potassium ferrate forms a reddish-black, non-hygroscopic, crystalline solid.

The net formation reaction on which all of the calculations of this report are based is as follows.



Since the ferrate ion is stable only in an alkaline medium



The investigation of the commercial production of such an oxidizing agent proposed a challenging problem. The research and development work related in this paper was carried out under the auspices of the Oregon State College Engineering Experiment Station and under the direct supervision of Professor Joseph Schulein.

As the work progressed, the scope of the problem broadened appreciably and many fundamental changes came to the original preparation method. In the

attempt to establish the critical values of the process control variables, it was found that the basic chemistry was either in question or far from complete. The engineering project was so dependent on this fundamental chemistry of higher valent iron that the chemical problems encountered were encompassed in the engineering investigation.

At the present time there is no commercial production of ferrate solutions or salts.

THE ORIGINAL INDUSTRIAL PROBLEM

The wet chlorination procedure recommended by Fremy (4) in 1841 is still the most common method of ferrate preparation in use today. The original goal of our research was the conversion of the laboratory scale wet chlorination preparation of potassium ferrate to a pilot plant scale and subsequent investigation of the pilot plant operation. Fremy's (4) preparation procedure described in the following paragraphs also covers Schreyer's (15) modifications and scheme of purification for the solid potassium ferrate.

Three hundred grams of potassium hydroxide are dissolved in 500 ml. of water. To the hot solution, 40 grams of pulverized ferric chloride are added with agitation. The reaction solution is about 8.4 molar potassium hydroxide at the start of the chlorination. Chlorine gas is bubbled through the solution as soon as the temperature has lowered to 55°C. The temperature is maintained between 55°-60°C. by means of agitation in a cold water bath. The length of time of chlorination is determined by chemical intuition.

The excess ferric hydroxide is filtered from the solution and potassium hydroxide is added slowly to

the filtrate. The temperature during saturation is maintained between 20°-30°C. The potassium ferrate which is practically insoluble in saturated potassium hydroxide is separated from the solution and air dried. The potassium ferrate precipitate contains large quantities of potassium chloride and potassium hydroxide as impurities. By four or five repeated reprecipitations from potassium hydroxide solutions most of the potassium chloride impurity is removed. The potassium ferrate solid is then added to 1,000 ml. of 95 per cent alcohol (3, 12) and agitated vigorously for one-half hour. The potassium ferrate is then filtered and washed with a small portion of ether (12) to remove the alcohol. Neither Frey nor Schreyer mentions yields obtained by following this procedure.

In studying the above, trouble was encountered immediately in the wet chlorination reaction. There was no readily available way of determining the progress of the reaction and chemical intuition proved erratic. The chlorine gas, a large percentage of which did not react with the sodium hydroxide, was entrained in a dense foam of the ferric hydroxide and viscous caustic solution. The foaming was troublesome and the chlorine

efficiency was prohibitively low. Temperature control was next to impossible as control of the chlorine flow rate, cooling water temperature, water flow rate, and agitation speeds was critical. Also, if the temperature went over 60°C., the entire ferrate solution underwent extensive and rapid decomposition.



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ELIMINATION OF THE CHLORIDE IMPURITY

The main impurity in the solid potassium ferrate was potassium chloride. As a waste or by-product of the ferrate reaction it presented an economic problem. As an impurity, its elimination was involved and costly. The inexpensive elimination of the chloride from the ferrate solution was accomplished as follows.

Taking advantage of the solubility of sodium ferrate in sodium hydroxide solutions was the first step. The ferrate ion was prepared in a sodium hydroxide solution rather than in the potassium hydroxide solution as previously used. The excess iron was removed by filtration and the filtrate saturated with sodium hydroxide. This precipitated the chloride ion as sodium chloride, leaving a relatively chloride free ferrate solution. Potassium hydroxide was then added to precipitate the potassium ferrate. The ferrate precipitate from this method of preparation was black, indicating a low chloride impurity.

ELIMINATION OF WET CHLORINATION PROCEDURE

Sodium hypochlorite was used by G. Blattner (2) in 1892 to oxidize ferric hydroxide to sodium ferrate. This suggested that the use of hypochlorite solutions offered answers to many of the problems encountered in the wet chlorination procedure.

The most important problem solved by the use of hypochlorite solutions was that of being able to study the reaction quantitatively. Through the use of known hypochlorite solutions, the effects of other constituents, studies of critical control variables, and yields could be determined. Temperature control was no longer a problem as the heat of formation of sodium hypochlorite was not introduced into the solution as in the wet chlorination method. The excess foaming from the wet chlorination method was also alleviated as the foaming from unreacted chlorine no longer occurred.

SEPARATION OF SOLIDS FROM CAUSTIC SOLUTIONS

The study of the filtration of the hydrated ferric oxide from the ferrate solutions was time consuming. The combination of viscous solutions and a gelatinous solid phase posed a difficult physical separation.

Both the ferrate and hypochlorite ions attack organic materials thus limiting the filtration media to corrosion resistant materials. For a laboratory separation of any appreciable volume it has been found that the best results are obtained by suction filtering of the slurry through a coarse asbestos mat on a Gooch type filter. This filtrate is then refiltered by suction through a fritted glass filter of medium or fine grade. Other media tried were wire screens, glass wool, Nylon cloth, and Vinyon cloth, but they gave no increase in filtration rate.

The ferric hydroxide, having a density about twice that of the caustic solution suspending it, was expected to separate from solution by centrifuging. Batch-wise centrifugal separation was time consuming but reasonably effective for removal of the larger particles. A low-speed centrifuge, 2,000 RPM, was used successfully for removal of the bulk of the ferric hydroxide. A continuous separation with a supercentrifuge, bowl speed of 25,000 RPM, was successful to some extent,

but the materials of construction of the equipment available were not suitable for use with the mixture of caustic, hypochlorite, and ferrate.

On an industrial scale a rubber or plastic lined centrifuge will probably handle the bulk of the separation. If the separation of ferric hydroxide is not complete in the centrifuge, a conventional filter with Nylon or Vinyon filter cloth will remove the finer particles. Both Nylon and Vinyon have been exposed to the extreme conditions expected in filtering these solutions. The two materials survived boiling in caustic, soaking twenty-four hours in strong hypochlorite, and standing in a ferrate solution for a period of forty-eight hours without any noticeable effect on the fabric.

PURIFICATION OF SOLID POTASSIUM FERRATE

The purification problem was practically eliminated as the chloride removal before precipitation gave a clean black precipitate. However, the chloride and caustic impurities which were present could be removed by taking advantage of their solubility in ethyl alcohol (12).

Trouble was experienced in washing the potassium ferrate with 95 per cent alcohol as recommended in Schreyer's purification procedure. The trouble seemed to lie in the fact that the heat of solution of the potassium hydroxide and potassium chloride surrounding the ferrate particles raised the local temperature to the point where oxidation of the alcohol took place easily. This alcohol oxidation may be avoided by one of two ways or by a combination of both. A large volume of alcohol, rapidly agitated when adding the potassium ferrate precipitate, reduces the oxidation as does lowering the temperature of the wash alcohol.

The ether wash (12) used to remove the alcohol film from the ferrate particles may be an unnecessary complication in a large scale process. An inert gas at low temperature drawn through the ferrate particles might be just as successful and certainly much simpler than the ether wash.

DECOMPOSITION BY HYDRATED OXIDES

Steel turnings, dissolved in hydrochloric acid and oxidized to ferric chloride with chlorine, was the starting material for the ferric hydroxide used in the early experimental work of this research. The erratic behavior of these solutions prompted an investigation of the effect of metallic oxides on a ferrate preparation using analytical grade ferric chloride to produce the ferric hydroxides.

Metallic oxides tried were those of cobalt, nickel, copper, beryllium, zinc, tin, copper, lead, magnesium, aluminum, mercury, and chromium. Nickel, cobalt, and copper in order of decreasing activity were the only oxides which catalyzed the hypochlorite decomposition. These observations are supported by the literature (1). The iron used for ferrate formation should therefore be free of nickel, cobalt, and copper.

The presence of nickel, cobalt, or copper would explain why Poggendorf (13) in his electrolytic preparation of potassium ferrate was not successful with all cast iron anodes and obtained negative results with wrought iron anodes.

SOLUTIONS RESULTING FROM FERRATE DECOMPOSITION

The bright green solutions resulting from the decomposition of some ferrate solutions have been attributed to the ferrite ion and to valence states higher than the ferrate (5). Technical grade ferric chloride was found also to give green decomposition solutions in our research, and it was found by analysis that these green solutions contained a large amount of manganese. The green color could be removed by the addition of hydrogen peroxide, and the resulting manganese dioxide removed by filtration, leaving a colorless filtrate. Solutions resulting from the decomposition of manganese free ferrate solutions were colorless.

A solution resulting from ferrate decomposition was analyzed for iron and was found to contain 0.0019 mols per liter. The addition of hypochlorite and sodium hydroxide brought the composition of the mixture to the conditions used for ferrate production. There was no color change or any other evidence of ferrate formation. This indicated the possibility of the ferrate reaction being totally dependent on the presence of a ferric hydroxide surface either as a catalytic surface for an ionic reaction or as an active surface which undergoes direct oxidation to the ferrate ion.

ANALYTICAL WORK FOR CONTROL ANALYSIS

For control analysis it was important to have a method of determining the ferrate ion concentration. Since the total iron determination of a solution is a routine analytical procedure, such a determination would offer an ideal measurement of ferrate concentration if the two could be related. With this idea in mind an analytical scheme was devised to evaluate this relationship.

Barium ferrate is a carmine-red precipitate formed by the addition of a soluble barium salt to an alkali metal ferrate solution (12). The barium ferrate is very stable, water-insoluble, and may be boiled without decomposition. This provided an excellent method for the quantitative separation of the ferrate ion from solution.

The total oxidizing power of a ferrate solution is due to both hypochlorite and ferrate ions. A considerable amount of preliminary work was done with hypochlorite solutions and mixtures of hypochlorite and ferrate. This work was done on a Fisher Titrimeter so that the potentiometric curves could be studied. Sodium bicarbonate as a buffer was found to stabilize the curves and sharpen the endpoint. There was no perceptible break in the potentiometric curve which

indicated that the oxidation potentials of hypochlorite and ferrate were proximate. The purple coloration of the ferrate ion faded slowly as the titration progressed, making the endpoint almost colorimetric. A platinum-calomel cell was found most suitable for this particular reaction.

The barium ferrate was precipitated from the ferrate-hypochlorite mixture by adding a slight excess of barium chloride. The precipitate was carmine-red with no barium ferrite or perferferrite impurity obvious. This precipitate was washed with cold water, decomposed with acid, and an iron determination made and compared with a total iron determination run on an aliquot of the same solution. All of the soluble iron was found to precipitate with barium.

The oxidizing power of the filtrate from the barium ferrate precipitation was then determined. The total oxidizing power of the solution should be the sum of the oxidizing values of the hypochlorite and the ferrate. This is indicated in the following data.

Analysis of a Ferrate Solution

Total Iron Analysis

Sample (ml. of FeO_4^- solution)	10	10	10
Volume 0.02 N $\text{K}_2\text{Cr}_2\text{O}_7$ (ml.)	51.80	51.80	51.90
Equiv. Volume of 0.100 N Na_3AsO_3 (ml.)	31.10 average		

 BaFeO_4 ppt. (Iron Analysis)

Sample (ml. of FeO_4^- solution)	5	5	
Volume 0.02 N $\text{K}_2\text{Cr}_2\text{O}_7$ (ml.)	25.78	25.96	
Equiv. Volume of 0.100 N Na_3AsO_3 (ml.)	15.52 average		

Filtrate Oxidizing Power

Sample (ml. of FeO_4^- solution)	5	5	5
Volume 0.100 N Na_3AsO_3 (ml.)	24.77	25.05	
	24.91 average		

Total Oxidizing Power of Ferrate Solution

Sample (ml. of FeO_4^- solution)	5	5	5
Volume 0.100 N Na_3AsO_3 (ml.)	39.76	39.65	39.52
	39.64 average		

Basis: 5 ml. of FeO_4^- solution

Total Oxidizing Power = 39.64 ml. of 0.100 N Na_3AsO_3

$\text{ClO}^- + \text{FeO}_4^- =$ Calculated total oxidizing power

$24.91 + 15.52 = 40.43$ ml. of 0.100 N Na_3AsO_3

Per cent deviation = 2%

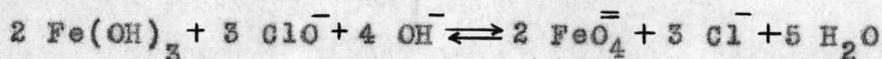
The method probably is more exact than the 2 per cent deviation shows. A logical source of this deviation might lie in the pipetting of small volumes of viscous caustic solutions.

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PROCESS VARIABLES

A net equation for the formation of the ferrate ion follows.



and the equilibrium constant

$$K = \frac{[\text{FeO}_4^{2-}]^2 [\text{H}_2\text{O}]^5 [\text{Cl}^-]^3}{[\text{Fe}(\text{OH})_3]^2 [\text{OH}^-]^4 [\text{ClO}^-]^3}$$

One consideration critical to the industrial process is the maximum ferrate concentration obtainable combined with a reasonable overall efficiency.

The variables which need investigation were indicated to be hydroxyl ion concentration, hypochlorite ion concentration, chloride ion concentration, hydrated ferric oxide reactivity, and temperature.

The use of the activity of ferric hydroxide in the equilibrium expression rather than the activity of the ferric ion is explained as follows. The activity of the iron is probably a composite activity consisting of the ferric ion activity and the ferric hydroxide surface activity.

Experimental Method

In the investigation of the ferrate reaction a batch volume of 400 ml. was used, employing a 1,000 ml. Erlenmeyer flask as the container. Sodium hydroxide solutions were prepared from commercial flaked caustic soda to a volume of approximately 200 ml. The caustic solutions were cooled to the temperature of melting ice, than a ferric chloride solution, 43.8 per cent by weight, was added slowly with sufficient agitation to maintain the low temperature throughout the slurry.

Sodium hypochlorite was then added slowly, care being taken to keep the temperature below that at which the ferrate oxidation reaction was to be carried out. The slurry was then made up to the 400 ml. volume and placed in a constant temperature water bath for the course of the reaction. The water bath used maintained the temperature within the limits of $\pm 0.5^{\circ}\text{C}$. Thorough agitation was required to prevent a foam layer from forming on top of the reaction mixture. This was accomplished by using turbulent off-center stirring which prevented the formation of foam.

Approximately 10 ml. samples were dipped from the slurry for each analysis. The slurry sample was filtered free of excess ferric hydroxide and the filtrate used

for analysis.

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The method of iron analysis was as follows. A 5 ml. aliquot of the ferrate filtrate was diluted to 10 ml., acidified with hydrochloric acid, and evaporated to about 4 ml. to remove the last traces of chlorine. The sample was diluted to 350 ml., 5 ml. of concentrated hydrochloric acid added, and then boiled with aluminum coils to reduce the ferric iron to the ferrous state. The sample was then cooled and titrated with standard potassium dichromate solution, using diphenylamine sodium sulfonate as an internal indicator.

The total oxidizing power determinations on the same filtered samples were carried out with the Fisher Titrimeter previously mentioned. 2 ml. aliquots were diluted to 400 ml., buffered with 5 grams of sodium bicarbonate, and titrated with standard sodium arsenite solution. The equivalents of sodium arsenite used represent the sum of the equivalents of hypochlorite and ferrate present.

The Effect of Hydroxyl Ion Concentration

Holding constant the ferric hydroxide concentration, the hypochlorite concentration, and the temperature; the sodium hydroxide concentration was varied from 4.75 molar to 14.25 molar. The results are shown graphically in Fig. 1.

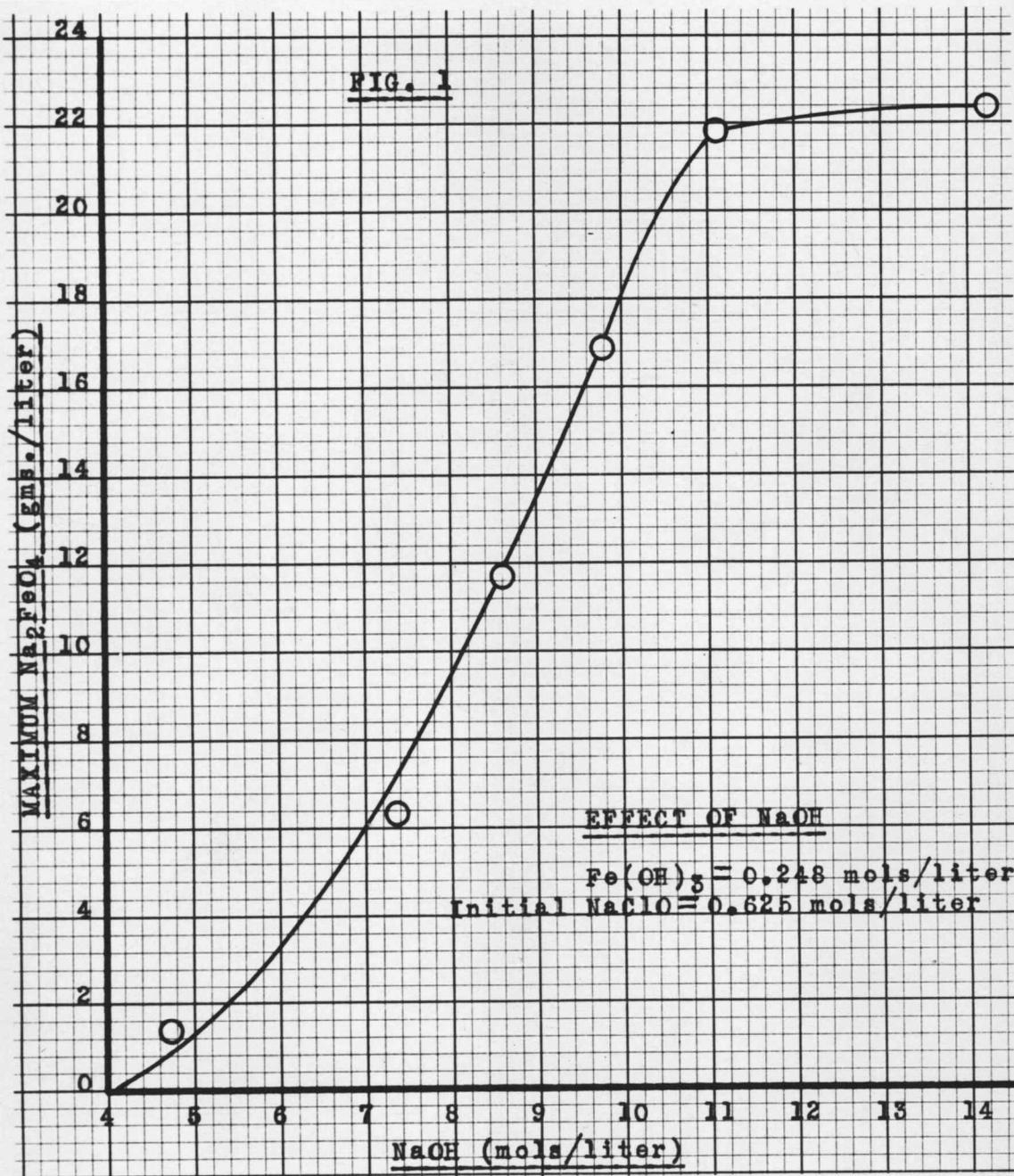
Since the curve flattens at about 11.0 molar, this would probably be the best sodium hydroxide concentration to use in an industrial application. The slightly increased yields resulting from higher concentrations would not compensate for the increased difficulty in handling and filtering the higher caustic ferrate solutions.

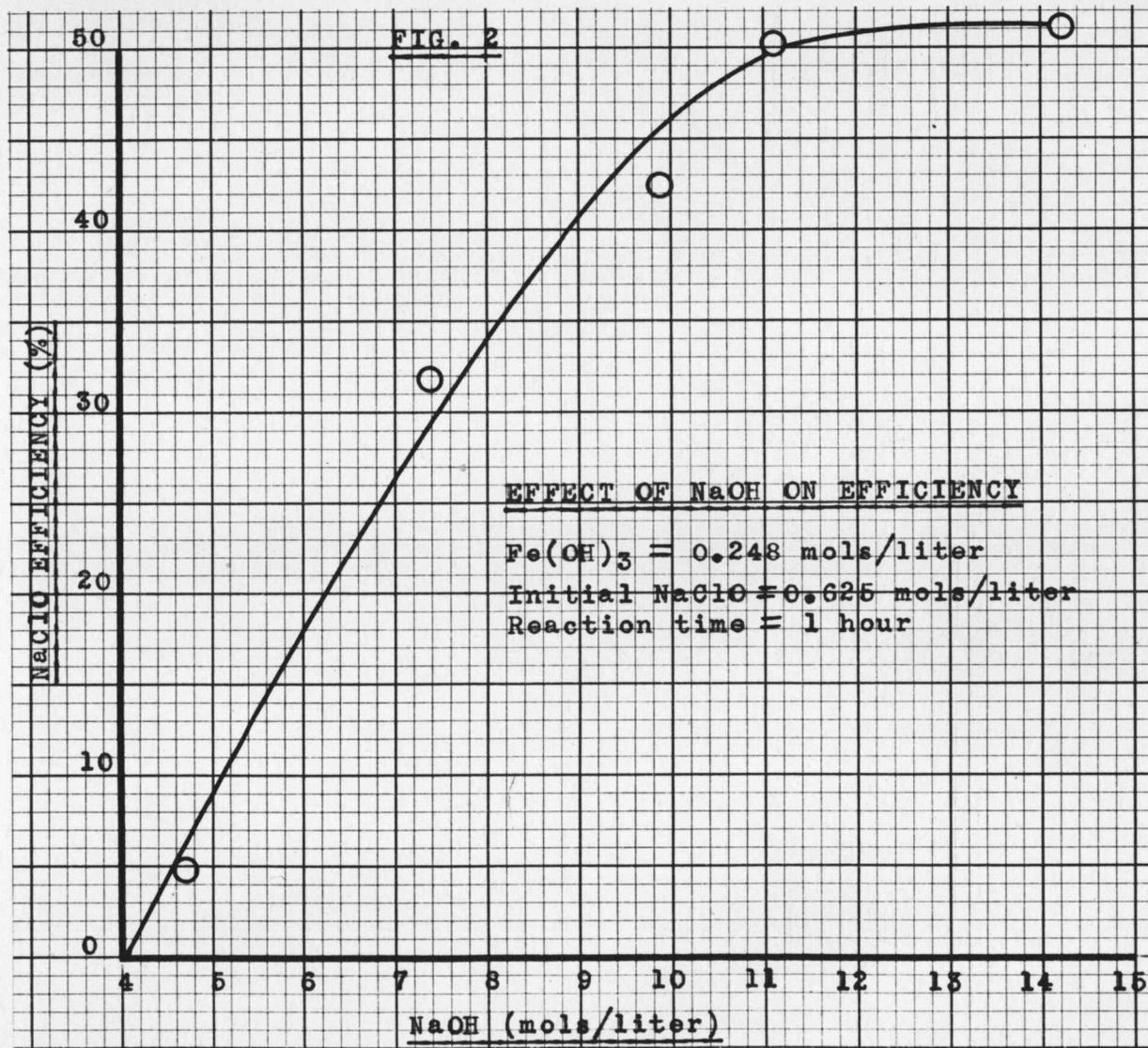
The efficiency of the net reaction also shows a considerable dependence on the hydroxyl ion concentration as illustrated in Fig. 2. The reaction efficiency is based on the hypochlorite used versus the theoretical requirement at any ferrate concentration.

$$\frac{(\text{Theoretical mols NaClO required to form ferrate})(100)}{(\text{Actual Mols NaClO used})} = \% \text{ Efficiency}$$

or from Equation (1)

$$\frac{(\text{Mols FeO}_4)(3)(100)}{(\text{Mols NaClO used})(2)} = \% \text{ Efficiency}$$





The hydroxyl ion concentration was the only variable found to have an important effect on the reaction efficiency.

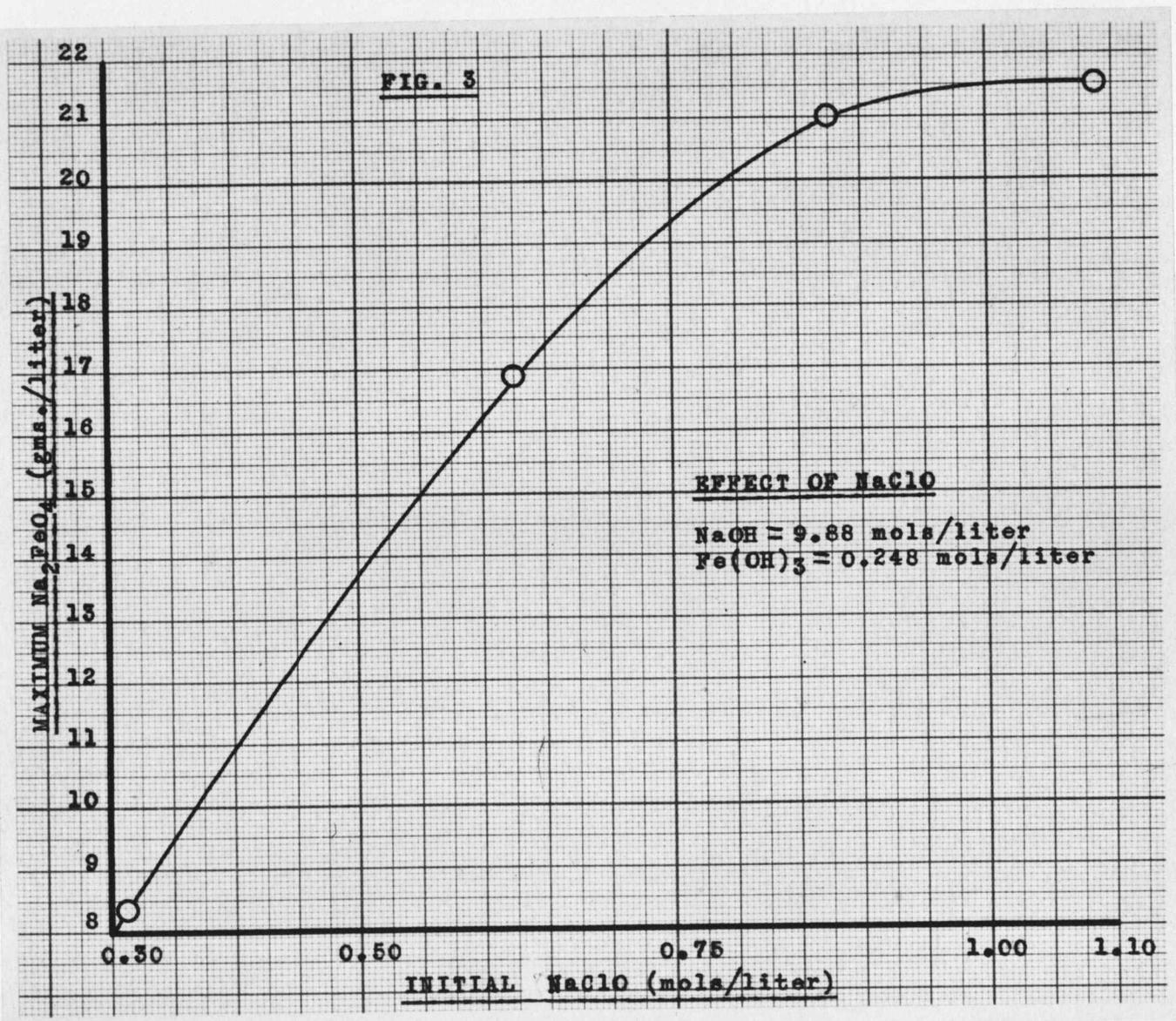
Effect of Initial Hypochlorite Concentration

The hypochlorite ion is the oxidizing agent which is reduced in the formation of the ferrate ion. The effect of varying its initial concentration holding the other variables constant is shown in Fig. 3.

Commercial sodium hypochlorite is not usually produced in concentration over 16 per cent by weight because of the instability of more concentrated solutions (1). The maximum concentration obtainable for industrial work runs about 2.73 mols per liter compared to 1.09 mols per liter at the highest concentration used in this work. However, since the curve starts leveling off at around 0.875 mols per liter, sufficient information was obtained for this investigation.

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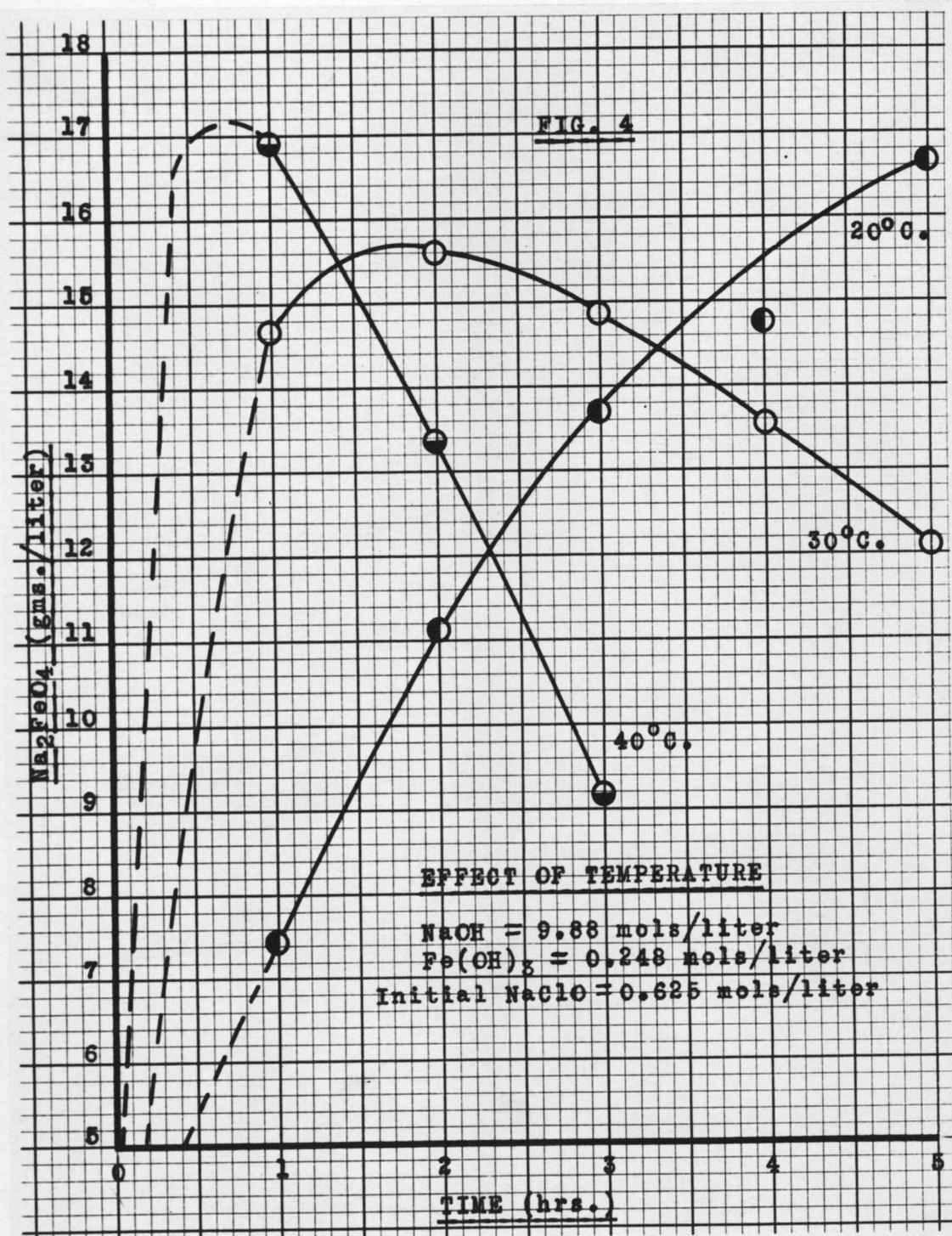
The Effect of Temperature

The temperature at which the ferrate reaction takes place has little or no effect on the yield, but has a very large effect on the rate of reaction. The ferrate decomposition rate is decreased with temperature lowering.

The point of maximum concentration occurs at about one hour with the temperature at 40°C. while at 20°C. the high point is reached around six hours as shown in Fig. 4.

The reaction is too difficult to handle at 40°C. for industrial purposes, and at 20°C., the reaction time is too long. A temperature of about 25-30°C. should give an easily controlled reaction suitable for commercial operation. The use of uncontrolled caustic concentrations resulting from the wet chlorination procedure is thought to be the contributing factor to the higher temperatures necessary for ferrate production previously reported in the literature (15).

The decline in ferrate concentration after the peak point is probably explained as follows. The formation and decomposition rates are just equal at the maximum concentration point. As the reaction progresses, the decomposition rate remains about



the same while the formation rate is constantly decreasing, bringing about a drop in ferrate concentration.

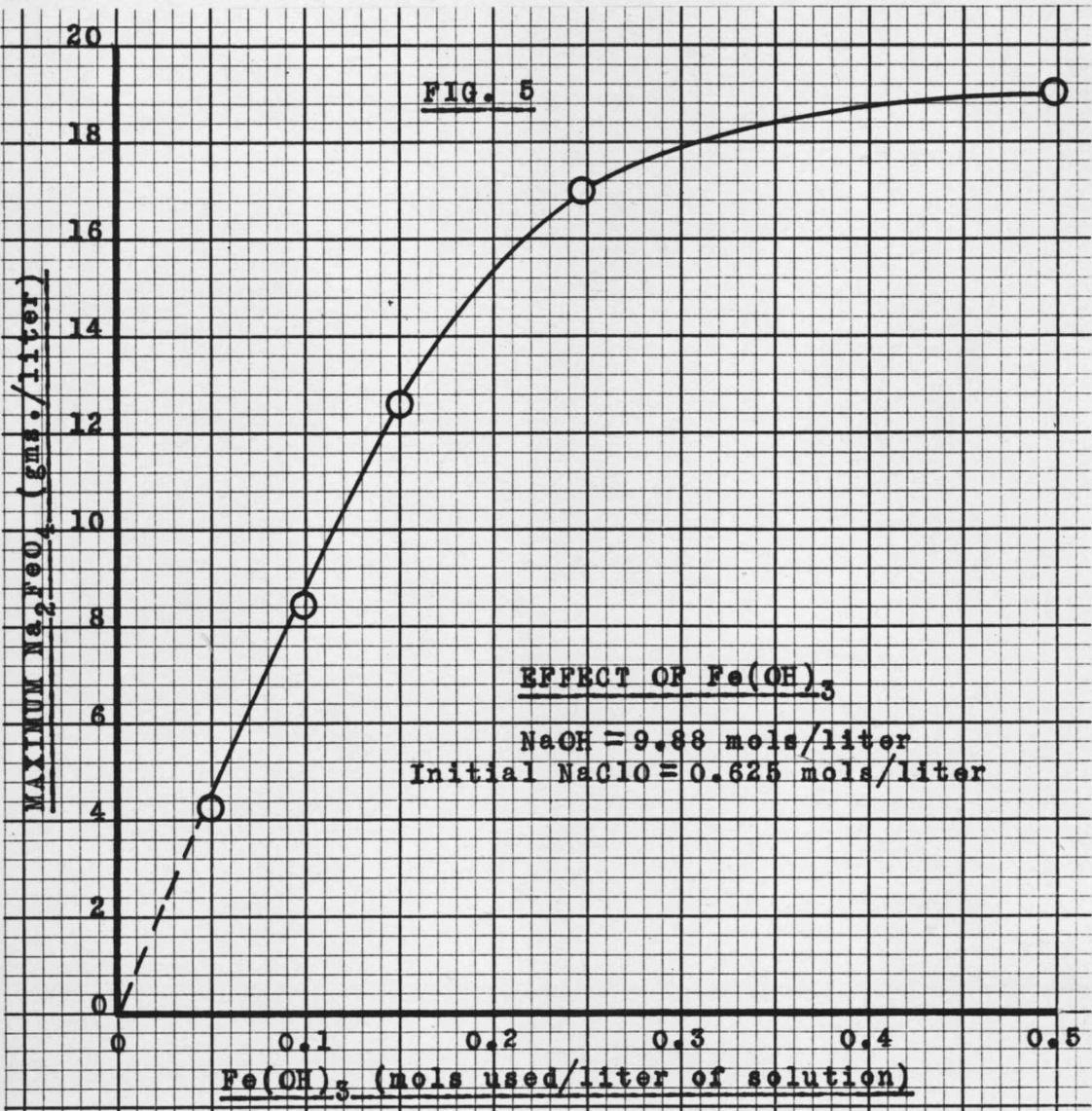


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The Effect of Ferric Hydroxide

Since the ferrate reaction was indicated to take place on the ferric hydroxide surface, an increase in this surface was expected to give an increase in ferrate concentration. This was found to be true up to a ferric hydroxide quantity of about 0.30 mols per liter of solution, where the curve flattened, giving little further effect, as illustrated in Fig. 5. This leveling off point can probably be raised as the hypochlorite concentration is raised unless other limiting factors are found.



The Effect of Aging on Ferric Hydroxide

While investigating the effect of ferric hydroxide reactivity, it was found that only about 40 to 50 per cent of the iron seemed to enter into the ferrate reaction. This is seen from the following data where the per cent of the iron used for the reaction represents iron in the higher valent state at the maximum ferrate concentration.

$\text{NaClO} = 0.625$ mols/liter

$\text{NaOH} = 9.88$ mols/liter

Temp. = 40°C .

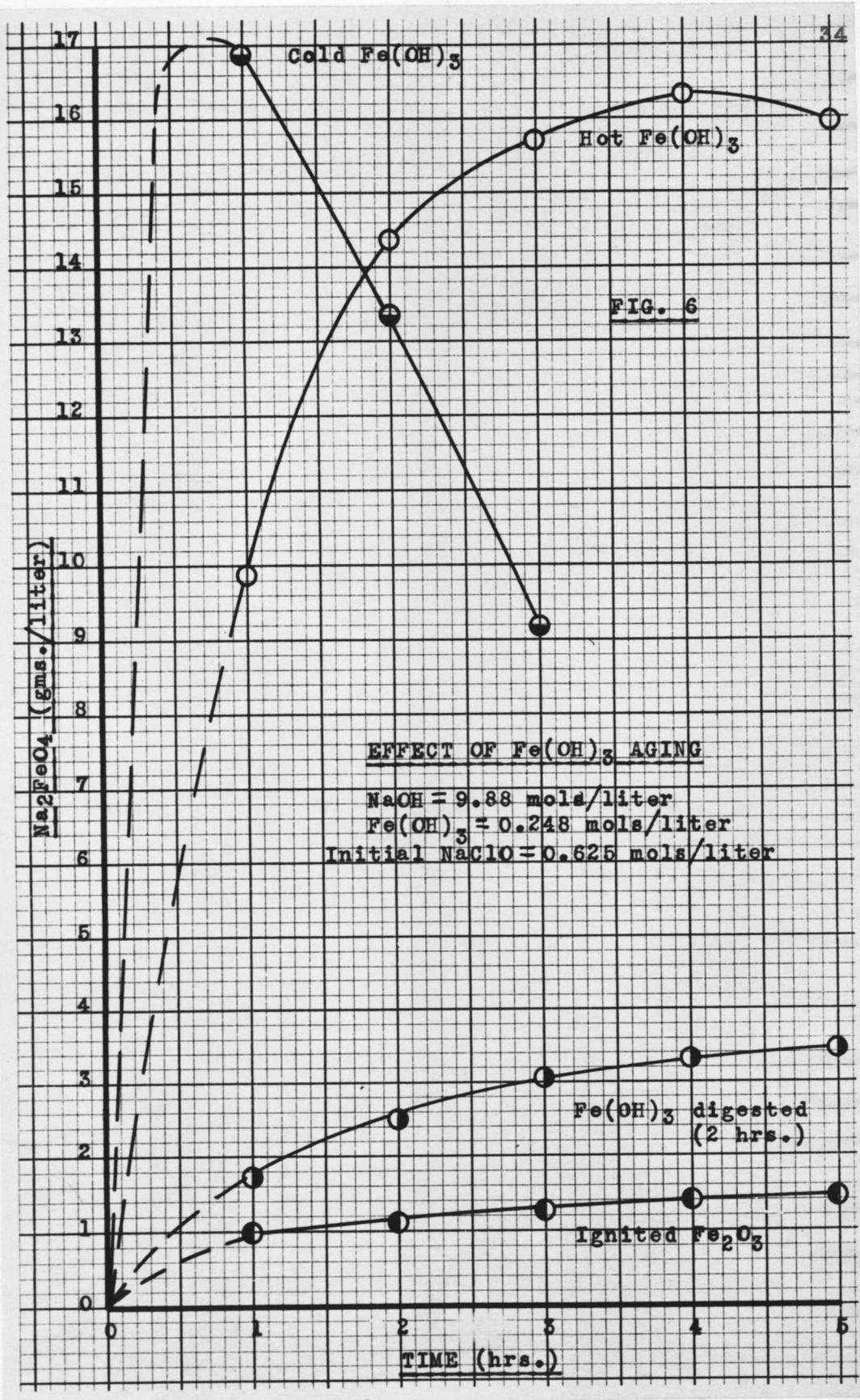
Iron (mols/liter)	0.0498	0.0995	0.149	0.249	0.498
Iron used (%)	51.8	50.8	50.9	41.0	45.8

Several possibilities were considered in attempting to explain why such a large percentage of the iron was apparently unavailable for reaction. When ferric chloride is added to strong sodium hydroxide there is a possibility of the formation of basic salts of ferric hydroxide (16) which might be unreactive. Another possibility is that there is a certain amount of unhydrated ferric oxide formed which would be extremely inactive.

In the attempt to confirm the above possibilities in the literature, the work of Krause and coworkers (8, 9, 10, 11) on the polymerization and aging of ferric hydroxide was found. There are two general classes of hydrated ferric oxide, the red and the yellow (17). The yellow type is very inactive while the red form is very active under certain conditions.

The activity of the red, or ortho-hydroxide, and its tendency to age were found to depend primarily on alkalinity and temperature. As alkalinity is decreased, the aging or polymerization rate is sharply increased. As the temperature at which the ortho-hydroxide is formed from the ferric salt is lowered, the activity is increased and the aging rates are again retarded. It would appear that the methods used for formation of the ferric hydroxide used in the ferrate reaction reported in the literature produced a relatively inactive form of the hydroxide and probably contributed to the lack of control and extremely low yield obtained by Schreyer (15).

The preparation of the ferric hydroxide at ice temperature did not appear to have too much effect on the yield, but the rate of reaction was increased by at least six times, as shown in Fig. 6. However, the use of this unaged ferric hydroxide did not seem to



change the percentage of the iron used for reaction or the efficiency of the reaction.

Ignited ferric oxide digested for two hours in strong caustic gave a low yield of sodium ferrate. Ferric hydroxide prepared in the usual way and then digested for two hours in strong caustic shows the drastic effect of aging by high temperatures as mentioned above.

The Effect of Sodium Chloride Concentration

From the equation for the equilibrium constant, it would seem that the chloride concentration would have an appreciable effect. It was found, however, that little change was brought about by reducing or increasing the chloride concentration.

This could be attributed to the following reasons. The ferric hydroxide can be washed clear of only about 50 per cent of the chloride by repeated washing and decanting (16). The chloride in the sodium hypochlorite solution may be partially removed by saturating with sodium hydroxide. By using these methods the lowest chloride concentration tested ran about 1.0 molar while the saturation concentration in 10.0 molar sodium hydroxide solution is approximately 1.5 molar which represented the maximum salt concentration used (7).

An excess of solid sodium chloride in the slurry does not have any noticeable effect on efficiencies, yields, or rates of reaction in ferrate preparation.

THE PREPARATION OF FERRATES WITH METALLIC IRON

The difficulties involved in the use of ferric hydroxide led to a test run with finely divided metallic iron--the theory being that the ferric hydroxide formed on the surface would be immediately oxidized to the ferrate state. The reaction solutions used were 9.88 molar sodium hydroxide and 0.625 molar with respect to sodium hypochlorite. The results are tabulated below.

	Run I	Run III			
Temp. (°C.)	23°	40°	----		
Iron (gm/liter of solution)	12.5	12.5	----		
Time of Reaction (hrs.)	23	23	44		
Na ₂ FeO ₄ (gms/liter)	0.768	1.060	1.338		
		Run II			
Temp. (°C.)	23°	---	---	---	---
Iron (gm/liter of solution)	37.5	---	---	---	---
Time of Reaction (hrs.)	23	48	73	97	121
Na ₂ FeO ₄ (gms/liter)	1.100	2.41	2.92	3.12	2.99

An increase in temperature from about 23°C. to 40°C. gave a corresponding increase in ferrate concentration at the end of twenty-three hours of approximately 38 per cent. Increasing the iron from

12.5 grams to 37.5 grams per liter of solution gave an increase of 43 per cent in the ferrate concentration. This indicated that the yield could be improved by these variables. At no time during the course of these runs was any ferric hydroxide obvious which might mean that the ferric hydroxide formed was very active and rapidly converted to ferrate.

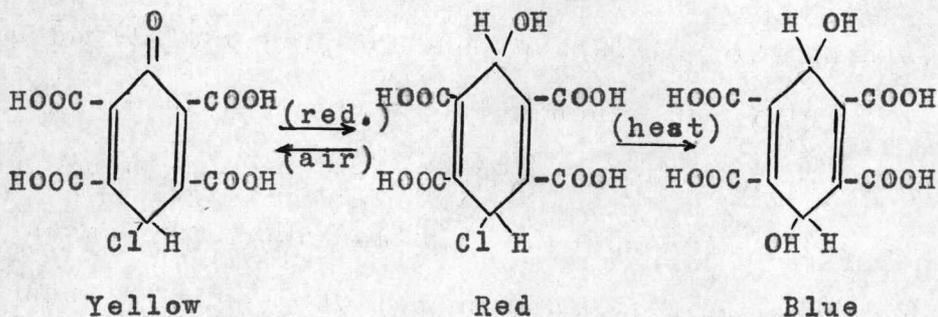
The industrial significance of this method of preparation has yet to be seen, but the apparent advantages are many. The filtering problem would be almost completely eliminated as separation of the metallic iron could easily be accomplished by magnetic means. This would greatly reduce the original equipment investment as no special separation equipment or materials of construction would be required.

The iron surface introduced into the slurry would then be limited only by the workability of the slurry. The hypochlorite concentration could possibly be maintained at a high level by electrolytic means during the course of the reaction. The potentialities proposed by these advantages certainly warrant further investigation.

USE OF FERRATE ION FOR CAUSTIC DECOLORIZATION

Commercial electrolytic caustic is characterized by a blue or purple color. The color is an impurity and is very objectionable from a sales standpoint. The industry at present usually removes the color by bleaching with chlorine followed by an adsorption settling step.

H. H. Heller (6) isolated an organic compound from used graphite electrodes which proved to be the cause of the blue caustic coloration. The compound was found to be a pyromellitic acid derivative, probably pyromellitic acid chloroquinone, a yellow acid. The blue coloration is produced during evaporation of the cell liquor to 50 per cent sodium hydroxide. This may be illustrated by the following formulas.



Bleaching with chlorine gives the 50 per cent caustic a distinct yellow coloration. Sodium peroxide changes the blue liquor to a deep yellow color.

However, solutions of the ferrate ion were found to decolorize the blue liquor completely, leaving a colorless solution comparative with a caustic solution made up from flaked sodium hydroxide. Schreyer (15) observed that a trace of ferrate caused the blue color to disappear, but no mention was made of the color of the resultant solution. The ferrate ion probably oxidizes the dye, breaking the aromatic ring, thus destroying the highly colored quinone structure.

The amount of sodium ferrate required for decolorization depends on the constantly changing concentration of the organic material in the cell liquor. However, an excess of ferrate solution is characterized by the purple coloration of the ferrate ion so decolorization control would be simple. The excess ferrate is easily reduced by peroxides or heating. A test run on commercial blue liquor is shown below.

Caustic Decolorization

Volume of blue caustic liquor (ml.)	200	300	400
Volume of 0.1452 molar FeO_4^- added (ml.)	2	2	2
Color of 50 per cent caustic liquor after 24 hours.	colorless	pale yellow	yellow

An estimate of the amount of sodium ferrate required for decolorization would be about two pounds per thousand gallons of blue liquor. In terms of volume, twelve gallons of an average 0.125 molar ferrate solution would be required per thousand gallons of blue caustic liquor.

The ferrate solution must be made up free of colored impurities. The worst offender here is manganese which, when oxidized to the manganate ion, has an intense green coloration. If the manganese elimination from the iron proved too costly, the manganate may be reduced with hydrogen peroxide to form manganese dioxide which would be removed in the settling steps.

A possible objection to the use of ferrate solutions for decolorization is the introduction of iron into the caustic. However, the amount of iron added would not be large and would be easily removed in the usual iron removal stage of caustic production.

The color comparisons of the decolorized caustic solutions have all been done by eye. A Klett-Summerson Colorimeter was tried, but failed to give useable results.

COST ESTIMATE FOR PRODUCTION OF SODIUM FERRATE SOLUTIONS

A possible use of ferrate solutions as mentioned previously could be for blue caustic decolorization. The following cost estimate was made on a ferrate installation capable of decolorizing 20,000 gallons of blue liquor per twenty-four period.

Operating Conditions

Temperature of reaction - - - - -	30°C.
Sodium hydroxide - - - - -	11.0 mols/liter
Ferric hydroxide - - - - -	0.3 mols/liter of solution
Sodium hypochlorite - - - - -	0.9 mols/liter
Time of reaction - - - - -	2 hours

From the blue caustic decolorization experiment it was found that a volume of 12 gallons of 0.125 molar ferrate solution would decolorize 1,000 gallons of blue liquor.

Basis: 250 gallons of 0.125 M Na_2FeO_4 per 24 hours, sufficient for treating 20,000 gallons of blue liquor.

$$\text{Na}_2\text{FeO}_4 \text{ produced} = \frac{(250)(3.785)(0.125)(166)}{(454)} = 43.3 \text{ lb.}$$

$$\text{Flaked NaOH for solution} = \frac{(250)(3.785)(11)(40)}{(454)} = 918 \text{ lb.}$$

To prepare 1.00 gallons of 16 per cent by weight sodium hypochlorite, 1.60 pounds of chlorine and 1.95 pounds of caustic are required (1).

$$\text{NaOH for NaClO} = \frac{(250)(3.785)(0.9)(74.45)(1.95)}{(454)(0.16)(1.00)(1.27)(8.34)} = 161 \text{ lb.}$$

$$\text{Cl}_2 \text{ for NaClO} = \frac{(161)(1.50)}{(1.75)} = 132 \text{ lb.}$$

$$\text{Iron for Fe(OH)}_3 = \frac{(250)(3.785)(0.3)(55.85)}{(454)} = 35 \text{ lb.}$$

$$\text{Iron used for ferrate} = \frac{(43.3)(55.85)}{(166)} = 14.6 \text{ lb.}$$

Estimated costs for the raw materials are as follows:

50% sodium hydroxide - - - - -	2.4 ¢/# NaOH
Flaked sodium hydroxide - - -	3.7 ¢/# NaOH
Chlorine - - - - -	2.0 ¢/# Cl ₂
Iron - - - - -	10.0 ¢/# Iron

Raw Material Costs

$$\text{Cost flaked NaOH} = (918)(0.013) = \$11.93$$

$$\text{Cost 50\% NaOH} = (161)(0.024) = 3.86$$

$$\text{Cost of chlorine} = (132)(0.02) = 2.64$$

$$\text{Cost of iron} = (35)(0.10) = \underline{3.50}$$

$$\text{Total} \quad \quad \quad \$21.93$$

Manufacturing Cost

Cost of NaClO manufacture = $(3.86 + 2.64)(0.5) =$	\$	3.25
Labor cost (5 hrs.) = $(5)(1.80) =$		9.00
Power, maintenance, etc. - - - - -		<u>2.00</u>
	Total	\$14.25

Equipment Costs

Reaction vessel (300 gal. steel) - - - -	\$	500
Stiring motor - - - - -		200
Pumps - - - - -		200
Leaf filter - - - - -		1,000
Storage vessel (100 gal.) - - - - -		<u>100</u>
	Total	\$2,000

Amortize equipment on 5 year basis

$$\text{Equipment Cost/day} = \frac{(2,000)}{(5)(360)} = \$1.11$$

Cost of Decolorization/20,000 gal. blue liquor/day

Raw material cost - - - - -	\$	21.93
Manufacturing cost - - - - -		14.25
Equipment cost - - - - -		<u>1.11</u>
		\$37.29

or Decolorization cost = 58.6 ¢/ton of NaOH

SUMMARY

The development of a method for the preparation of solid potassium ferrate includes the following changes over previous methods.

1. The formation of the ferrate ion in sodium hydroxide solution.
2. The elimination of the wet chlorination method, involving the use of sodium hypochlorite solutions instead.
3. The removal of the chloride from solution before precipitating the potassium ferrate.
4. The precipitation of potassium ferrate from a chloride free sodium ferrate solution.
5. The necessity for using raw materials free of nickel, cobalt, and copper.

A method suitable for control analysis was developed and confirmed for determination of ferrate concentration, involving a total iron determination of the ferrate solution.

The green solutions resulting from ferrate decompositions were found to contain manganese as the coloring material, the manganese free ferrate decomposition solutions being found to be colorless.

The effects of the following process variables in the ferrate reaction were studied; sodium hydroxide concentration, initial sodium hypochlorite concentration, ferric hydroxide reactivity, sodium

chloride concentration, and temperature. It was found that the aging of the ferric hydroxide was critical to the rate of reaction.

Sodium ferrate was prepared with a powdered metallic iron and the reaction explained.

The ferrate ion was used for blue caustic decolorization and an estimated made of the amount of sodium ferrate required for decolorizing average blue liquors. On the basis of the decolorizing experiments, a cost estimate was made for commercial decolorization.

SUGGESTIONS FOR FUTURE INVESTIGATION

1. A pilot-plant study of the ferrate reaction and the solid potassium ferrate preparation.
2. The solubility of potassium ferrate in various hydroxyl ion concentrations.
3. Find the nature of the decolorization of the dye in strong caustic with the ferrate ion and the products of this oxidation.
4. A thorough investigation of the ferrate preparation from metallic iron.
5. Investigate the use of the ferrate ion as an oxidant especially in the organic field.
6. Investigate the possibility of there being a critical concentration of the ferrate ion in solution, in excess of which concentration the ferrate ion is extremely unstable.
7. A thorough investigation of ferric hydroxide aging and polymerization in the ferrate reaction.

BIBLIOGRAPHY

1. Allied Chemical and Dye Corporation. Solvay Technical and Engineering Service. Chlorine Bleach Solutions. Bulletin No. 14, 1949.
2. Blattner, G. Action des Oxydes metalliques sur les hypochlorites alcalins et alcalino-terreux. Bull. Soc. Chim. (3) 7:705, 1892.
3. Eidmann, W., and Moser, L. Ueber Strontium ferrat. Ber. 36:2290, 1903.
4. Fremy, E. F. Compt. Ren. 12:23, 1841; 14:424, 1842.
5. Goralevitch, D. K. Russ. Journ. Phys. Chem. Soc., 58:1129, 1896.
6. Heller, H. H. The Color of Electrolytic Caustic Liquor. Trans. Electro. Chem. Soc., 87:50, 1945.
7. Hooker, A. H. Chem. and Met. Eng. 23, 1920.
8. Krause, A., and Ciokowna, M. Struktur und Polymerisation des braunen Orthoferrihydroxids. Zeit. anorg. allgem. Chem. 204, 20, 1932.
9. Krause, A., Lakosciukowna, H., and Cichowski, J. Der Reaktions Mechanismus der Bildung Von Bohms Goethit und der Einfluss der H-Konzentration auf die Alterung des Orthoferrihydroxyds bei hoheren Temperaturen. Zeit. anorg. allgem. Chem. 209, 282, 1932.
10. Krause, A., and Lewandowski, A. Der Alterungsprozess des Orthoferrihydroxyds und die Konstitution des Goethits (α -FeOOH). Zeit. anorg. allgem. Chem. 206, 328, 1932.
11. Krause, A., and Torno, H. Struktur und quantitative Trennung gealterter Eisen (III) hydroxyde. Zeit. anorg. allgem. Chem. 211, 98, 1933.

12. Moser, L. Zur Kenntniss der eisen sauren Salze. Journ Prakt. Chem. (2) 56:425, 1897.
13. Poggendorf. Pogg. Ann. 54:161; 373, 1841.
14. Retgers, J. W. Der Isomorphismus der Ferrate mit den Sulfaten, Seleniaten U. S. W. Zeit. Phys. Chem. 10:529, 1892.
15. Schreyer, James M. Higher Valence Compounds of Iron. Thesis at Oregon State College, 1948.
16. Sheldon, J. A Study of Ferric Hydroxide Precipitated by Urea and its use in Quantitative Separations. Doctoral Thesis, University of Michigan, 1940.
17. Welo, Lars. A., and Baudisch, Oskar. Active Iron. Chem. Rev. 15, 45, 1934.

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APPENDIX

ORIGINAL DATA

Run	Reaction Time-hrs.	Temp. C°.	NaOH Conc. mols/liter	Initial NaClO mols/liter	Iron Added mols/400ml.	Total Iron 5 ml. sample Vol. of 0.02 N $K_2Cr_2O_7$ (ml.)	Total Oxidiz- ing Power 2 ml. sample Vol. of 0.100 N Na_3AsO_3 (ml.)
1	1	40	9.88	0.250	0.0995	14.85	15.58
	2	"	"	"	"	21.60	16.13
	3	"	"	"	"	23.60	13.29
	4	"	"	"	"	24.55	11.99
	5	"	"	"	"	23.99	10.30
3	1	40	7.38	0.250	0.0995	8.31	20.68
	2	"	"	"	"	9.28	16.09
	3	"	"	"	"	9.61	13.14
	4	"	"	"	"	8.83	10.10
	5	"	"	"	"	7.77	8.54
5	1	40	8.63	0.250	0.0995	13.87	22.37
	2	"	"	"	"	16.37	17.36
	3	"	"	"	"	17.59	14.94
	4	"	"	"	"	17.25	12.45
	5	"	"	"	"	16.21	10.66
8	1	40	10.31	0.250	0.0398	8.02	24.20
	2	"	"	"	"	10.85	20.96
	3	"	"	"	"	12.00	19.38
	4	"	"	"	"	12.42	18.21
	5	"	"	"	"	12.62	16.83

9	1	40	9.88	0.250	0.0597	10.15	23.71
	2	"	"	"	"	14.61	20.99
	3	"	"	"	"	17.84	19.45
	4	"	"	"	"	18.90	16.98
	5	"	"	"	"	19.03	16.19
12	1	40	9.88	0.250	0.0199	4.45	24.35
	2	"	"	"	"	5.57	22.20
	3	"	"	"	"	5.96	21.05
	4	"	"	"	"	6.43	19.97
	5	"	"	"	"	6.45	19.03
13	1	40	9.88	0.250	0.0995	1.51	23.40
	2	"	"	"	(Fe ₂ O ₃)	1.70	22.76
	3	"	"	"	"	1.89	22.40
	4	"	"	"	"	2.11	21.80
	5	"	"	"	"	2.22	21.37
14	1	40	9.88	0.250	0.0995	2.60	25.35
	2	"	"	"	(digested	3.82	24.55
	3	"	"	"	2 hrs.)	4.59	23.64
	4	"	"	"	"	4.98	23.32
	5	"	"	"	"	5.20	22.33
16	0.5	20	9.88	0.250	0.0995	7.48	24.53
	1	"	"	"	"	11.21	22.20
	2	"	"	"	"	16.73	21.25
	3	"	"	"	"	20.60	10.84
	4	"	"	"	"	22.22	-----
5	"	"	"	"	25.09	19.52	
19	1	40	9.88	0.435	0.0995	32.32	31.37
	2	"	"	"	"	27.93	23.49
	3	"	"	"	"	24.40	19.40

20	1	40	4.75	0.250	0.0995	2.21	14.61
	2	"	"	"	"	1.32	8.40
21	1	40	9.88	0.125	0.0995	12.58	6.00
	2	"	"	"	"	6.25	2.17
22	1	40	11.12	0.250	0.0995	32.80	17.20
	2	"	"	"	"	26.17	10.40
	3	"	"	"	"	20.00	6.92
24	1	40	9.88	0.250	0.0995	25.48	16.68
	2	"	"	"	0.0	20.13	10.18
	3	"	"	"	"	13.80	6.90
25	0.5	40	14.25	0.250	0.0995	28.50	18.47
	1	"	"	"	"	33.52	15.48
	2	"	"	"	"	31.14	11.29
28	0.5	40	9.88	0.250	0.1990	28.50	14.96
	1	"	"	"	"	18.72	7.40
	2	"	"	"	"	5.28	1.95
29	0.5	40	9.88	0.350	0.0995	32.53	30.20
	1	"	"	"	"	31.61	22.89
	2	"	"	"	"	27.59	14.99
30	1	30	9.88	0.250	0.0995	22.26	19.51
	2	"	"	"	"	23.50	16.50
	3	"	"	"	"	22.40	13.12
	4	"	"	"	"	20.41	11.15
	5	"	"	"	"	18.22	9.18

SAMPLE CALCULATIONS

Basis: 400 ml. batch volume

Oxidizing power from ferrate (2 ml. sample)

$$\frac{(\text{ml. of } 0.02 \text{ N } K_2Cr_2O_7)(2)(0.02)(3)(10)^3}{(5)(0.10)(10)^3} = \text{equiv. ml. of } 0.100 \text{ N } Na_3AsO_3$$

Mols ferrate present

$$\frac{(\text{ml. of } 0.02 \text{ N } K_2Cr_2O_7)(0.02)(400)}{(10)^3 (5)} = \text{mols } FeO_4$$

Na_2FeO_4 (gms/liter)

$$(\text{mols } FeO_4 \text{ in } 400 \text{ ml.})(2.5)(166) = \text{gms/liter}$$

K_2FeO_4 (gms/liter)

$$(\text{mols } FeO_4 \text{ in } 400 \text{ ml.})(2.5)(198) = \text{gms/liter}$$