

Ferrate Ion:  $\text{FeO}_4^{2-}$  as a  $\text{Cl}_2$  and  $\text{MnO}_4^-$  Replacement in Water Purification

Principal Investigator  
R. Kent Murmann

Student Assistants  
Martin Hoppe  
Laling Fang  
Scott Young  
Martha Burnett  
Sahba Jalahi

Grant Numbers: 14-08-0001-G 1235-05  
U.S. Geological Survey  
U.S. Department of the Interior

Missouri Water Resources Research Center  
University of Missouri  
Sinclair Road - Route 3  
Columbia, Missouri 65203

The research on which this report is based was financed in part by the Department of the Interior, U.S. Geological Survey, through the Missouri Water Resources Research Center.

The contents of this publication do not necessarily reflect the views and policies of the Department of the Interior, nor does mention of trade names or commercial products constitute their endorsement by the U.S. Government.

# "FERRATE ION: $\text{FeO}_4^{2-}$ AS A $\text{Cl}_2$ and $\text{MnO}_4^-$ REPLACEMENT IN WATER PURIFICATION"

R. Kent Murmann

## INFORMATIVE ABSTRACT

A method has been devised by which solid samples of  $\text{K}_2\text{FeO}_4$  can be stabilized with respect to decomposition through a double-mixed salt with inexpensive  $\text{K}_2\text{SO}_4$ . This solid solution is stable over a wide range of compositions and can be prepared directly by electrolysis in a continuous process.

The mechanism of stabilization of solutions of  $\text{FeO}_4^{2-}$  by  $\text{IO}_4^-$  has been studied and it is found to prevent solid oligomers of Fe(III) from forming which are the major catalytic species. This occurs through complexation to form a symmetrical ion which has been isolated and its crystal structure determined. There is a direct correlation between the time of complete removal of  $\text{IO}_4^-$  and the start of the catalytic path. It is concluded that the kinetics of decomposition in the presence of metal-ion complexes is a function of trace impurities in the solvent and that "clean" kinetics cannot be observed.

The reaction of  $\text{CH}_2\text{O}$ ,  $\text{HCOO}^-$ , and  $\text{NO}_2^-$  with  $\text{FeO}_4^{2-}$  were studied and the rates shown to be first order in substrate and oxidant, increasing with acidity and are consistent with a  $2e^-$  slow step followed by a rapid reaction or reactions. The third oxygen in  $\text{NO}_3^-$  (from  $\text{NO}_2^-$  oxidation) comes from  $\text{FeO}_4^{2-}$  as shown by  $\text{O}^{18}$  measurements.

Enhancement of the rates of  $\text{NH}_3$  reaction were found with traces of oxidizable metal ions. But the products of the reaction were many and the mechanism is not certain.

A study of the formation of  $[\text{Fe}(\text{o phen})_3]^{+2}$  during  $\text{CH}_2\text{O}$  oxidation by  $\text{FeO}_4^{2-}$  in the presence of ophen shows that it definitely forms but we were not able to establish that Fe(II) was generated from Fe(IV).

## STATEMENT OF PURPOSE AND OBJECTIVES

(Duration June 1, 1986 to June 31, 1987)

That there is a serious need to replace  $\text{Cl}_2$  and  $\text{MnO}_4^-$  at least partially in the purification of many types of water is well documented. Both reagents have serious drawbacks to their continued use at the present levels. Ferrate ion is a natural for their replacement in many, though not all, respects. Although research has been going on slowly since about 1970 when we suggested its potential we still have not reached the stage where it is practical and even the patents which should point the way that industry will take are highly misleading, often vague and non-reproducible and have not been very constructive in making a useful product. One of the leading reasons for the lack of progress is that few basic studies have been made to provide the underlining foundation which would allow educated decisions to be made concerning the most likely directions for success. This work explores several basic features of the chemistry of  $\text{K}_2\text{FeO}_4$  in an attempt to understand the main mechanism by which the ion oxidizes other substances. Obviously there probably are many modes of reaction but the hope is that the majority will fall into some pattern. So one main question has to do with whether Fe(VI) usually goes to Fe(IV) in the primary step and then Fe(IV) rapidly in one or more step goes to Fe(III). This is not an easy question to answer and one which this study does not answer. It does however, provide some additional information which must be considered in any discussion of the nature of the primary oxidation step.

The nature of the water solution decomposition is important mechanistically and also practically. The product must be stable to

transportation and storage and must remain in solution long enough to react with substances to be removed or converted. This has been in doubt since the first days of  $\text{FeO}_4^{2-}$  discovery and even now the rates are not reproducible from laboratory to laboratory or even with one laboratory. Coupled with this is the disagreement in the rate law for the "simple" decomposition. These studies concentrate on the catalytic effect of some foreign substances and on the product when coordinating agents are not present. It is now clear I think that kinetics will not shed any new light on the nature of the water oxidation. It is so subject to the presence of trace ions in the water, the  $\text{K}_2\text{FeO}_4$ , and the buffer or complexing agent that it is a point best bypassed at this stage to be returned to at a later date. In this work we had as an objective to establish a direct link between the rate and the appearance of semi-collodial  $\text{Fe}(\text{OH})^-$  gels, the prevention of this rate enhancement by  $\text{IO}_4^-$  (which is well known) and the establishment of the nature and strength of the complex formed between  $\text{Fe}(\text{III})$  and  $\text{IO}_4^-$ . An exciting prospect for increasing the stability of  $\text{K}_2\text{FeO}_4$  and perhaps other salts of it we suggested some time ago was to be found in forming a mixed solid solution with an inert, cheap salt which was isomorphous with  $\text{K}_2\text{FeO}_4$ . So we did the crystal structure of  $\text{K}_2\text{FeO}_4$  and showed it to be the same structure as  $\text{K}_2\text{SO}_4$  and  $\text{K}_2\text{CrO}_4$ . So one main objective was to see if a range of solid solutions could be formed and to see if they would have good practical properties such as stability in a humid atmosphere.

A final objective was to attempt to find a means of enhancing the rate of oxidation of certain substrates such as  $\text{NH}_3$  when they are at low concentration.  $\text{NH}_3$  is a good example because when dilute, it is quite

slow to react with  $\text{FeO}_4^{2-}$ . One reason for this may be the mis-match of electrons 3-2 for relatively stable products. A way around this is to aggregate  $3e^-$  (oxidizing agent) by coordinating  $\text{FeO}_4^{2-}$  with an oxidized metal ion which is capable of  $1e^-$  oxidation. So an effort was made to determine if  $\text{FeO}_4^{2-}$  will coordinate and if, when coordinated, it would be more reactive toward  $\text{NH}_3$  or  $\text{NH}_4^+$  when in dilute aqueous solution.

So the objectives were to add to our understanding of

- a. the mechanistic nature of the primary oxidative process.
- b. the catalytic effect of colloidal-solid Fe(III) oligomers and the moderating effect of  $\text{IO}_4^-$ .
- c. the formation of solid solutions of  $\text{K}_2\text{FeO}_4$  and the effect on stability.
- d. the manner in which foreign metal ions affect the rate of water oxidation and substrate reaction.

#### REVIEW OF EXPERIMENTAL METHODS

$\text{K}_2\text{FeO}_4$  was prepared by  $\text{OCl}^-$  oxidation of purified  $\text{Fe}(\text{OH})_3$ ,<sup>1</sup> utilizing purified DMSO. The iron was especially low in Mn a common serious contaminant. It was analyzed by Cr(III) oxidation and was found to be 95-98% pure.<sup>2</sup> No decomposition of the solid occurred when kept over anhydrous  $\text{CaSO}_4$ .

For the decomposition experiments teflon or polyethylene flasks were used which had been "pre-oxidized" with  $\text{FeO}_4^{2-}$ . Distilled water was de-ionized and treated with  $\text{FeO}_4^{2-}$  which was allowed to decompose. The  $\text{Fe}(\text{OH})_3$  was removed by settling or centrifugation. Salts such as  $\text{KNO}_3$ ,  $\text{PO}_4^{3-}$ ,  $\text{BO}_3^{3-}$  were also treated with  $\text{FeO}_4^{2-}$  to remove reductants before use. The  $\text{FeO}_4^{2-}$  concentration was usually determined spectrally

at 5100A(1100).<sup>3</sup> No changes in the absorption maximum were found at any time which could be attributed to lower oxidation states of iron except Fe(III).  $\text{CH}_2\text{O}$ ,  $\text{HCOO}^-$  could not be easily purified and were used as obtained while  $\text{KNO}_2$  was twice recrystallized.

Kinetics of self-decomposition or reaction were followed on a temperature controlled spectrophotometer and the data treated by a nonlinear least squares program which utilized weighted values for the absorbance values, usually  $\pm 0.002A$ . Reactions were followed for at least two half-lives.

The x-ray data on single crystals was obtained on a Nonius diffractometer-PDP controlled and the structures solved utilizing standard CAD4 programs. Semi-spherical crystals of approximately 0.2 mm diameter were selected, the unit cell determined with 25 standard reflections and Patterson interpretation used for the initial phasing. All atoms were located utilizing difference maps and in the later stages anisotropic parameters were applied to the heavy atoms. Most hydrogens were not located due to the complexity of the structure and so the oxidation state of the iron was not known. This was determined by Mossbauer spectra which established the III state. The formula  $\text{K}_6\text{Na}_2[\text{Fe}_4\text{I}_3\text{O}_{24}\text{H}_7] \cdot 14\text{H}_2\text{O}$  was established with  $a=b=13.070(2)$ ,  $c=18.470(2)A$ ,  $v=2732.4(5)A^3$ ,  $z=3$ ,  $D_x=2.785(s)$  and  $D_o=2.75(3) \text{ Mgm}^{-3}$  and the space group R32. The final R value was 0.038 with the largest shift to error ratio in the final stage of refinement being 0.13.

The  $^{18}\text{O}$  measurements were made on a Nuclide RMS mass-spectrometer. In most experiments the  $^{18}\text{O}$  was contained in the  $\text{FeO}_4^{2-}$  for the reaction  $\text{FeO}_4^{2-} + \text{NO}_2^- \rightarrow \text{NO}_3^- + \text{Fe(III)}$  but in other cases only the  $\text{H}_2\text{O}$  was enriched in  $^{18}\text{O}$ . The reaction was carried out at pH 10.0-10.5 utilizing

0.5M KF, 0.2 Na<sub>2</sub>CO<sub>3</sub>, 0.15M NaH<sub>2</sub>PO<sub>4</sub> and 0.05M KOH. The CO<sub>3</sub><sup>-2</sup> and PO<sub>4</sub><sup>3-</sup> were removed with PbCl<sub>2</sub> and the NH<sub>4</sub>NO<sub>3</sub> isolated with NH<sub>4</sub>Cl. Thermal decomposition on Pt gave N<sub>2</sub>O which was purified by VPC and analyzed for the 46/44+45 ratio. The solvent FeO<sub>4</sub><sup>2-</sup> and NO<sub>2</sub><sup>-</sup> <sup>18</sup>O content was determined by conversion to CO<sub>2</sub> in a sealed tube, purification by UPC and <sup>18</sup>O analysis of (46/44+45) mass ratio. Standards showed less than 2% exchange during the collection-purification-analysis process.

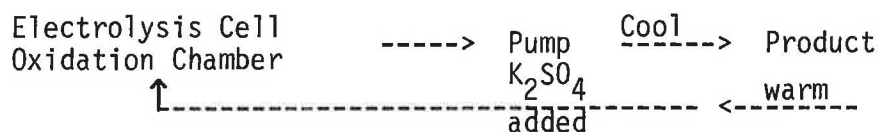
The solid solution studies<sup>4</sup> were made in H<sub>2</sub>O containing 0.001M IO<sub>4</sub><sup>-</sup>. Mixtures of K<sub>2</sub>FeO<sub>4</sub> + K<sub>2</sub>SO<sub>4</sub> or K<sub>2</sub>FeO<sub>4</sub> + K<sub>2</sub>CrO<sub>4</sub> were added to a known amount of H<sub>2</sub>O which was less than that required for complete solution. After equilibration the solution was removed and analyzed for FeO<sub>4</sub><sup>2-</sup>. An alternate method consisted of preparing a saturated solution using known amounts of the salts, adding KOH which caused crystallization and analyzing both solution and solid. From these values the FeO<sub>4</sub><sup>2-</sup>/CrO<sub>4</sub><sup>2-</sup> or FeO<sub>4</sub><sup>2-</sup>/SO<sub>4</sub><sup>2-</sup> ratio in the solid and in solution was calculated for various total mole ratio's. Changes in the KOH concentration had no observable effect on the ratio's obtained.

Preparation of solid solution of K<sub>2</sub>FeO<sub>4</sub>/K<sub>2</sub>SO<sub>4</sub> were made by cooling solution mixtures of the two salts. The crystals were washed with MeOH and carefully dried. To test their stability they were placed in a vessel containing saturated NaOAc in contact with solid NaOAc at 20°C. The relative humidity is 76% under these conditions. At measured intervals samples were analyzed for FeO<sub>4</sub><sup>2-</sup> content.

Magnetic measurements<sup>5</sup> were made by the Gouy method over a series of temperatures on the ground solid obtained from single crystals.

The attempted continuous preparation of solid solution of K<sub>2</sub>FeO<sub>4</sub>-K<sub>2</sub>SO<sub>4</sub> were carried out in a plastic-glass apparatus with a

metering pump. Solid Fe electrodes were used, 20% KOH solution saturated with  $K_2SO_4$  and containing 0.01M  $KIO_4$ . The scheme was



After a period of four hours with 4 amps of current the product (~30% Ferrate) began depositing as crystals. It contained only a trace of insoluble rust. The electrical efficiency was calculated to be 35% based on the total production but only a fraction of that was obtained as a solid product. In many ties, rust began to form in the cell causing decomposition of the  $FeO_4^{2-}$  and the trial had to be stopped.

The measurement of the formation of  $Fe(o\text{phen})_3^{2+}$  was done using the oxidation of  $CH_2O$ . An excess of  $FeO_4^{2-}$  was used and the solution was essentially saturated with ophen. The pH was 9.0 with phosphate ion and in many cases some  $ClO_4^-$  was present. The  $[Fe(o\text{phen})_3](ClO_4)_2$  was extracted into 0-dichlorobenzene after the addition of  $NaClO_4$ . After drying the absorbance was measured at 5080A. In some cases Fe(III) was substituted for  $FeO_4^{2-}$ . The results are reported as moles  $Fe(o\text{phen})_3^{+2}$ /mole of  $CH_2O$  consumed.

Reaction of  $NH_3$  in the presence of metal ions was conducted using various complexes and by having the metal ion present with  $NH_3$  at the time of  $FeO_4^{2-}$  addition. In some cases the  $NH_3$  concentration was determined utilizing a specific electrode while in other case evidence for enhanced reaction was suggested by the rapid loss of  $FeO_4^{2-}$  color.



## PRINCIPAL FINDINGS AND THEIR SIGNIFICANCE

A. We reinvestigated the decomposition of  $\text{FeO}_4^{2-}$  in water and came to the following conclusions:

1. The rate generally follows a rate law which has at least one term which is greater than 1 in  $[\text{FeO}_4^{2-}]$ . While there is a slightly better fit to the data with 1st and 2nd order terms the 3/2 order is almost as good as within the error and considering the better fit one should get with two terms versus one, we conclude that one cannot mechanistically substantiate either based on this data. A better criteria might be whether the first order constant is constant with varying starting  $[\text{FeO}_4^{2-}]$  concentrations. From our data it is clear that the error in  $k_1$  is large, not reasonably constant and subject to the solution conditions. The presence of complexing agents does not alter these conclusions.

2. Impurities introduced in the water, in the  $\text{K}_2\text{FeO}_4$ , in the buffers and anti precipitants have a large effect on the rate, especially  $k_1$  and so all reagents and solvents used have to be pre-oxidized and freed from impurity metal ions.

3. The buffer (Borate, phosphate, fluoride, periodate) or anti-precipitant does not have a large effect on the rates and thus interaction directly with  $\text{FeO}_4^{2-}$  is not very important.

4. The onset of cloudyness or precipitation is very effective in promoting decomposition to  $\text{O}_2$ . Periodate ion is extremely effective in preventing precipitation and thus stabilizes the system. The complex involved is not known but in this study we have isolated a complex which has the same visible spectrum as solutions resulting from the decomposition of  $\text{FeO}_4^{2-}$  in  $\text{IO}_4^-$ . Its structure is reported later. A

significant experiment, which was very repeatable, was to place together  $\text{FeO}_4^{2-}$  and  $\text{IO}_4^-$  in dilute base with the  $\text{FeO}_4^{2-}$  in molar excess.

Decomposition proceeds slowly and normally according to 1st order kinetics (at these low  $\text{FeO}_4^{2-}$  concentrations) until all of the  $\text{IO}_4^-$  is used up by complexation as calculated from the loss of  $\text{FeO}_4^{2-}$  and the 4/3 (Fe/I) ratio as given by the formula of the complex;  $[\text{Fe}_4\text{I}_3\text{O}_{24}\text{H}_7]^{8-}$ . When this point is reached the remainder of the  $\text{FeO}_4^{2-}$  is lost very rapidly and soon after the point cloudiness is apparent. We were not able to confirm the observation that there was significance to a 2/1 I/Fe ratio<sup>6</sup> with regard to stability. These data establish that as long as there is sufficient periodate ion in solution to complex the Fe(III) the  $\text{FeO}_4^{2-}$  is stabilized. The formation constant for the complex must be very large since the break occurs sharply and at the exact equivalence point.

5. There may be a tendency for  $\text{FeO}_4^{2-}$  to associate with other oxy anions through oxygen bridging and perhaps even to itself (inspite of the charge). Note later that the kinetics of the  $\text{NO}_2^-$ - $\text{FeO}_4^{2-}$  reaction do not extrapolate to the expected value at  $[\text{NO}_2^-] = 0$ . This suggests an equilibrium association preliminary to reaction.

B. The kinetics of reaction of  $\text{CH}_2\text{O}$  and  $\text{HCOO}^-$  have been followed and show first order behavior with respect to  $\text{FeO}_4^{2-}$  and substrate. The first order disappearance graph of  $\text{FeO}_4^{2-}$  with excess substrate is not linear, bending in the direction suggesting a second order term in  $\text{FeO}_4^{2-}$ . Attempts to decide if this second order  $\text{FeO}_4^{2-}$  term also involved substrate was inconclusive. So none of our data can differentiate between the rate terms

$$\begin{array}{l} k(\text{FeO}_4^{2-})(\text{S}) + k'[\text{FeO}_4^{2-}]^2[\text{S}] \\ \text{or} \quad k[\text{FeO}_4^{2-}][\text{S}] + k'[\text{Fe}_2\text{O}_4^{-2}]^2 \end{array}$$

The other factors measured by others are confirmed ie. only small differences between substrates, small increases with increasing ionic strength, large rate increases with acidity. We are impressed by the fact that the rate is so uniform for substrates which are uncharged organic molecules. This may suggest that the main change in getting to the activated state may be limited to the ferrate ion itself. Just for consideration it might be  $\text{FeO}_4^{2-} \rightarrow \text{FeO}_3 + \text{O}^{2-}$  where the  $\text{O}^{2-}$  is intimately associated with the solvent. The 2nd order term might be considered " $[\text{O}_3\text{Fe-O-FeO}_3]^{2-}$ ".

A test of this is to determine the amount of  $\text{O}_2$  released while substrate was also reacting. Our results on this are not very conclusive nor accurate. The  $\text{O}_2$  was determined by M.S.<sup>7</sup> and we also compared loss of substrate vs loss of Ferrate. In both cases, under these conditions employed, the amount of self-decomposition was 30% or less of what would have been predicted from the rates of self-decomposition and reaction with substrate. Thus we tentatively conclude that both reactions ie self-decomposition and reaction with substrate are dependent on some intermediate or activated state and that state can either react with water or with the other substrate.

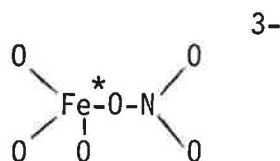
With  $\text{NO}_2^-$  in excess the reaction follows the rate law  $[\text{NO}_2^-][k[\text{FeO}_4^{2-}] + k'[\text{FeO}_4^{2-}]^2]$  but as stated earlier the second term may not have  $\text{NO}_2^-$  in it. The product is solely  $\text{NO}_3^-$  and little if any oxygen is produced. The data below are representative

$[\text{NO}_2^-]$	$10^3 k_1 (\text{s}^{-1})$	$k_2 (\text{m}^{-1} \text{s}^{-1})$
0	.062(1)	.0035(20)
0.10	4.08(4)	10.2(1)
0.20	5.25(6)	14.2(2)
0.30	7.51(8)	16.0(3)
0.40	9.79(9)	18.8(3)
0.50	13.1(2)	21.5(4)

Clearly it is first order in  $\text{NO}_2^-$  but there is an intercept probably caused by an equilibrium forming  $\text{O}_3\text{Fe-O-NO}_2^{3-}$ .

The  $^{18}\text{O}$  results are quite clear that greater than 2 2/3 of the three oxygens of  $\text{NO}_3^-$  come from  $\text{NO}_2^-$  and  $\text{FeO}_4^{2-}$ . Since it is known that  $\text{FeO}_4^{2-}$  exchanges its oxygens at a rate only slightly slower than it reacts with  $\text{NO}_2^-$  one would expect less than three. More important however is the fact that Fe(IV) is not expected to transfer any oxygen to  $\text{NO}_2^-$  because of its very fast exchange rate. Although it is likely that the second order reaction with  $\text{NO}_2^-$  may be very fast also.<sup>8,9</sup>

Thus the calculated value for oxygen transfer to  $\text{NO}_3^-$  is 2 2/3 if the first step transfers quantitatively and the last step(s) not at all. We conclude that the activated complex is



which breaks up into  $\text{NO}_3^-$  and  $\text{FeO}_3\text{aq}^{2-}$ . The latter ion rearranges before reacting with another  $\text{NO}_2^-$ .

#### $^{18}\text{O}$ Transfer Results

<u>Sample</u>	<u>Solvent (%)</u>	<u><math>\text{N}_2\text{O}(\%)</math></u>	<u><math>\text{NO}_3^-(\%)^a</math></u>	<u>#O Trans.</u>
1	.319	.219	.242	.67
2	.319	.219	.242	.67
3	.319	.221	.248	.61
4	.545	.242	.298	.72
5	.545	.247	.313	.68

The structures of  $\text{K}_2\text{FeO}_4$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{K}_2\text{CrO}_4$ ,  $\text{K}_2\text{MnO}_4$  are all the same with small variances in unit cell dimensions and atom-atom distances and

angles. It seemed reasonable that they would form solid solutions of almost any composition. Such was found to be the case for the two systems investigated  $K_2FeO_4$  with  $K_2SO_4$  and with  $K_2CrO_4$ . When solutions of the salts are evaporated the crystals have a composition related to but different from that in solution. When water or  $KOH-H_2O$  is used as the solvent the solid contains a lower  $FeO_4^{2-}/SO_4^{2-}$  ratio compared to the solution. It was thought that these solid-solutions would be more stable than the pure compound and might provide a way of preparing a more useful product. Table (1) gives the relationship between solution and solid composition at equilibrium. Note that there are no discontinuities. The crystals obtained are pink to black as one goes toward the highest Fe concentration. An excellent feature is that the mixed crystals seem to form more easily and more uniformly than pure  $K_2FeO_4$  and large size-uniform size and color crystals are easier to obtain in the middle of the composition range. Because of the uniform size the the lower solubility the crystals are more easily washed and dried. I think this contributes to their stability. If one watches a batch of  $K_2FeO_4$  crystals turning brown individual crystals react, a few at a time. Impurities on the surface especially  $H_2O$  and  $KOH$  contribute markedly to the start of decomposition of an individual crystal. The mixed salt has a cleaner surface and thus is not as affected by this process. Table (2) contains some data on the decomposition of these mixed salts in a high humidity.<sup>10</sup> As can be easily seen, the solid solutions are much more stable and it appears that around .50 mole fraction gives good protection and could be easily strived for on a industrial scale. If a trace of  $IO_4^-$  were incorporated into the crystallization liquid the stability might be even greater.<sup>11</sup> It might be advantageous to look at the sodium system. It probably is more

complicated as evidenced by the many compositions of  $\text{Na}_2\text{SO}_4$  hydrates. I don't think anyone knows at the moment the nature of  $\text{Na}_2\text{FeO}_4$  obtained from water or how or if it would form solid solutions with the  $\text{SO}_4^{2-}$  analogue. This would have the advantage of cheapness however and could be valuable if other factors did not complicate the chemistry.

Knowing that one can crystallize solid solutions of  $\text{K}_2\text{SO}_4$ - $\text{K}_2\text{FeO}_4$  suggests that one could partially alleviate the decomposition problem of high concentrations of  $\text{FeO}_4^{2-}$  by removing it as formed as the double salt. We attempted to test the feasibility of a continuous process in which solution is slowly circulated past a electrolysis cell which runs best at  $\sim 45^\circ$  and the  $(\text{FeO}_4\text{SO}_4)$  salt is partially removed as a crystalline material by cooling to a lower temperature. We achieved about 30% conversion (the  $\text{H}_2$  and  $\text{O}_2$  could be sold) in the initial stages of conversion and did obtain a small amount of the solid-solution but ran into problems with the formation of rust which clogged the circulation tubes. Frankly it was a partial success and I think could be developed into a commercial process with better experiments. It is obvious that considerable advantage would be present if one had to supply only electricity,  $\text{KOH}$ , iron and  $\text{K}_2\text{SO}_4$  to give a stable  $\text{K}_2\text{FeO}_4$ - $\text{K}_2\text{SO}_4$  product.

TABLE 1

## Phase Diagram Data

Ave. mole fraction $K_2FeO_4^a$	Mole fraction $K_2FeO_4^b$
0.10±2	trace
0.21±2	0.012±1 <sup>c</sup>
0.38±2	0.076±5 <sup>c</sup>
0.45±2	0.057±5 <sup>d</sup>
0.52±2	0.084±5 <sup>d</sup>
0.59±2	0.196±10 <sup>c</sup>
0.63±2	0.183±10 <sup>c</sup>
0.72±2	0.395±10 <sup>c</sup>
0.74±2	0.397±10 <sup>c</sup>
0.83±2	0.643±10 <sup>c</sup>
0.85±2	0.668±10 <sup>d</sup>

a) Average mole fraction in solution.

b) Mole fraction in solid.

c) Precipitated from solution by addition of sat. KOH and cooling.

d) Precipitated by cooling only.

Note: All errors are estimated based upon the procedure.

TABLE 2

Decomposition of Ferrate-Sulfate Crystals at 76% Rel. Hum.

Temp. = 25°C

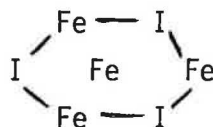
Mass % $K_2FeO_4$	Time for Complete Dec. (days)
98.0	.50 <sup>a</sup>
82.8	.88 <sup>a</sup>
60.9	-- <sup>b</sup>
51.9	-- <sup>b</sup>
26.7	ND <sup>c</sup>
20.3	ND <sup>c</sup>
20.1	ND <sup>c</sup>
18.6	ND <sup>c</sup>
9.4	ND <sup>c</sup>
7.6	ND <sup>c</sup>
2.0	ND <sup>c</sup>

- (a) Crystals became moist looking after approx. 1 hr. but no decomposition noticeable until about 2 hrs. from complete decomposition.
- (b) Approx. 10% dec. after 2 days but no additional decomposition during the next 19 days.
- (c) No decomposition after 21 days.



The X-ray structure of  $K_2FeO_4$  shows the ion to be tetrahedral with only minor distortion due to lattice deformation. The average M-O distance is 1.656(b)Å while for  $K_2CrO_4$  it is 1.659(4) and for  $K_2MnO_4$  1.660(8). The IR for the M-O stretch is consistent with a slight lengthening of the Fe-O bond. Oxygen exchange rate comparisons between the oxyanions and solvent do not follow any explainable pattern.

We were fortunate that the crystallizing solutions for the complex between Fe(III) and  $IO_4^-$  contained both  $Na^+$  and  $K^+$  because otherwise no crystalline material is obtained. The structure was difficult to resolve however and hampered by the high symmetry and the small number of independent data which could be measured. The structure of the ion is complex and unique. It consists of a hexagon of heavy atoms alternating Fe, I with the fourth Fe in the center



The ring iron and iodine atoms are octahedrally bonded together through bridging oxygens and the central iron bonded to the ring via 6 capping oxygens. There is considerable disorder in the system whereby the iron and iodine centers are transposed.<sup>12</sup> The necessity of having both  $Na^+$  and  $K^+$  in the structure is related to the close distance of approach 3.46Å which is too short for a  $K^+ - K^+$  interaction.

The Mossbauer spectra, obtained at 78°K show two independent sites. These are in the ratio 3 to 1 consistent with the X-ray structure. The isomer shift values of 0.47(2) and 0.45(2) mm/sec and quadrupole splitting values of 0.95(2) and 0.49(2) mm/sec clearly indicate that the oxidation state in both types is +3.

The magnetic susceptibility was measured from 78 to 296°A, shows after diamagnetic corrections,  $\mu_{\text{eff}}$  to be 4.6(1) with no field or temperature dependence. The moment is much lower than 5.92 BM expected for high spin Fe+3 however it is clearly not low spin, 1.7BM.

The importance of identifying the complex lies in showing its extreme stability in basic media which allows  $\text{IO}_4^-$  to react almost quantitatively with Fe(III) and prevent hydroxo complexes from precipitating. Why these hydroxo-Fe(III) species behave as a catalyst is not understood. A moments thought however suggests that electron transfer from the polymer to associated  $\text{FeO}_4^{2-}$  would generate Fe(V) or Fe(IV) with the electron diffused over many metal ion sites. This would allow  $1e^-$  reactions with  $\text{H}_2\text{O}$  rather than the  $2e^-$  probably required by  $\text{FeO}_4^{2-}$ .

The rather facile reaction of  $\text{FeO}_4^{2-}$  with  $\text{H}_2\text{O}_2$ ,  $\text{NO}_2^-$  and  $\text{SO}_3^{2-}$  coupled with 0 transfer in the last two cases suggests that ferrate ion prefers to react by a 2 electron process. What happens to the Fe(IV) after that is not at all understood. Clearly it would seem that it would easily go to Fe(III). However, there is some evidence that Fe(II) is produced in some reactions. The main evidence of this is the formation of  $[\text{Fe}(\text{open})_3]^{+2}$  during reduction of  $\text{FeO}_4^{2-}$  with various substrates. Since this is a rather important concept we expended considerable effort to confirm or deny this observation. In summary of our results, we did find that  $[\text{Fe}(\text{open})_3]^{+2}$  is always formed when  $\text{CH}_2\text{O}$  reacts with  $\text{FeO}_4^{2-}$  with excess  $\text{FeO}_4^{2-}$ . The amounts are small: yields of .06/mole  $\text{H}_2\text{CO}$  or less. In the absence of  $\text{FeO}_4^{2-}$  or of Fe(III) about 1/3 to 1/4 of that amount is found. Since  $\text{FeO}_4^{2-}$  reacts rapidly with Fe(II), if it is formed it must compete with  $\text{FeO}_4^{2-}$  and open for

reaction. (Any  $[\text{Fe}(\text{o phen})_3]^{+3}$  formed would be converted to the +2 state in our experiments). We conclude that by some means Fe(II) is being produced most likely by  $2e^-$  reduction of Fe(IV) but that the importance of this reaction in the usual reduction of  $\text{FeO}_4^{2-}$  is not known. For the present it is best to say that we do not have any significant evidence concerning the fate of the Fe(IV) generated by  $2e^-$  reduction of  $\text{FeO}_4^{2-}$ .

Our attempts to catalyze the reaction of  $\text{FeO}_4^{2-}$  with  $\text{NH}_3$  are not very far along. We have investigated the reaction of about twenty complexes of Ni, Cu, Ag, Mn, Os, Mo, V all containing nitrogen or amine ligands. Almost invariably reaction occurs much more rapidly than with free  $\text{NH}_3$  but this may be a concentration effect. One product always obtained is  $\text{N}_2$  but in many cases the complex also catalyzed the decomposition of ferrate ion and a major quantity of  $\text{O}_2$  was obtained. In a few cases reaction was slow such as with  $[\text{Co}(\text{en})_3](\text{NO}_3)_2$ . Attempts to prepare solid salts containing a replaceable  $\text{H}_2\text{O}$  such as  $[\text{Co}(\text{NH}_3)_5\text{OH}_2](\text{FeO}_4)\text{Cl}$  were unsuccessful because the  $\text{NH}_3$  was oxidized even in basic media. Co(II) as the perchlorate does form a substance which is probably  $[\text{Co}(\text{H}_2\text{O})_5\text{OFeO}_3]$ . It probably can be isolated in a pure form but so far we have not been able to do so because of loss of  $\text{O}_2$ . Also, salts which were somewhat more stable included  $[\text{Co}(\text{en})_2(\text{NH}_3)\text{Cl}]\text{FeO}_4$  and  $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{FeO}_4$  but of course these cannot coordinate  $\text{FeO}_4^{2-}$  in order to make it more stable.

From these observations it appears that when  $\text{NH}_3$  is coordinated to a metal ion it often is more susceptible to oxidation by  $\text{FeO}_4^{2-}$ . Perhaps this can be used to advantage in the sense that for instance, the presence of  $\text{Mn}^{2+}$  may cause the facile oxidation of  $\text{NH}_3$ . It is expected that Fe(VI) will rapidly oxidize Mn(II) to Mn(IV) which then

can oxidize  $\text{NH}_3$  which would be coordinated to it. A more likely example might be the  $\text{Ag}^+ \rightarrow \text{Ag}^{+3}$  couple. In preliminary runs we have tested this hypothesis in that we have monitored solutions containing 3ppm  $\text{NH}_3$  and  $10^{-3}$  metal ion for  $\text{NH}_3$  using a specific ion electrode. The addition of  $\text{FeO}_4^{2-}$  does lower the  $\text{NH}_3$  concentration more rapidly than in the absence of at least one metal ion,  $\text{Ag}^+$ . No changes were observed with  $\text{Mn}^{2+}$  and  $\text{Cu}^{2+}$ . These experiments are promising and are in progress.

LITERATURE CITED:

1. G.W. Thompson, L.T. Ockerman, J.M. Schreyer, J. Am. Chem. Soc. 1951, 73, 1379.
2. J.M. Schreyer, G.W. Thompson, L.T. Ockerman, Anal. Chem., 1950, 22, 1426.
3. H. Goff, R. Kent Murmann, J. Am. Chem. Soc. 1971, 93, 5998.
4. Martin Hoppe, M.S. Thesis, University of Missouri.
5. Measurements were carried out at the University of Missouri, Rolla Mo, Courtesy of Dr. Gary Long.
6. This is suggested several places in the literature in a rather casual manner. We could find no solid evidence for such an observation.
7. Mixtures of N<sub>2</sub> and O<sub>2</sub> were obtained. The N<sub>2</sub> used as a carrier gas. Std mixtures were compared and Toepler pumps used to collect all gases.
8. J.D. Rush, B.H.J. Bielski, J. Am. Chem. Soc., 1986, 108, 523.
9. B.H.J. Bielski, M.J. Thomas-Communication.
10. This procedure is probably not too close to environmental conditions since the temperature was held constant. The raising and lowering of the temperature would facilitate condensation on the crystal surface were impurities lay. This would be expected to cause premature decomposition.
11. Using a Cu-IO<sub>4</sub><sup>-</sup> complex as has been suggested in a patent would have no advantage here or with other types of samples.
12. A list of atom parameters, structure factors, B's for the structure can be obtained by request.