

AN ABSTRACT OF THE THESIS OF

-----Charles Boyd-----for the--MS--in--Inorganic Chemistry
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Title--Adsorbtion by strontium salts of traces of iron from
-----caustic soda solutions.-----

Abstract Approved: Redacted for privacy
(Major Professor)

Caustic soda solutions used in the Rayon industry for the production of viscose must be comparatively free of iron impurity. The presence of this impurity affects the quality of the thread produced.

In industrial practice, the removal of the iron impurity from the caustic soda solution is accomplished by agitating finely ground Strontium minerals in the solution. It is found that when the strontium mineral settles from the caustic soda solution, the iron content of the solution is markedly decreased.

It was the purpose of this work to study the mechanism by which finely ground Strontium minerals remove iron impurities from caustic soda solutions.

It was found that the iron impurity in commercial caustic occurs in the form of a ferrate ion, FeO_4^{2-} with possibly some FeO_3^- and $\text{Fe}_2\text{O}_4^{2-}$ ions.

The removal of this impurity is due to the adsorbtion of these ions upon the finely ground strontium mineral. At 30°C strontium sulfate is a better adsorbent than strontium carbonate. However, at higher temperatures, strontium carbonate approaches strontium sulfate in adsorbative capacity. Also, increase in temperature increases the amount of iron impurity adsorbed from caustic soda solution by a given weight of strontium mineral.

ADSORPTION BY STRONTIUM SALTS OF TRACES
OF IRON FROM CAUSTIC SODA SOLUTIONS

by

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ADSORPTION BY STRONTIUM SALTS OF TRACES OF IRON FROM CAUSTIC SODA SOLUTIONS

Introduction

Crude caustic soda solutions as produced by electro-chemical means contain iron compounds as an impurity. This impurity is thought to be due to iron compounds occurring in the raw materials used in the electrolyzing process and to the use of iron vessels in the subsequent evaporation.

In the rayon industry, caustic soda solutions are used for the production of the viscose solution. It has been shown that the viscosity of the viscose is markedly changed by the presence of impurities, particularly metallic compounds, thus affecting the size and quality of the thread produced. Therefore, it is important that the iron impurity be removed from the caustic soda used in the manufacturing of rayon.

In some industrial processes (4) this removal is accomplished by agitating finely ground strontium sulfate and strontium carbonate ores in a fifty percent solution of the raw caustic soda. Upon the settling of the ore through the solution, it is found that the iron impurity has been concentrated in the ore and that the caustic soda solution is comparatively low in iron concentration.

Although strontium ores have been employed in

purifying caustic soda solutions for a number of years, little is known concerning the mechanism involved. It is the purpose of this work to study the form in which the iron occurs as an impurity in commercial caustic soda, to refine the method of analysis for iron in minute amounts in caustic soda, to investigate the nature of the mechanism by which iron impurities are removed from caustic soda solutions by strontium ores, and to study the factors influencing this removal.

Occurrence of Iron in Crude Caustic Soda

Several mechanisms may be postulated for the removal of iron impurities from caustic soda by strontium ores depending upon the form in which the iron occurs as the impurity.

If it is present as a hydrated iron oxide suspended in the solution, the removal may be attributed to an adsorptive process or to a mechanical sweeping by the ore particles settling through the solution. However, if it is present in some soluble form such as a ferrate or ferrite ion, the possibility of mechanical sweeping may be disregarded.

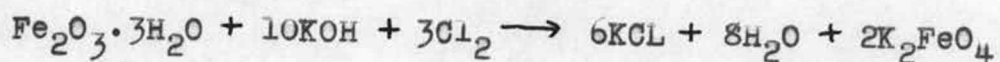
Therefore, a knowledge of the form in which the iron occurs in the crude caustic soda is pertinent to the problem of its removal.

Before purification, the crude caustic solution is highly colored, usually purple. Earlier researchers investigating the higher valence forms of iron, describe the violet and purple solutions obtained when iron salts in concentrated alkali were treated with strong oxidizing agents. It was later explained that the coloration in these solutions was due to the formation of the ferrate ion (9). E. Fremy described the color of potassium ferrate in alkali solution as being red-violet (9).

A study of the methods for making potassium and sodium ferrates shows that the necessary conditions and oxidizing agents for the production of ferrate are also

present in the electrolytic cell used in preparing the caustic.

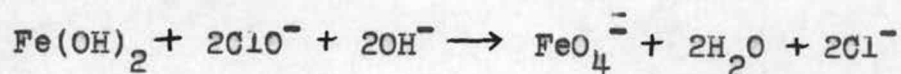
E. Fremy (9) obtained a solution of potassium ferrate by passing chlorine gas through a concentrated solution of potassium hydroxide in which ferric oxide was suspended. The reaction is given as:



C.A.O. Rosell also used chlorine (11) as the oxidizing agent in the production of alkali ferrate solutions. M. Muspratt and E.S. Smith found that sodium hypochlorite would produce the same results (10).

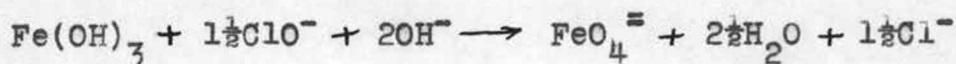
Free energy calculations show that the oxidation of ferric and ferrous hydroxide to ferrate ion by the hypochlorite ion is a feasible reaction. V.L. Bohannon and A.C. Robertson (1) have estimated that the standard free energy of formation at 25°C of the ferrate ion lies between -106,885 calories and -182,155 calories. In this paper the smaller value was used as a limiting case, and the standard free energy values for the other substances involved in the equations were taken from tables of accepted values (8).

For the reaction:



ΔF_{298}° was found to be equal to -73,695 calories.

For the reaction:



ΔF_{298}° was found to be equal to -40,335 calories.

These values indicate that the above equations would tend to be spontaneous.

F. Haber and W. Pick (5) observed that solutions of ferric and ferrous salts in concentrated alkali solution could be oxidized electrolytically to ferrates.

According to H.G. Elledge (3) the red color produced in certain hypochlorite bleaching solutions is not due to alkali ferrates but to permanganate. Accordingly, analyses were made on a sample of crude caustic soda solution obtained from the Pennsylvania Salt Manufacturing Company at Tacoma, Washington. No detectable amount of manganese was found to be present. Other substances such as molybdenum and chromium were analysed for and not detected. A faint trace of nickel was indicated by the dimethylglyoxime test, but the amount of precipitate was too small to be weighed. The iron content of this commercial sample was found to be approximately twenty parts per million.

Since the above facts suggest that the iron impurity in commercial caustic soda occurs in the form of a ferrate, it was decided to compare the color of a known solution of sodium ferrate with the color of the sample of the commercial caustic soda solution. Accordingly, a solution

of sodium ferrate was produced by passing chlorine gas through a suspension of hydrated ferric oxide in fifty percent, chemically pure sodium hydroxide solution. The temperature was maintained at forty degrees centigrade. The resulting purple colored solution had much the same appearance in color as the sample of crude caustic soda solution obtained from the Pennsylvania Salt Manufacturing Company.

In consideration of the above facts, it is believed that the iron impurity in commercial caustic soda solutions produced by the electrolysis of brine occurs in the form of the ferrate and, possibly, the ferrite ions.

It was found that a dilute solution of sodium ferrate in fifty percent sodium hydroxide turned from a purple to a green color upon exposure to sunlight. The same color transition was observed for the purple-colored commercial caustic soda solution.

Since sodium ferrite is described as being yellow-green in color (6), it is believed that the change in color of the sodium ferrate solution may be due to the photo chemical decomposition of the ferrate to the ferrite ion.

Analytical Procedure

The analyses for iron were run by a colorimetric method which depends upon the formation of the complex ion $\text{Fe}(\text{CNS})_6^{3-}$ in acid solution (7). The resulting solution is colored red. However, the color development is found to be easily inhibited by the presence of other compounds in the solution (12).

Since the analyses were to be run on sodium hydroxide solutions which had been acidified with hydrochloric acid, the effect of various amounts of sodium chloride upon the color development was studied. Table I shows the inhibition of color development by sodium chloride at different iron concentrations. The values in the main body of the table are the differences between the measured iron content and the actual iron content. Figure I shows these differences plotted against the square root of the ionic strengths of the solutions. It can be seen from these data that in any accurate determination of iron in caustic soda solutions employing this method, a correction for the salt effect is necessary. The analytical procedure employed is as follows:

A sample of the caustic soda to be analysed was weighed out, the size of the sample depending upon the iron concentration. For a fifty percent caustic soda solution having an iron content of fifteen parts per million, it was found that a six gram sample would produce the best

color for comparison. The sample was then neutralized with concentrated hydrochloric acid, and a three milliliter excess of the acid was added.

Table I. Inhibition of the $\text{Fe}(\text{CNS})\frac{2}{6}$ color development by various amounts of sodium chloride for different iron concentrations (values in the main body of the table are the differences between the actual iron concentration and the apparent iron concentration).

Actual Iron Concentration g/liter	Wt 50% Caustic Soda Sample			
	0.00g $\sqrt{\mu}=1.12$	1.00g $\sqrt{\mu}=1.32$	5.00g $\sqrt{\mu}=1.94$	10.00g $\sqrt{\mu}=2.50$
0.00300	0.00000	0.00016	0.00040	
0.00200	0.00000	0.00006	0.00021	0.00033
0.00100	0.00000	0.00002	0.00011	0.00016
0.00020	0.00000	0.00000	0.00000	0.00000

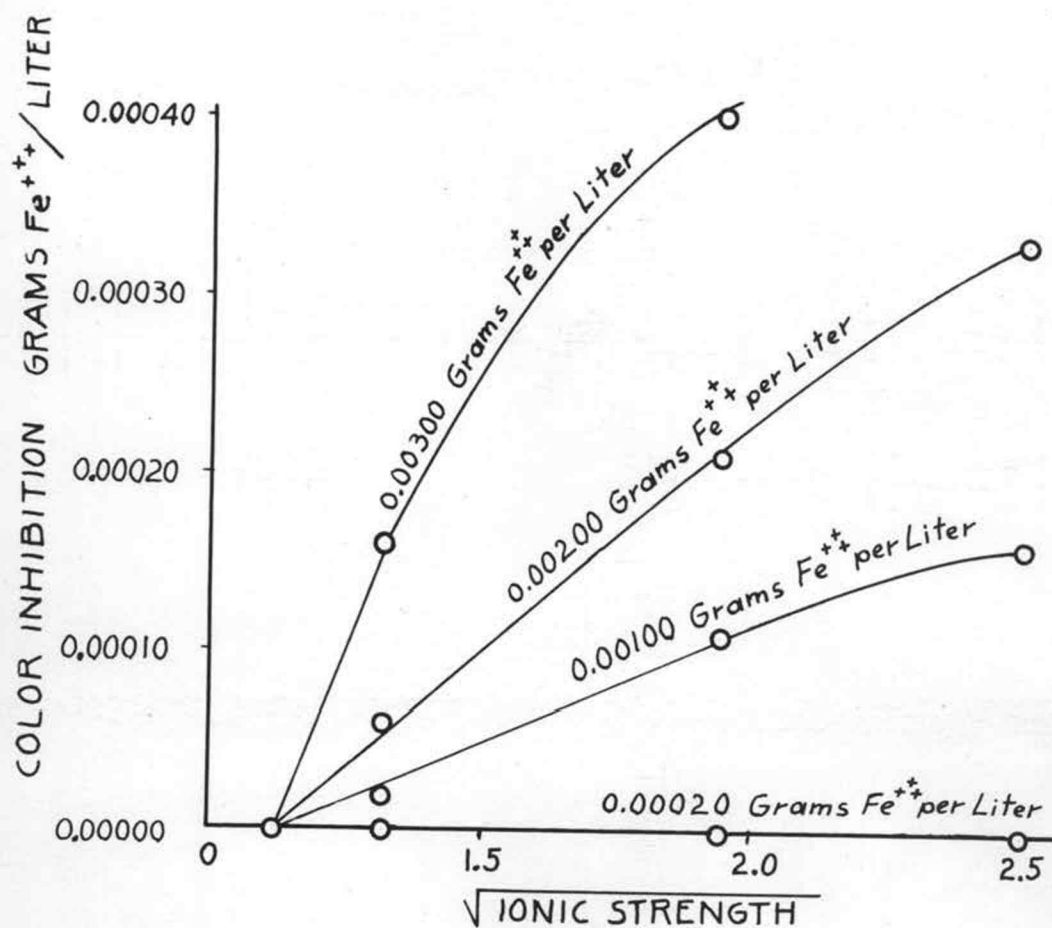


FIG. I

Inhibition of $\text{Fe}(\text{CNS})_6^{\equiv}$ Color Development by Sodium Chloride for Various Iron Concentrations.

Since it is necessary that the iron be present in the ferric state for color development, a few drops of tenth normal potassium permanganate solution were added. This step was omitted in the analyses on the crude caustic solutions since they contain a quantity of hypochlorite. The chlorine liberated by the hypochlorite upon acidification with hydrochloric acid was enough to insure that all the iron was present in the ferric state. It was found that it was unnecessary to remove the free chlorine formed as it had no apparent effect upon the $\text{Fe}(\text{CNS})\frac{2}{6}$ color formation.

The treated sample was then transferred to a colorimetric tube, and ten milliliters of a solution containing twenty grams of ammonium thiocyanate per liter were added. The solution was then diluted to a volume of fifty milliliters with distilled water.

Three milliliters of concentrated hydrochloric acid and ten milliliters of the ammonium thiocyanate solution were then added to a second colorimetric tube to be used as a standard.

In order to correct for the salt effect, a quantity of sodium chloride equivalent to that formed by the neutralization of the sample had to be added to the standard tube. This was accomplished by adding a measured volume of stock solution containing a known amount of sodium chloride. The volume added was calculated from the

weight of the sample.

An iron solution containing 0.00001 grams of ferric iron per milliliter was then added to the standard tube from a buret, and the volume of the solution was adjusted with distilled water until the color development and the levels of the solutions in both tubes were the same.

From the volume of standard iron solution required to give a color development in the standard tube equal to that in the sample tube, the iron concentration in the caustic soda solution may be calculated according to the equation:

$$\text{Fe concentration in ppm} = 10 \frac{\text{mls. Fe standard}}{\text{weight of sample in grams}}$$

With practice it was found that color differences corresponding to two tenths of a milliliter of iron standard solution could be detected. In a determination requiring ten milliliters of iron standard, this would give an accuracy of about two percent for the method.

Removal Of Iron Impurities From Caustic Soda Solutions

The investigation of the mechanism by which iron impurities are removed from caustic soda solutions by finely ground strontium sulfate and strontium carbonate ores was carried out in the following manner:

100 gram samples of the caustic soda solution having a predetermined iron concentration, were placed in four-ounce wide mouth bottles. These were then fitted with rubber stoppers and placed in a constant temperature bath to attain the temperature at which the removal was to be studied.

After the caustic soda samples had reached thermal equilibrium, weighed portions of the purifying agent to be studied were added, and the resulting mixture was agitated with a stirring motor to insure uniform dispersion.

The bottles were then allowed to remain in the constant temperature bath until the purifying agent had settled out of the caustic soda solution. This usually required a period of about one week.

After the purifying agent had settled out, the supernatant caustic soda solution was sampled and analysed according to the procedure outlined previously.

Runs were made in this fashion using the crude caustic soda solution obtained from the Pennsylvania Salt

Manufacturing Company and also using a fifty percent caustic soda solution in which ferrous hydroxide had been suspended.

The purifying agents studied were strontium sulfate and strontium carbonate which had been passed through a two hundred mesh sieve. The results of these runs are summarized in tables II and IV.

To test the adsorption theory, the data from these runs were plotted according to the Freundlich adsorption isotherm:

$$x/m = kc^n$$

or putting this in logarithmic form for plotting:

$$\log x/m = n \log c + K$$

Where x is the quantity of material adsorbed, m , the weight of the adsorbent, and c , the equilibrium concentration in the main body of the solution of the substance being adsorbed.

The results of these plots are given in figures II and III.

For purposes of comparison, additional runs using the sulfates and carbonates of calcium and barium as purifying agents were made, using the crude commercial caustic soda solution. The results of these runs are given in table VI.

Table II. Removal of Ferrate from Commercial Fifty Percent Sodium Hydroxide Solution by Strontium Sulfate and Strontium Carbonate at 30°C (in each case a 100 gram sample of sodium hydroxide solution was used).

Ore Used	Weight Ore	Original Iron Conc.	Final Iron Conc.	Decrease In Conc.
SrCO_3	0.100g	24.7 ppm	15.0 ppm	9.7 ppm
SrCO_3	0.200	24.7	8.0	16.7
SrCO_3	0.300	24.7	6.8	17.9
SrCO_3	0.500	24.7	2.61	22.1
SrCO_3	0.750	24.7	1.46	23.2
SrCO_3	1.000	24.7	1.17	23.5
SrSO_4	0.100	24.7	5.61	19.1
SrSO_4	0.200	19.0	3.84	14.2
SrSO_4	0.300	19.0	1.41	17.6
SrSO_4	0.500	19.0	0.73	18.3
SrSO_4	0.750	19.0	0.41	18.59
SrSO_4	1.000	19.0	0.40	18.6
blank	-----	17.7	17.7	00.0

Table III. Data for the Removal of Ferrate from Commercial Caustic Soda Solution by Strontium Sulfate and Strontium Carbonate at 30°C Calculated According to the Freundlich Adsorption Isotherm Equation.

SrCO_3 (through 200 mesh)

Decrease In Conc. x	Weight Ore m	x/m	log x/m	Final Iron Conc. c	log c
9.0 ppm	0.100g	90.0	1.954	15.0 ppm	1.176
16.7	0.200	83.5	1.922	8.0	0.903
17.9	0.300	59.7	1.776	6.8	0.833
22.1	0.500	44.2	1.645	2.61	0.415
23.2	0.750	30.9	1.490	1.46	0.164

SrSO_4 (through 200 mesh)

Decrease In Conc. x	Weight Ore m	x/m	log x/m	Final Iron Conc. c	log c
19.1 ppm	0.100	191.0	2.281	5.61 ppm	0.749
17.6	0.300	58.7	1.769	1.41	0.149
18.3	0.500	36.6	1.564	0.73	-0.137
18.6	0.750	24.8	1.395	0.41	-0.387
18.6	1.000	18.6	1.270	0.40	-0.398

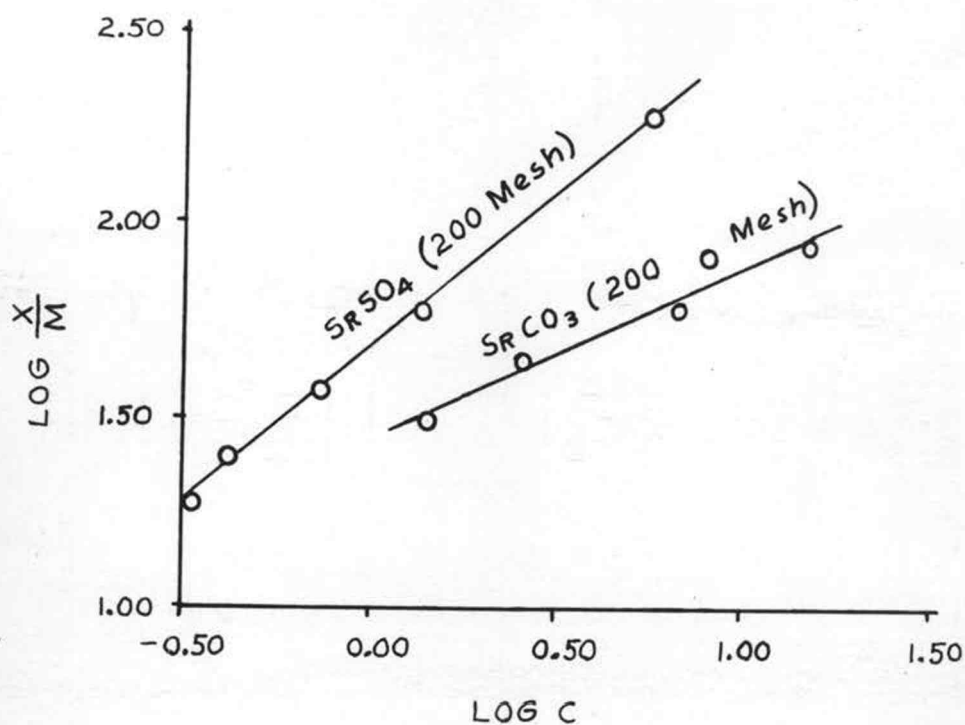


FIG. II

Data for the Removal of Iron from Commercial Caustic Soda Solutions at 30°C. Plotted According to the Freundlich Adsorption Isotherm Equation.

Table IV. Removal of Suspended Ferrous Hydroxide from Fifty Percent Sodium Hydroxide Solution by Strontium Sulfate and Strontium Carbonate at 30°C (in each case a 100 gram sample of sodium hydroxide solution was used)

Ore Used	Weight Ore	Original Iron Conc.	Final Iron Conc.	Decrease In Conc.
SrCO_3	0.100g	22.0 ppm	5.04 ppm	17.0 ppm
SrCO_3	0.200	22.0	4.17	17.8
SrCO_3	0.300	22.0	1.92	20.1
SrCO_3	0.400	22.0	1.23	20.8
SrCO_3	0.500	22.0	0.62	21.4
SrCO_3	0.750	22.0	0.48	21.5
SrSO_4	0.100	22.0	4.94	17.1
SrSO_4	0.200	22.0	5.50	16.5
SrSO_4	0.300	22.0	0.90	21.1
SrSO_4	0.400	22.0	0.42	21.6
SrSO_4	0.500	22.0	0.46	21.5
SrSO_4	0.750	22.0	0.68	21.3
blank	-----	22.0	20.7	1.3

Table V. Data for the Removal of Suspended Ferrous Hydroxide from Fifty Percent Sodium Hydroxide Solution by Strontium Sulfate and Strontium Carbonate at 30°C Calculated According to the Freundlich Adsorption Isotherm Equation.

SrCO_3 (through 200 mesh)

Decrease In Conc. x	Weight Ore m	x/m	log x/m	Final Iron Conc. c	log c
17.0 ppm	0.100g	170	2.230	5.04 ppm	0.702
17.8	0.200	89.0	1.949	4.17	0.620
20.1	0.300	67.0	1.826	1.92	0.283
20.8	0.400	52.0	1.716	1.23	0.090
21.4	0.500	42.8	1.631	0.62	-0.208
21.5	0.750	28.7	1.458	0.48	-0.319

SrSO_4 (through 200 mesh)

Decrease In Conc. x	Weight Ore m	x/m	log x/m	Final Iron Conc. c	log c
17.1 ppm	0.100g	171	2.233	4.94	0.694
16.5	0.200	82.5	1.917	5.50	0.740
21.1	0.300	74.0	1.869	0.90	-0.046
21.6	0.400	54.0	1.732	0.42	-0.377
21.5	0.500	43.0	1.634	0.46	-0.337
21.3	0.750	28.4	1.453	0.68	-0.167

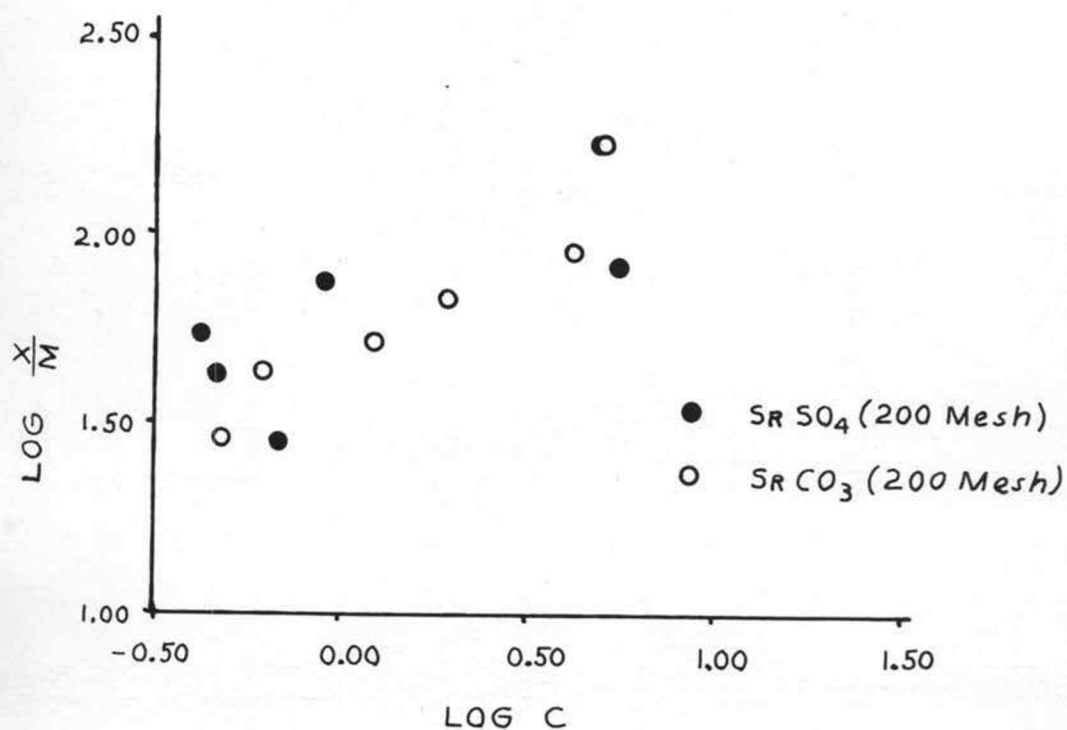


FIG. III

Data for the Removal at 30°C. of $\text{Fe}(\text{OH})_2$ Suspended in Fifty Per Cent Sodium Hydroxide Solution Plotted According to the Freundlich Adsorption Equation.

Table VI. Removal of Ferrate from Commercial Caustic Soda Solutions by Calcium and Barium Sulfate and Carbonate at 30°C (in each case 100 grams of the caustic solution having an original iron concentration of 13.6 p.p.m. were used)

Substance	Weight of Substance	Decrease In Iron Concentration
BaSO_4	0.100	0.3ppm
BaSO_4	0.500	2.4
BaSO_4	1.000	7.2
BaCO_3	0.100	0.4
BaCO_3	0.500	0.0
BaCO_3	1.000	0.4
CaSO_4	0.100	2.1
CaSO_4	0.500	7.2
CaSO_4	1.000	9.0
CaCO_3	0.100	2.1
CaCO_3	0.500	7.4
CaCO_3	1.000	10.4

The Effect of Temperature on the Rate of Removal of Ferrate From 50% Commercial Caustic Soda Solutions

The effect of temperature upon the rate of removal of ferrate from fifty percent caustic soda solution by strontium sulfate and strontium carbonate was studied in the following manner:

150-gram samples of the crude caustic soda solution obtained from the Pennsylvania Salt Manufacturing Company were placed in four-ounce wide mouth bottles. These were then allowed to come to the temperature at which the removal was to be studied.

0.500 grams of the purifying agent were then agitated in the caustic soda solution, and the resulting mixture was allowed to settle. The mixtures were maintained at the proper temperature during the time in which the experiments were being run.

A pipet was arranged so that samples of the caustic soda solution could be withdrawn at the same level from each of the bottles. Samples were taken in this fashion at measured time intervals and analysed for the iron content.

It can be seen that the decrease in the iron content thus measured is due to the settling out of the purifying agent from the caustic soda solution. Therefore, by plotting iron concentration against time, a measure of the settling rate of the purifying agent in the caustic

soda solution may be obtained.

Runs were made in this fashion for strontium sulfate and strontium carbonate which had been passed through a 200 mesh sieve. The temperatures studied were 30°C, 50°C, and 70°C. The results of these runs are shown graphically in figures IV, V, and VI.

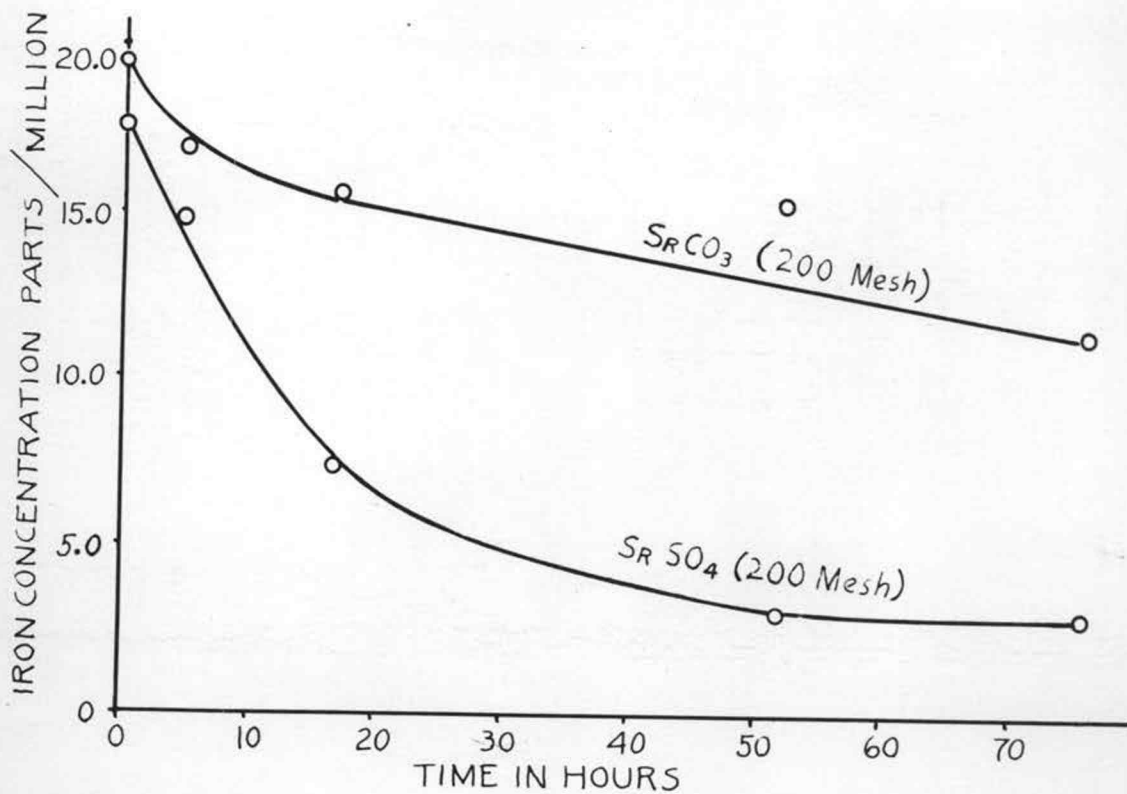


FIG. IV

Variation with Time in the Removal of Iron Impurity from Commercial Caustic Soda Solution at 30°C.

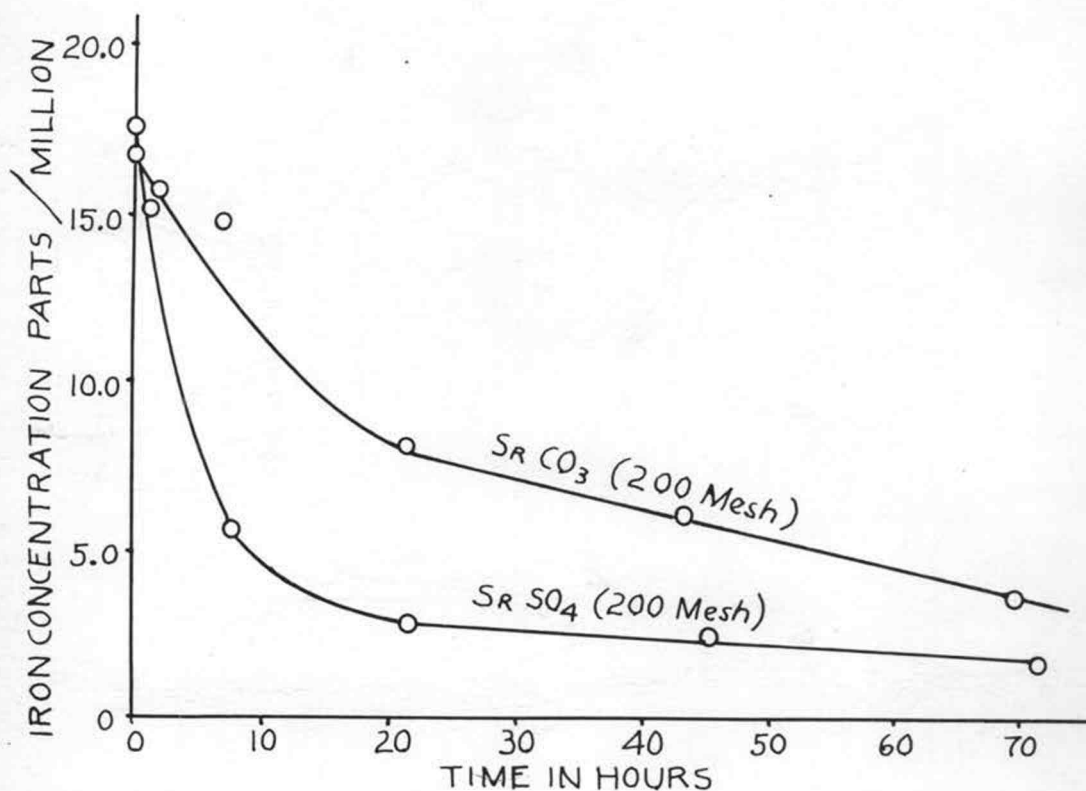


FIG. V

Variation with Time in the Removal of Iron Impurity from Commercial Caustic Soda Solution at 50°C.

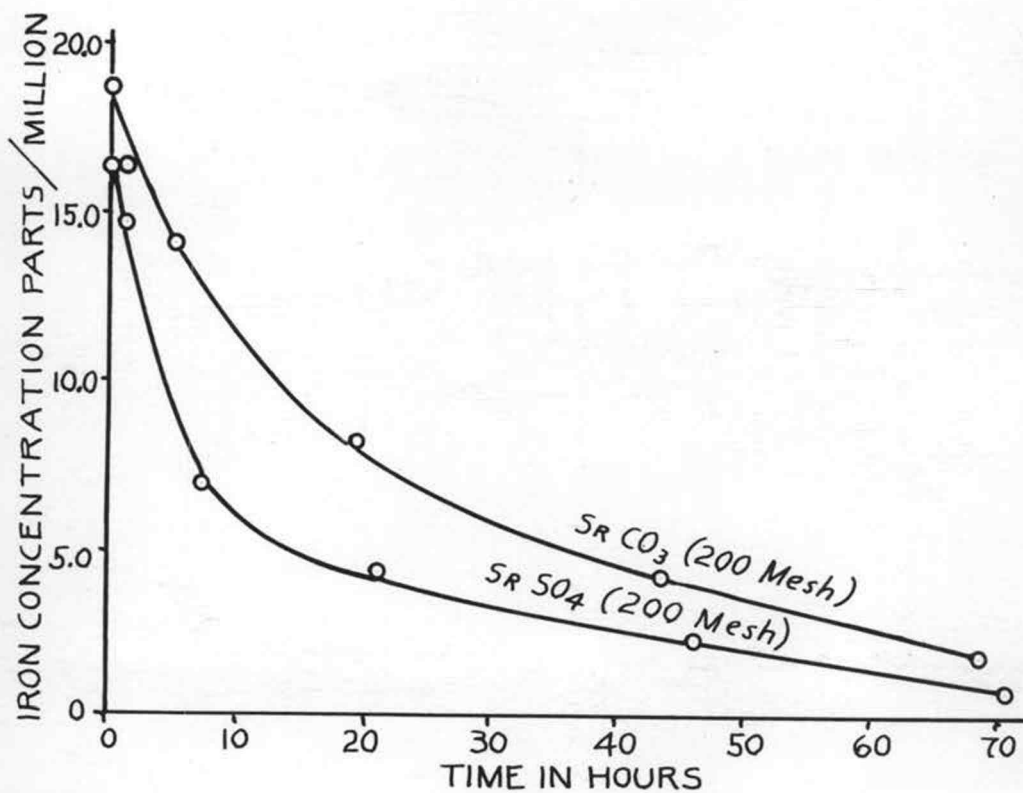


FIG. VI

Variation with Time in the Removal of Iron Impurity from Commercial Caustic Soda Solution at 70°C.

Discussion of Results

Table II gives the experimental results obtained for the variation of the removal of the iron impurity from commercial caustic soda solutions with different amounts of strontium sulfate and strontium carbonate. Figure II shows these values plotted according to the Freundlich adsorbtion isotherm equation:

$$\log x/m = n \log c + K$$

Table IV shows the same type of data obtained for the variation of the removal of suspended ferrous hydroxide from fifty percent sodium hydroxide solution by strontium sulfate and strontium carbonate. These values are also plotted according to the Freundlich adsorbtion isotherm equation in figure III.

In the case of the ferrous hydroxide suspended in the fifty percent sodium hydroxide solution, the removal is independent of the type of purifying agent and varies only with the quantity of purifying agent added. This can be seen from an examination of table IV.

An examination of figure III shows that the removal of suspended ferrous hydroxide from sodium hydroxide solutions does not conform with the Freundlich adsorbtion isotherm equation.

It is therefore believed that the removal of the suspended ferrous hydroxide from sodium hydroxide solutions is due to the mechanical sweeping of the

suspended particles by the finely ground strontium ore settling through the solution.

In comparison to this, the data for the removal of the iron impurity from commercial caustic soda solutions does follow the Freundlich adsorption equation as can be seen from figure II. Also, at 30°C strontium sulfate is seen to be a better purifying agent per unit weight than strontium carbonate. This cannot be attributed to the difference in density of the two materials. The strontium sulfate has a density of 3.96 grams per ml., and the strontium carbonate has a density of 3.70 grams per ml. (2). This means that for a unit weight of material having a definite particle size, there is a greater number of strontium carbonate particles than there are strontium sulfate particles, and, consequently, the strontium carbonate would expose a greater surface area than would the strontium sulfate.

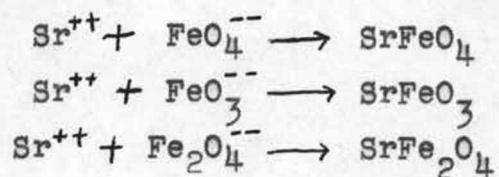
Therefore, since the strontium sulfate does remove more of the iron impurity than does the strontium carbonate even though the exposed surface area is less, it can be concluded that the strontium sulfate is a better purifying agent than the strontium carbonate at 30°C.

From the evidence to support the belief that the iron impurity occurs in the form of the ferrate ion and from the nature of the curve obtained in figure II,

it is concluded that the removal of iron impurities from commercial caustic soda solutions by strontium sulfate and strontium carbonate occurs in the following manner:

The ferrate ion is adsorbed upon the surface of the strontium ore particles, and an equilibrium is reached between the quantity of ferrate adsorbed and the quantity remaining in the solution. The strontium ore then settles from the solution taking with it the ferrate which has been adsorbed.

The mechanism by which the ferrate is adsorbed can be explained by an exchange reaction occurring at the surface of the adsorbent. The adsorbing agent is slightly soluble in the caustic soda solutions liberating around the particles, alkaline earth ions. However, the alkaline earth ferrates have been shown to be insoluble in caustic soda solutions (9). It is therefore believed that the concentration of alkaline earth ions liberated by the dissolving of the adsorbent, exceeds the solubility product of the alkaline earth ferrate. Thus an equilibrium is attained between ferrate ions in solution and alkaline earth ferrate which is precipitated out, probably upon the surface of the adsorbent material.



On the basis of this postulated mechanism, it can be seen that the efficiency of iron removal from caustic soda solutions depends mainly upon two factors:

The solubility of the adsorbent material, and the solubility of the alkaline earth ferrate.

The curves obtained for the variation with time of the iron content at a given level in the caustic soda solutions do not give much indication of the change in the rate of settling of the adsorbent with temperature as was hoped. However, they do show that an increase in temperature does increase the amount of iron impurity removed from the caustic soda solution by the adsorbent.

Also, at the higher temperatures around 70°C , the amount of iron impurity removed by strontium carbonate approaches the amount of iron removed by the strontium sulfate.

Summary

1. Much of the iron impurity in commercial caustic soda solutions produced by electrochemical means occurs in the form of a ferrate, FeO_4^{2-} , with possibly some FeO_3^- and $\text{Fe}_2\text{O}_4^{2-}$ ions.

2. The removal of this impurity by finely ground strontium ores is due to the adsorption of the ferrate upon the ore particles, which, in turn, settle from the solution.

3. At 30°C , strontium sulfate is a better adsorbent than strontium carbonate.

4. Increase in temperature increases the amount of iron impurity removed from the solution by a given amount of strontium mineral. At higher temperatures, strontium carbonate approaches strontium sulfate in ability to remove iron impurities.

5. In colorimetric iron analyses of caustic soda solutions, depending upon the formation of the complex ion $\text{Fe}(\text{CNS})_6^{2-}$, corrections must be made for the inhibition of color formation by the presence of electrolytes in the solution.

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