DISSOLUTION OF FERRIC HYDROXIDE IN SEQUESTERED ALKALI

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Sodium gluconate and certain other sequestering agents in alkaline solutions have been recommended for the derusting of iron and steel. This article is concerned with a quantitative approach to the solubility of precipitated ferric hydroxide in sodium hydroxide solutions containing various sequestering agents and under a variety of conditions.

EXPERIMENTAL DETAILS

Preliminary experiments.—In the early stages of this work we found that the condition of the iron oxide or hydroxide greatly affected its solubility in sequestered caustic solutions. For example various ferric oxide preparations and powdered rust possessed very low solubility in sequestered alkali whereas freshly precipitated ferric hydroxide dissolved more readily. In addition, ferric hydroxide, upon standing even in moist condition became less soluble in sequestered alkali so that subsequent experiments were always carried out with freshly precipitated ferric hydroxide.

Analysis for iron.— A standard analytical procedure was used for the analysis of the iron dissolved by the alkaline solutions. A 25-ml. aliquot containing 0.004 moles of iron, in most cases, was acidified slightly with hydrochloric acid and one ml. of potassium iodide solution (120 g. KI per 200 ml. of water) was added along with one ml. of soluble starch solution. The solution was titrated with 0.1 N sodium thiosulfate solution to the discharge of the blue, purple, and finally the pink color.

Preparation of ferric hydroxide.—A molar solution of ferric chloride hexahydrate was prepared. Forty ml. of this solution (0.04 moles of iron) were treated with 20 ml. of concentrated ammonium hydroxide, and the precipitated ferric hydroxide was collected by filtration and washed with distilled water.

Dissolution experiments.—Appropriate amounts of sodium hydroxide pellets and sequestering agent were weighed into a 250-ml. volumetric flask, and a clear solution was prepared using carbon dioxide-free (boiled) distilled water. This solution was added to the 0.04 moles of freshly-precipitated ferric hydroxide and the mixture was stirred mechanically for varying periods of time. Approximately 35-ml. aliquots were removed periodically and the ferric hydroxide which had not dissolved was removed by centrifugation. A 25-ml. aliquot of the clear supernatant mother liquor representing 0.004 moles of iron in the original mixture was analyzed for its iron content by the above-described procedure.

DISCUSSION OF RESULTS

Figure 1 illustrates the variation in the quantity of ferric hydroxide

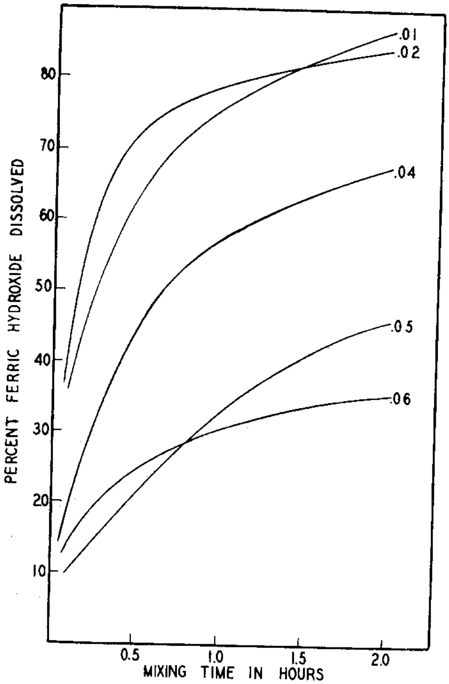

FIG. 1—Dissolution of 0.01 to 0.06 moles of ferric hydroxide per 250 ml. of 3% sodium hydroxide containing 0.3% sodium gluconate.

dissolved in 3% sodium hydroxide containing 0.3% sodium gluconate over a period of two hours. In this experiment it becomes apparent that the amount of ferric hydroxide dissolved, that is the percent of the total ferric hydroxide present, begins to level off after a two-hour period. Therefore, in future experiments either a one- or two-hour mixing time was employed and we arbitrarily used 0.004 of a mole of ferric hydroxide per each 25-ml. aliquot since this concentration of iron appeared to give the greatest weight percent dissolution.

In earlier experiments it was found that if the sodium hydroxide-sodium gluconate solutions were allowed to stand overnight in glass containers the dissolution of ferric hydroxide by these solutions was somewhat poorer than by freshly prepared solutions. This was attributed to the presence of silicate in these caustic solutions and it was found that introduction of a small amount of sodium silicate into the chelated sodium hydroxide solutions did indeed reduce the capacity of the solution for the dissolution of ferric hydroxide. Another factor which appeared to affect adversely the dissolution of iron was the presence of carbon dioxide. Upon bubbling this gas through the chelated caustic solution while mixing with ferric hydroxide, substantially less

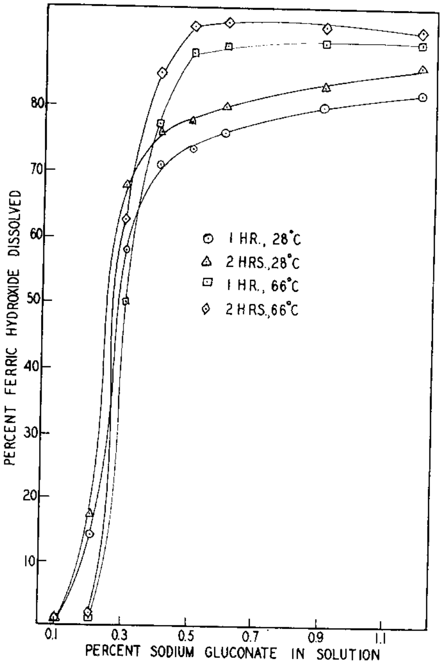

FIG. 2.—Dissolution of 0.04 mole of ferric hydroxide per 250 ml. of 3% sodium hydroxide containing varying amounts of sodium gluconate.

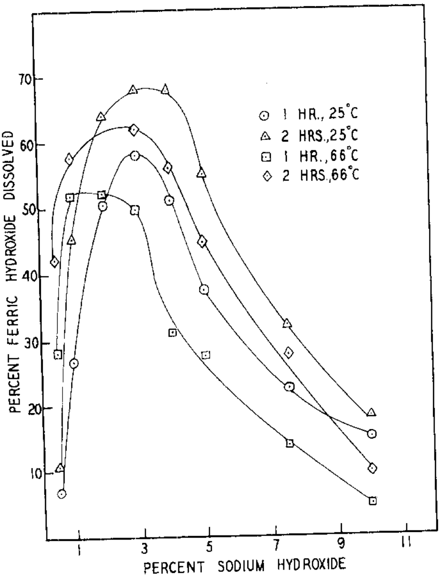

FIG. 3.—Dissolution of 0.04 mole of ferric hydroxide in 250 ml. of 0.3% sodium gluconate solution containing varying amounts of sodium hydroxide.

iron was dissolved. Therefore, all solutions were prepared with carbon dioxide-free water.

The effect of the amount of sodium gluconate on the dissolution of ferric hydroxide was next studied. To a 250-ml. solution containing 0.04 mole of iron and 3% sodium hydroxide varying percentages of sodium gluconate from 0.1 to 1.2% were added. The percentage of the total iron present which dissolved over a one- and two-hour period at 28° and 66° C. was measured and the results are shown in Figure 2. It becomes apparent that in all cases approximately 0.5% sodium gluconate gave optimum results and that the 66° C. temperature and/or a two-hour mixing time gave greater dissolution of the ferric hydroxide. It is interesting to calculate the molar ratio of sodium gluconate which gave optimum dissolution of the ferric hydroxide. At 66° with a two-hour mixing time, 85% of the 0.004 mole of iron per 25-ml. aliquot was dissolved by 0.5% or 125 mg. of sodium gluconate. Therefore, 0.0034 moles of iron were sequestered by 0.00057 moles of sodium gluconate or approximately six moles of iron per mole of sodium gluconate under these conditions.

Another series of experiments was carried out by varying the caustic strength of the solution as illustrated in Figure 3. In this case 0.04 moles of ferric hydroxide per 250 ml. of various caustic solutions containing 0.3% sodium gluconate were mixed one and two hours at 25° and 66° C. The caustic strength was varied from 1 to 10% and it became

TABLE 1.—Percent Dissolution of 0.04 Moles of Ferric Hydroxide per 250 ml. of 3% Sodium Hydroxide and 0.4% Chelating Agent at 25° C. for Two Hours.

Chelating agent	% ferric hydroxide dissolved
Sodium gluconate	70-75
Potassium acid saccharate	78
Sodium D-gluconate	85
Sodium D-mannonate	74
C-29*	74-78
Sodium D-glucoheptonate	75
Sodium D-galactoheptonate	65
Sodium D-galactonate	60
Sodium mucate	5
Sodium glucuronate	4
Sodium galacturonate	1
Versene Fe-3 specific	0.8
Versene	0.06
Sodium tripolyphosphate	0.06
Tetrasodium pyrophosphate	0.06

* A commercial sequestering agent produced by Blockson Chemical Company.

evident that optimum dissolution of ferric hydroxide occurred with from 2 to 4% sodium hydroxide.

After the optimum conditions had been established for the dissolution of ferric hydroxide by sodium gluconate in sodium hydroxide solution a number of other sugar acids and other chelating agents were substituted for the sodium gluconate and the dissolution of ferric hydroxide was measured. The results obtained are compared to sodium gluconate in Table 1.

SUMMARY

The above-described experiments indicate that the polyhydroxy monocarboxylic acids such as gluconic acid possess the ability to dissolve ferric hydroxide in caustic solutions. The optimum conditions indicate the use of 3% sodium hydroxide with 0.5% sugar acid for two hours using freshly precipitated ferric hydroxide. It should be emphasized that the oxides or hydroxides of iron as found in rust are not as readily soluble in these chelated solutions.