

ELECTROLYTIC REMOVAL
OF RUST
FROM
IRON AND STEEL

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PREFACE

Iron and steel is at present, and is coming more and more, to be one of the most important materials with which the engineer has to deal.

Contrary to the opinion of most people, iron and steel, and metals in general, have little permanence as compared to that of certain minerals and rocks, some of which have come down to us from ancient times in a state of remarkable preservation. Ancient metal articles, on the other hand, are the exception rather than the rule. This may be due to there being originally many more stone implements than metal ones, or, which seems more probable, to the corrosion of all but the exceptionally well protected metal articles.

In the field of corrosion, by far the most important aspect is that of preventing the formation of rust, rather than the removal of that which has already formed, but, in many instances, articles of iron and steel have their commercial value, but not their utility value, greatly impaired by a more or less slight coating of rust.

At the suggestion of Dr. H. P. Cady, this thesis was begun with the purpose in mind of dev-

eloping an economical method for the restoration to this class of materials their former commercial value by an electrolytic pickling of the article, whereby the rust is cheaply removed.

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NATURE OF RUST AND RUSTING

Before an intelligent study of the problem at hand can be made, it will be necessary to look in some detail into the nature of rust on iron and steel, its composition, mode of occurrence, theories as to its formation, etc.

The phenomenon known as rusting is far from being a simple one. Bengough * gives the following factors as being of importance in the rusting of iron:

1. Chemical composition of the metal.
2. Contact with other more or less electro-positive substances which are metallic conductors.
3. Stray electric currents passing to or from the sample.
4. Quantity of dissolved oxygen in the moisture in contact with the sample.
5. Rate of motion of the water.

* Hudson and Bengough, Iron and Steel. Page 157.

6. Presence of acids, bases, or salts in the water.
7. Presence of previous rust.
8. The temperature.
9. Physical condition of the metal.
10. Quantity of light falling on the metal.

With all the possible variations of the above factors, one would hardly expect the composition of any two different samples of rust to be the same, but the variations in composition of samples from widely differing conditions is not as great as might be expected, as the following analyses show:

	Rod	Rail	Sheet	Chain
Free water ---	.12%	.11%	.24%	.08%
Fe ₂ O ₃ -----	85.41	84.92	80.96	80.55
Fe ₃ O ₄ -----	5.41	1.77	4.41	10.66
FeCO ₃ -----	.84	2.24	.95	.81
MnO ₂ --- ---	.41	.73	.54	.06
Carbon -----	.15	.93	1.17	.20
Combined water	5.90	6.60	9.42	3.88
SiO ₂ & insol.	.14	.05	1.50	1.44
Undetermined	1.74	2.76	1.05	2.94

The free metal in these samples was totally destroyed by rusting and the composition differs somewhat from the following analyses of dried samples taken from the inside of some iron tanks.

*Sample	1	2	3	4	5
Fe ₂ O ₃ ----	55.73	51.12	64.60	65.13	68.89
FeO -----	32.86	36.57	25.74	25.66	23.18
FeCO ₃ ----	11.40	12.31	9.66	9.21	7.93

It will be seen from this that ordinary iron rust consists, essentially, of a more or less hydrated ferric oxide with varying quantities of ferrous oxide, as such or in the form of magnetic oxide, and ferrous carbonate. The layer of rust next to the mother metal seems to be richer in ferrous iron than the outer layers, and this is what would be expected from the probable mode of its formation, as will be shown later.

Rust is not, in general, crystalline but is granular and amorphous and seems to take the form of flakes, probably because of its initial formation in local spots and further spread from these spots. It adheres to the specimen with greater or less

* This and the preceding table were taken from A. Sang, Corrosion of Iron and Steel, page 4.

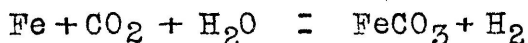
tenacity depending upon the relative importance of the various factors affecting its formation. Its electrical conductivity varies widely also, from a practical non-conductor if dry and soft, to a fairly good conductor if wet and firm.

Theories of Rusting.

There are, at present, two theories for the explanation of the formation of rust, as well as one or more of little apparent value. Any theory, to be satisfactory, must take into consideration and coordinate the various factors affecting the formation of rust, as given on pages 6 and 7.

The carbon dioxide theory of rusting is the oldest plausible one and has been strongly supported by many experimenters. It supposes the action of rusting to be a purely chemical one, the carbon-dioxide forming carbonic acid with water, and the acid attacking the iron with the liberation of hydrogen and the formation of ferrous carbonate, which is then oxidized to ferric oxide with the regeneration of the carbon dioxide. The following

equations illustrate the reactions.



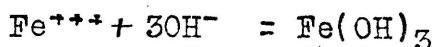
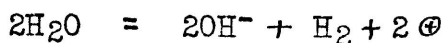
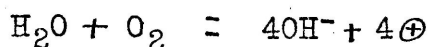
Since the carbon dioxide is regenerated, the process is a cyclic one, with modifications for the formation of ferrous oxide and ferrous carbonate which are nearly always present in rust.

The theory is logical, and since a mere trace of carbon dioxide is all that is necessary to cause it to function, and carbon dioxide is present in all water, it is very hard to conclusively prove or disprove the theory. In any case, it is proved beyond a doubt that rusting is much more rapid if carbon dioxide is present than if it is absent and all other conditions are the same.

Electrolytic Theory of Rusting.

Sir Humphry Davy seems to have been the first to connect the impurities in the iron with its rate of rusting, and thus start a new theory of rusting known as the electrolytic theory, which correlates everything that the carbon dioxide theory does and still is more comprehensive than the latter.

Rusting, according to this theory, can take place only when the iron is not uniformly pure so that one part may become electro-negative to another, and the necessary water must be impure enough to carry current and act as an electrolyte. Under these circumstances, all the conditions necessary for the formation of an electrolytic cell are present and ferrous iron is supposed to go into solution at the positive areas while dissolved oxygen is reduced and goes into solution as hydroxyl ions at the positive areas, or hydrogen is evolved with the formation of hydroxal ions. The ferrous iron is oxidized to ferric by the dissolved oxygen and precipitated by the hydroxyl ions. The following equations represent these reactions.



The ferric hydroxide loses more or less water and rust is the result.

This theory explains why carbon dioxide, salt, base, or any acid would hasten rusting, for anything

that increases the conductivity will increase the galvanic action. This theory explains why stray electric currents hasten corrosion and why rusting is observed to initiate in spots, rather than to form uniformly over the whole surface as might be expected from a consideration of the carbon dioxide theory. It is a well known fact that temperature and physical condition of the metal would effect the electrolytic potential between two dissimilar areas. The overvoltage of hydrogen would be less on some areas than on others either due to the nature of the metal or the physical condition. If the overvoltage happened to be especially low on some areas, corrosion would be rapid. Any movement of the water would prevent concentration polarization of the products of electrolysis and assist corrosion. Light probably acts as a catalyst as it does in many reactions.

It is an often observed fact that iron rusts much more rapidly, once rusting has started. This is readily accounted for by this theory since a potential difference has been actually measured between iron and a rusty piece, the rust being electro positive to the bright iron, i.e. the bright iron being the region where Fe^{++} ions are

produced. This potential difference causes the ring of iron surrounding the spot of rust to begin corroding and thus spread the area of rust until the whole surface becomes coated. Under certain conditions the rust does not seem to spread but eats deeper and deeper into the iron. This is probably due to the presence in the iron of impurities which extend to some depth and thus carry the current deeper, rather than allowing it to spread.

Dr. W.H.Walker suggested and carried out in conjunction with Dr. Cushman, some experiments which illustrated beautifully the nature of rusting. A solution called "feroxal" reagent was prepared by neutralizing a hot solution of gelatin or agar-agar with 1/100 normal KOH, with phenolphthalein as an indicator, and then adding a few drops of a dilute potassium ferricyanide solution. A bright specimen of iron was dipped into the reagent, which solidified on cooling and retarded diffusion because of its colloidal state. The negative spots on the specimen were indicated by the formation of a blue coloration of ferrous ferricyanide, while the positive spots were indicated by a red coloration of the phenolphthalein, indicating the presence of

hydroxyl ions. These OH^- ions were produced by the evolution of gaseous hydrogen or by the dissolving of oxygen electrolytically, and then the iron at the negative areas went into solution with the aid of the positive charges thus produced, as explained before.

By means of this reagent these men found that the location of the negative spots in materials which had been mechanically worked was initially in the places where the deformation had been greatest, but after a while conditions would be reversed, and previously positive regions would now become negative ones and vice versa, probably due to the deposition of rust. In this way, through alternate rustings, the whole piece became coated.

For a more detailed treatment of the field of corrosion and rusting, the reader is referred to the brief though comprehensive treatment by Alfred Sang in his book entitled "The corrosion of Iron and Steel" (McGraw-Hill 1910) and to the bibliography at the end of this paper.

Some mention should be made here of the magnetic oxide of iron, Fe_3O_4 , which is referred to several times in this paper. This magnetic oxide differs from ordinary rust in many of its physical and

chemical properties. It is formed by the direct oxidation of the iron at elevated temperatures, and occurs in the steel industry when the metal is rolled. It is necessary to remove this 'roll scale' before further rolling can be done on the metal. This oxide adheres very tenaciously to the metal and seems to be a good conductor of electricity, differing from ordinary red rust markedly in this latter respect.

PRESENT STATUS OF PICKLING AND RUST REMOVAL

As mentioned before, various industrial processes require that the metal surface be clean. Since practically all industrial raw material is new, or at least remelted metal, and practically all this metal is rolled or heat treated, the objectionable oxide is in the form of roll scale rather than rust proper. Obviously, this must be removed before rerolling, galvanizing, tinning, plating, or glazing can be accomplished. At present this is done in most plants by the methods in use for many years, namely, straight chemical pickling in dilute acids. Mechanical and electrolytic methods are used in some cases.

Chemical Pickling

This is carried out by immersing the iron in a solution of sulphuric acid of from 4 to 5%, until upon removal of the article the surface is sufficiently clean for the purpose at hand. Sometimes, if the presence of a salt of the halogens is not objectionable, instead of using acid as such, the spent-cake or acid salt from the manufacture of hydrochloric and nitric acid is used. Investigations of the reactions occurring in this process made by Carl Herring * and others have shown that

* Nov. 1, 1915, Removing Iron Scale by Pickling, Theory vs Practice Met. and Chem. Eng. vol. 13, - pg. 785.

the removal occurs principally by the solution of some of the metal under the scale with the resulting mechanical flaking of the scale itself.

Mechanical Removal.

For certain other types of articles such as steel structures, large castings etc., the foregoing process would not be practicable. In these cases mechanical methods are usually used for the removal of the layer of oxide. Two of the most important of these methods are the sand blast and the steel wire brush. The sand blast is by far the better and more economical but must be operated in a shop with special precautions for the workman. The steel wire brush is used to a large extent when old structural steel is to be repainted. Both are outside of the scope of this paper but should be mentioned here for the sake of completeness.

Electrolytic Pickling.

The electrolytic method of pickling developed and patented (U.S. Pat. No. 855,667. and 827,179) by Mr. C. J. Reed in 1907, will be considered in somewhat more detail. The patent specifications call for a sulfuric acid solution of 1.2 specific gravity, a temperature of about 60 degrees centigrade

and a current density of from 40 to 70 amperes per square foot, (4.27 to 642 amperes per square decimeter). The ferrous sulphate formed is removed by cooling to zero degrees centigrade. The article to be pickled is, of course, to be made the cathode.

The fundamental principle on which the process is founded is as follows: The iron in the form of roll scale is partly in the ferric and partly in the ferrous form, ($\text{Fe}(\text{FeO}_2)_2$ or Fe_3O_4) and before it can be dissolved and sent into solution, it must all be in the ferrous form. This is accomplished in the process by reducing the ferric iron to the ferrous by means of the electric current, the reaction at the cathode being essentially reduction as will be shown later. (See page 41). At the same time, that portion of the metal which has been already cleaned is prevented from being dissolved in the acid. (See page 44).

In checking up on the inventor's work, M.D. Thompson* and F.W. Dodson pickled identical pieces of steel by the electrolytic and straight acid processes under the extreme conditions most and

*Dec. 15, 1917. The Electrolytic Pickling of Steel. Met. and Chem. Eng. vol. 17, page 713.

least favorable to the electrolytic process, with the following results:

There was a great saving in time under both of the extreme conditions when the electrolytic method was used. One of the specimens, a piece of boiler plate, required two and one-half hours by the ordinary and eight minutes by the electrolytic method. The amount of acid used was about the same by both methods. There was an appreciable loss of good metal by the ordinary method. The cost of the electricity must be considered in the electrolytic method but the saving in steel more than compensated for the cost of the current. The advantages seemed to be more in favor of the electrolytic method, the thicker the scale was.

PRINCIPLE AND THEORY OF ELECTROLYTIC REDUCTION

It is probably best to spend some time in consideration of the theory of electrolytic reduction in general before taking up the specific experiments tried in connection with the reduction of iron oxide.

When electricity is passed thru an electrolyte, positive charges are assumed to enter the electrolyte at the anode or positive electrode and an equal number of positive charges to leave at the cathode or negative electrode. It is quite evident then, that positive charges must pass from the solution to the cathode. This necessitates that ions in the solution loose positive charges and be reduced. Of course we have the converse of this taking place in a few cases, namely where material from the cathode goes into solution as negative ions. This is however just as much a case of reduction as the former. We can state then as a general rule that there is always reduction at the cathode.

In most cases there are two or more possible things to be reduced. Thus, in the electrolysis of a solution of CuSO_4 , there are the following

possibilities of reduction:-

- (a) Reduction of Cu^{++} to Cu^+ .
- (b) Discharge of Cu^{++} to Cu .
- (c) Discharge of 2H^+ to H_2 .

In all such cases, that reduction is accomplished which takes place with the greatest ease under the circumstances existing at the time of the electrolysis. The substance that is reduced with the greatest ease is, in general, the one requiring the lowest voltage.

Since practically all electrolysis takes place in water solutions it is quite evident that one of the ever prominent possibilities of reduction is the discharge of hydrogen ions. This is in general not desired, as hydrogen that is evolved as a gas is a measure of the inefficiency of the process.

In the past it has been a common opinion that in the reduction of a substance electrolytically, hydrogen ions first give up their charge and then react in the atomic or 'nascent' state with the substance to be reduced. This opinion is becoming less common as there is no reason to believe that the hydrogen ions give up their charge and are

reoxidized by the other substance. It is held instead of this that the second substance is reduced directly.

There are several things that have a prominent influence on the ease of reduction of the various oxidizing agents during electrolysis. Some of these are listed below, and will be discussed in the order given.

1. Nature of the oxidizing agent.
2. Concentration of the oxidizing agent.
3. Nature of the electrode.

Possibility of alloy.

Catalytic effect.

Overvoltage

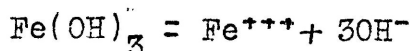
4. Current density.
5. Temperature.
6. Catalysts in the electrolyte.

Nature of the Oxidizing Agent.

By the nature of the oxidizing agent is meant its strength as an oxidizing agent. It is quite evident that the strength of a substance as an oxidizing agent will control to a large extent its ease of reduction.

Concentration of Oxidizing Agent

By the concentration of the oxidizing agent is meant the amount present at the cathode in the reducible form. It is quite evident that the more plentiful a substance is, the lower will be the voltage required to attract the ions to the electrode fast enough to carry all of the current. Thus it requires a higher voltage to liberate hydrogen at a given rate in an alkaline solution than it does in an acid solution because of the great difference in the hydrogen ion concentration. It is evident then that as far as this one consideration goes, one would find it easier to reduce a given substance, without the liberation of hydrogen, when working in an alkaline solution than in an acid solution. However, in the particular case under consideration, there is another effect that the hydrogen and hydroxyl ion concentrations have. Rust is in general assumed to be $\text{Fe}(\text{OH})_3$. At least it seems safe to assume that any ionization that might occur is as follows:-



Let their concentrations be represented by c , c' , and c'' respectively. Since $\text{Fe}(\text{OH})_3$ is present

in the solid state c can be regarded as constant. Then $c' \times (c'')^3 = K$. For every increase of OH^- ions there is a proportionate decrease of the H^+ ions, since the product of the concentrations of H^+ and OH^- is a constant, but on the other hand the concentration of Fe^{+++} ion is decreased by the third power. Hence in our particular case it is quite possible that hydrogen would be less liable to be evolved in an acid solution than in an alkaline solution, because of the fact that in the acid solution there would be many more Fe^{+++} ions present for reduction.

Nature of the Electrode.

The nature of the electrode is not so very much under the control of the operator in a process such as we hoped to develop, for it would be necessary to use the material as it happened to come to the operator. However there is little doubt but that the effect of the electrode on the reduction should be studied.

It is known that where there is an alloy formed at the cathode as in the case of amalgams, often the decomposition potential is materially lowered. In the reduction of iron oxide however

there is little hope of using this principle to advantage. It is possible, however, that the alloy of hydrogen and iron has an influence but it was not possible to study such phases of the question, due to the short time allotted to the work.

In the reduction of many substances in solution, such as organic compounds, it is found that some particular kind of an electrode works much better than others with no apparent reason for doing so. This effect, for the sake of something better, is ascribed to catalytic effect of the electrode. As stated before, the material which supports the rust one desires to reduce must of necessity be used as the electrode. However it is quite possible that rust on some particular kinds of material can be reduced much easier than the average, due to the catalytic effect of that material. In fact it was found in the experiments that samples appearing very much alike and treated as nearly under the same conditions as possible gave different results. This may be due to the catalytic effect of the material and it may be due to some particular combination of circumstances, for with so many variables affecting the

reduction, it is quite difficult to keep them all constant for a series of observations. The influence of the electrode material is well shown in the accompanying diagram * of cathode potential current curves for the reduction of a slightly alkaline N KNO_3 solution (figure 3). The reduction is apparently catalysed far more powerfully at some electrodes than at others.

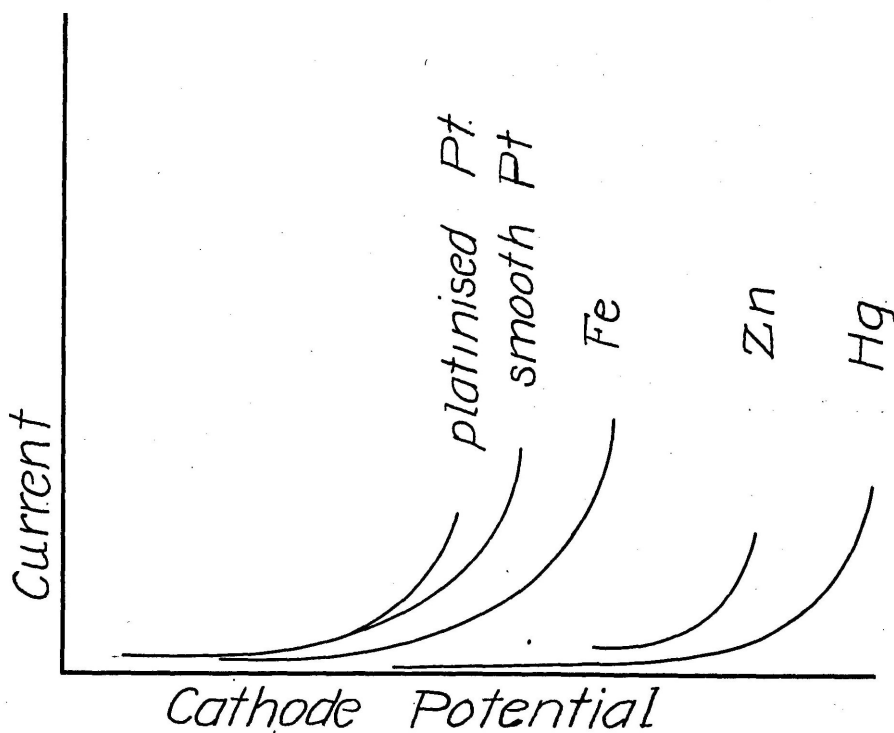


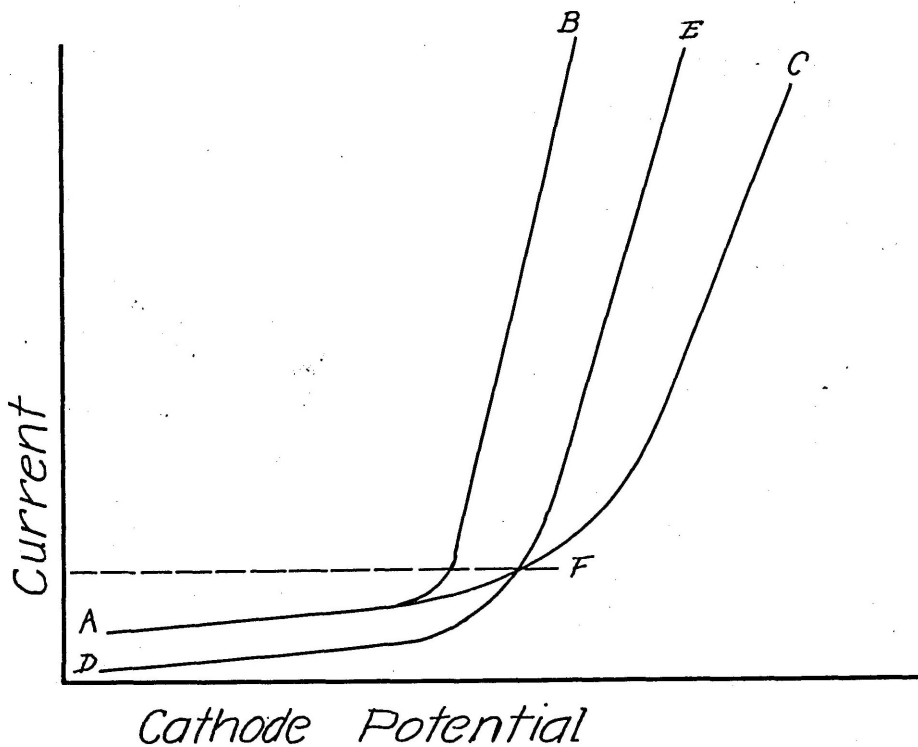
Figure 3.

* A.J.Allmand. (1920) The Principles of Applied Electrochemistry. Page 129.

The nature of the cathode can also affect electrolytic reduction by increasing the polarization needed for hydrogen ion discharge. This is known as overvoltage, which is defined as the voltage, over the reversible voltage of the cell, that is required for continuous electrolysis. The cause of overvoltage is not definitely known, but it is known that the voltage required for continuous discharge of substances such as hydrogen gas at some electrodes is considerable more than at others. It is quite evident that anything that raises the voltage required for hydrogen discharge is beneficial, for it is quite possible in some cases to raise the voltage of a cell in this way above that required to reduce the desired oxidizing agent.

Current Density.

Reduction in general takes place with a greater efficiency with a low current density, for if the current density is raised too high, the voltage will exceed the decomposition potential of hydrogen. However in a few cases, such as that shown in the curves of figure 4 it is best to use a high current



* Figure 4

density. Let AB be the cathode-potential current curve for reversible hydrogen discharge, and the curve DE the curve for the reduction process. It is obvious that if the electrode used allows reversible hydrogen ion discharge,

* From A.J.Allmand (1920) The Principles of Applied Electrochemistry. Page 129.

then no reduced product will be formed, - all the current will give hydrogen. But if the hydrogen overvoltage be at all considerable, then the hydrogen ion discharge curve will have the form AC and at current densities above that corresponding to F, reduction, still accompanied by hydrogen evolution, will begin. With a high current density a rather large per cent of the electricity will be used in the desired reduction process.

Temperature.

An increase in temperature in general assists in the reduction of a substance. This results in a general way from the fact that convection is increased, viscosity is decreased, speed of the ions, and diffusion are increased. However, with the reduction of substances accomplished only thru the overvoltage of hydrogen and high current density as mentioned in the case above, temperature increase is a detriment as it decreases the overvoltage of hydrogen.

Catalysts.

Finally, the velocity of reduction can often be essentially increased by the addition of some catalyst to the electrolyte. Titanium and

vanadium salts are often active. Thus quinone can be readily reduced in acid solution to hydroquinone in the presence of titanium chloride, whereas, in the absence of this salt the reduction stops at quinhydrone.* The mechanism of catalysis in this particular case is clear. The TiCl_4 is readily reduced cathodically to TiCl_3 ; this salt, a powerful chemical reducing agent, reacts rapidly with the depolariser present, being reoxidized to TiCl_4 in the process, and the cycle continues.

*A.J.Allmand. The Principles of Applied Electrochemistry. Page 130.

EXPERIMENTS AND RESULTS

Materials.

The experiments were conducted on various rusty materials that might be picked up around the premises. A few experiments were conducted on rolled steel, for the removal of the roll scale. This material was obtained from the scrap at Fowler shops. A considerable number of rusty pipe fittings were obtained from the university plumbing shop. Quite a large number of three inch wood screws were obtained from the physics department. These were quite satisfactory in that they were quite uniform, and the effect of a change of conditions could be studied with some degree of accuracy. A sheet of rusty transformer iron was also obtained and cut into rectangles of suitable size.

Apparatus.

Figure 1 shows a diagram of the wiring as installed. S_2 is a switch used for connecting with the 110 volt university direct Current power line. R_3 is a 4.25 ohm resistance which may be shunted out by closing switch S_4 . R_2 is a 4 ohm

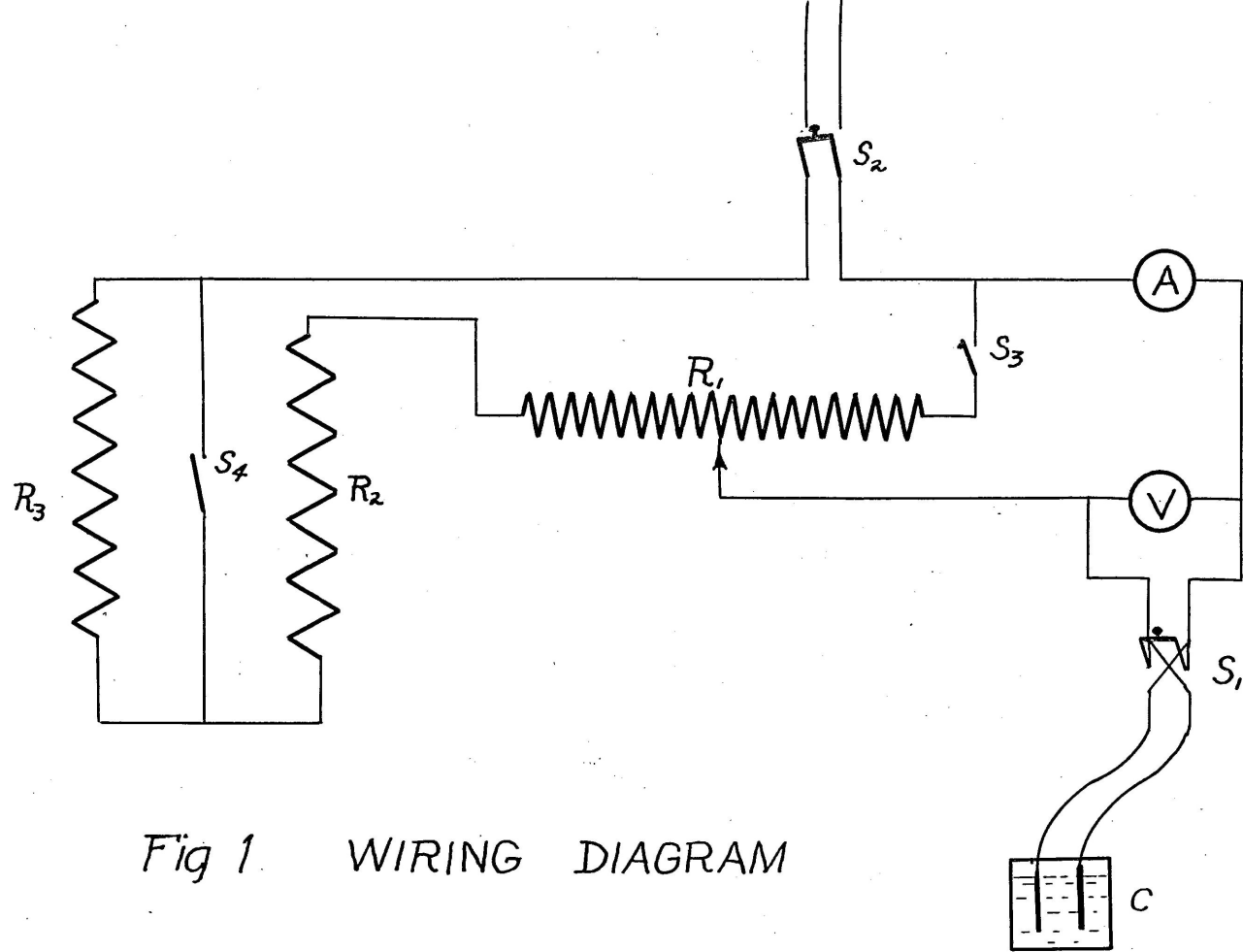


Fig 1. WIRING DIAGRAM

resistance that is in the circuit continuously. S_1 is a reversing switch for reversing the current in the electrolytic cell C. R_1 is a 10.5 ohm variable resistance. A is an ammeter and V is a voltmeter. S_2 is a switch which may be closed and currents for the cell C shunted off of the variable resistance R_1 . With the various combinations it is possible to obtain currents varying continuously from .1 to 15 amperes.

The construction of the electrolytic cell is shown in figure 2. The containers for the electrolyte were made by cutting the tops from 2 and 3 liter bottles by means of a hot wire, and using the bottoms. The electrodes were clamped to a ring stand as shown. The rod A is a round $5/8$ inch wood dowel-pin stick.

When it was desired to study the effect of a change in temperature or concentration, two of these cells were connected in series and screws immersed equally in the two cells. In this way current density and quantity of electricity could be made exactly the same in each case.

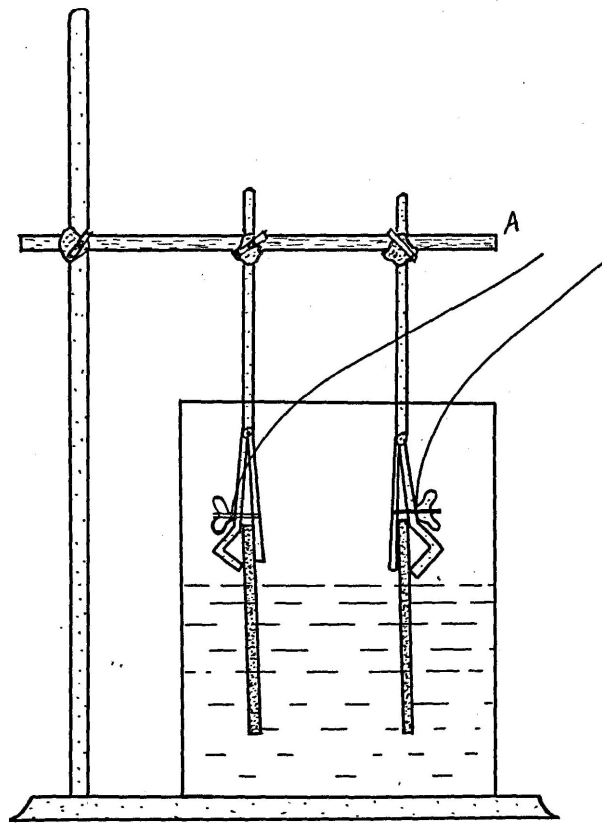


Fig 2
Electrolytic Cell

EXPERIMENTAL

Since the main object of this thesis was to find some solution that could be successfully used as an electrolyte in the reduction or removal of iron oxides from small articles of commerce, the experimental part of the work consisted mainly in trying various solutions as electrolytes using in general rusty articles as electrodes and noting any change in their appearance. It is evident that any report of the experimental work must then of necessity be the telling of a more or less disconnected series of experiments. It is also evident that any report of results must be general, for the operators were unable to find any satisfactory method of accurately recording the exact results of the experiments. The only method available seemed to be merely the observation of the specimens before and after treatment. Such results are extremely hard to convey accurately to the reader. The effects of changes in such things as current density, and temperature were very difficult to find for the above reason, and the fact, that it was impossible to get two specimens that one could rest assured had the same quantity and quality of rust on before treatment. It would have been very satisfactory indeed if results could have been recorded with such accuracy that curves

could have been drawn showing the rate of reduction at various current densities, temperatures, and the like, but it could not be done, so let us turn our attention to the results such as they are.

The discussion of the experiments will be divided roughly as follows.

A. Cathode treatment.

1. Neutral solutions.
2. Basic solutions.
3. Acid solutions.
4. 'Special' or complex-ion solutions.

B. Anode treatment.

Neutral Solutions.

Neutral solutions were not tried out very extensively and the results were very much the same in every case. Saturated solutions (at 20°C) of sodium chloride and sodium sulfate and a 5 per cent solution of potassium nitrate were used. In each case there was doubtless some reduction as a considerable portion of the rust would turn black. However there would usually remain some red rust and the whole would adhere rather closely to the iron. The solutions worked best when hot but even then the

results were not satisfactory.

Alkaline Solutions.

We will now turn our attention to alkaline solutions with which more work was done and more satisfactory results were obtained. In all cases of straight alkaline reduction, the specimens did not come from the alkaline bath in a suitable state for use, but were given a second treatment in a neutral bath as anode or in an acid bath as cathode. This second treatment will be discussed under acid solutions.

It was found that a considerable portion of the scale was removed mechanically and that reduction took place to some extent. By watching the specimen after the current was turned on one could notice the scale dropping off. After a specimen had been run for a few minutes most of the red scale had been removed and the few remaining spots were very loosely attached. The rest of the surface was covered with a loosely adherent black substance. This loosening effect was not due to pure chemical action of the sodium hydroxide as a specimen was immersed in a sodium hydroxide solution of equal strength (20 per cent) for 17 days with apparently no effect.

It was found that the voltage across the cell would drop from about 10 volts to 8 or 9 volts during the electrolysis when a current of 10 amperes was being passed between electrodes 10 or 12 centimeters apart and about 70 square centimeters in area. This fall in voltage was doubtless due to the removal of the red rust which is known to be a poor conductor of electricity. With the current density mentioned above, a specimen could be cleaned to the state mentioned above in about 4 minutes.

A 4 per cent solution of sodium carbonate was tried. This worked very much as sodium hydroxide did. A solution containing 5 per cent sodium hydroxide and 5 per cent sodium carbonate was tried. This seemed to give slightly different results than straight sodium hydroxide solution. When a cell containing this electrolyte was run in series with another cell containing 5 per cent sodium hydroxide, and similar material run in both cells at the same time, the cell containing the mixture seemed to give slightly better results in that there was less black deposit and it often had a slightly different shade of color. The difference in the results obtained with the two electrolytes was quite slight however and was not studied further.

A solution containing 5 per cent potassium nitrate and 5 per cent sodium hydroxide was used. Another solution containing 5 per cent sodium hydroxide and saturated with sodium chloride was tried. Both of these solutions worked fairly well, especially hot but it seemed that both of them were inferior to straight sodium hydroxide solution.

Solutions of sodium hydroxide varying in concentration from 4 per cent to 12 per cent were tried to see what effect the concentration had. It was found that any of these solutions apparently worked as well as the 20 per cent solution already mentioned. In the remainder of the experiments with sodium hydroxide a solution of about 5 to 6 per cent was used.

Solutions of sodium hydroxide were tried at various temperatures between 2 degrees and 100 degrees centigrade. No decided difference was noticed in the lower part of the range but after a temperature of about 40 to 60 degrees was reached it could be noticed that there was a difference. By using temperatures above this range and using a slightly rusty 3 inch wood screw

as cathode, about half immersed, and a current of .1 to .2 amperes, the rust would be entirely blackened for about a minute before any hydrogen would be evolved. It would usually take about 3 or 4 minutes to darken the rust. The hydrogen evolution always started quite suddenly. On the other hand when the solution was run cold there would be a few small spots of red rust on the screw when the hydrogen started to come off and these spots would be removed very slowly on continued electrolysis. The black layer remaining adhered much more closely to the metal and was more uniform when the specimen was treated hot than when treated cold..

An effort was made to find out whether this black deposit remaining was finely divided iron or a low oxide of iron. Some of it was removed to filter paper and then immersed in a copper sulfate solution, the supposition being that if it were metallic iron, copper would be deposited. After standing several hours the filter paper and deposit was thoroughly washed and treated with nitric acid. This was then neutralized with an excess of ammonium hydroxide. No blue color resulted, which goes to show an absence of copper and that the black material

was an oxide of iron. It is possible that the original material on the iron was a deposit of finely divided iron and was oxidized by the air before it could be placed in the copper sulfate solution. Altho it would be finely divided and wet it does not seem probable that it would oxidize so rapidly, for care was taken to make the transfer as rapidly as possible.

Acid Solutions.

When screws that had been reduced in sodium hydroxide were placed in dilute sulfuric acid they would be cleaned in a few minutes. However if they were made the cathode in a sulfuric acid solution they would be cleaned in a very much shorter time. A sulfuric acid solution containing 50 cubic centimeters of concentrated sulfuric acid to every 350 cubic centimeters of water was used. In view of the fact that roll scale is very effectively removed in this manner and is a lower oxide of iron, mainly Fe_3O_4 , it seems reasonable to suspect that this black deposit is some lower oxide of iron.

Roll scale on a piece of rolled steel showed no change when treated as cathode in a sodium hydroxide solution. As a verification of the patents already

mentioned, a sample coated with roll scale was treated as cathode in the sulfuric acid bath. The sample was completely cleaned in about 2 minutes. Acid of the same concentration had apparently no effect at room temperature on a similar sample in the same length of time when no current was passed.

Articles coated with red rust were treated as cathode in the sulfuric acid bath. Unless the layer of rust was rather thick, continued action for ten or fifteen minutes would clean the article. From all appearances however the action was entirely chemical. The rust seemed to fall off in flakes due to the acid dissolving the iron from beneath it. Spots of rust would remain after treatment which would still be red indicating no reduction had taken place. Articles placed in sulfuric acid and agitated for an equal period showed nearly as good a surface as those treated electrolytically.

Theory of Cathode Reduction of FeO or Fe_2O_3 .

The fact that the lower oxides of iron are so speedily removed by electrolysis in acid solution

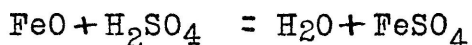
while, at least with Fe_2O_3 , reduction takes place much easier in alkaline solutions, seems rather unusual and deserves further attention.

One supposition is that the oxide is further reduced electrolytically to a lower oxide of iron or to iron which in its finely divided state is rapidly dissolved by the acid. It was shown in the discussion of the theory of reduction, that one might suspect reduction to take place more easily in acid solution than in basic solutions in the case of material having hydroxyl ions. Altho this did not prove out in practice with Fe_2O_3 , one would, never the less, not be surprised to see it work out with the lower oxides. One might also argue that the hydrogen liberated by the current would reduce the surface of the electrode exposed to the acid at any one time and thus tend to reduce straight chemical reaction instead of increase it, - hence some sort of electrolytic reduction must take place. Mr. Carl Herring* mentions the fact that when a clean iron plate

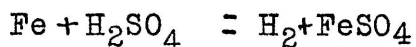
* Nov. 1, 1915, Removing Iron Scale by Pickling, Theory vs Practice. Met. and Chem. Eng. vol. 13, -page 785.

is immersed in sulfuric acid and made the cathode, the reaction between the acid and the iron is very slight indeed as compared with the action that takes place when no current is passing. This, he ascribes to the protection offered to the iron by the layer of gaseous hydrogen.

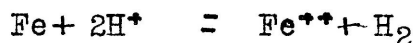
While the above explanation seems more or less logical and was one of the first ones to occur to the writers, there seems to be a more logical explanation. It is as follows:- Assume for simplicity that the black scale after reduction in sodium hydroxide to be ferrous oxide, FeO. This would react with sulfuric acid as follows:



The underlying iron would tend to react thus:



That is, the iron is oxidized thus:



It is evident that in either of these reactions, which are both chemical, the big necessity is a generous supply of H^+ ion in the immediate vicinity of the plate. When we pass current with the iron plate as cathode, hydrogen ions travel to the cathode and all the hydrogen that is liberated by the current must come in contact with the electrode as ions first.

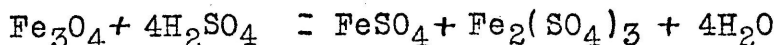
Then since the number of hydrogen ions coming in contact with the plate would be greatly increased by the current, one would suspect that both of the above reactions would be greatly accelerated. However, with the second reaction it should be noted that it is an oxidation reaction. The tendency of the current is to cause reduction at the cathode. That is, any Fe^{++} ions that might form would be held at the cathode by the current with a strong tendency for them to be reduced. This tendency of the Fe^{++} ions to collect and be reduced apparently overcomes any tendency for the iron to dissolve. Of course the ferrous ions formed by the reaction of FeO and H_2SO_4 would be held at the cathode too, but in this case it is not necessary that the iron be oxidized for the formation of the ferrous ions. It would seem logical then, to suspect that the passage of current would hasten the solution of FeO and retard the solution of Fe . In the case of roll scale, or Fe_3O_4 , it is only necessary to assume that the ferric iron is reduced before it is dissolved by the acid while the ferrous iron is dissolved directly as such.

Since the above is mere speculation that appealed to the logic of the writers, who are inexperienced in this field, it seems advisable to quote the opinion of a more experienced man*, whose theory on the subject was the only one the writers could find in the literature. The reader is at liberty to accept either theory, as he sees fit.

After making a few pertinent remarks on the subject and stating that he found magnetic oxide to be not soluble in acids, Mr. Hering goes on to state:

"A possible reason for its not being soluble is the equation, - $\text{Fe}_3\text{O}_4 + 3\text{H}_2\text{SO}_4 = 3\text{FeSO}_4 + 3\text{H}_2\text{O} + \text{O}$ which shows that free oxygen would have to be evolved if it (Fe_3O_4) were soluble. As this oxygen was combined with the iron it presumably requires a supply of energy to free it." -----

It doesn't seem to the writers, however, that it is necessary to assume that oxygen would be evolved. Part of the iron might go into solution as ferric iron, thus:



* Carl Hering. Nov. 1, 1915. Removal of Iron Scale by Pickling, Theory vs Practice. Met. & Chem. E. Page 785.

However, let us continue with Mr. Hering's line of thought.

"As the oxide is already in a low state, from the energy standpoint, little if any energy can be expected to be set free by its solution. Hence it seems to be necessary to supply some energy from external sources. In the usual pickling process this is supplied by the dissolving of some of the metal itself, whereby good metal and acid must be consumed."

After telling the facts of electrolytic pickling as cathode in dilute sulfuric acid, and that the magnetic oxide is soluble under these conditions, he continues:

"The reason, apparently, is that the tendency to develop hydrogen at the cathode reduces the higher oxide to the lower one, which then is soluble chemically; or perhaps the higher oxide or the partially reduced oxide is dissolved electrochemically, as we know it is in the case of the peroxide of lead on the cathode in a nitrate of lead bath.

"Another factor is that the energy which it seems must be supplied when this oxide is to be

dissolved in sulfuric acid is now supplied by the current.-----"

Let us turn our attention once more to the actual experiments performed in the laboratory.

A solution containing 50 grams of potassium nitrate, 50 cubic centimeters of concentrated sulfuric acid and 1000 cubic centimeters of water was tried. Rusty iron treated as cathode showed little or no effect.

A solution of 10 cubic centimeters of hydrochloric acid and 500 cubic centimeters of saturated sodium chloride solution was tried. Also a solution containing 15 cubic centimeters of concentrated sulfuric acid in a saturated solution of sodium sulfate was tried. In neither case was there any cleaning action worth mentioning at the cathode.

Complex-ion Solutions.

The first special or complex-ion solution tried was a mixture of 5 per cent sodium hydroxide and .5 per cent sodium cyanide. This worked very well on screws containing a light coat of rust. A screw after being treated as cathode

4 or 5 minutes with .2 to .3 amperes came out clean without any black scale remaining. When this was tried on pipe fittings having a heavy coat of rust it did not work at all well. However, when the cyanide content was raised to about 3 per cent the results were quite satisfactory. The fitting came out clean with very little black deposit. The following equations and explanation show how the operators think the cleaning comes about.

$\text{Fe}(\text{OH})_3$ ionizes to Fe^{+++} and 3OH^- . The Fe^{+++} are reduced to Fe^{++} , but these ferrous ions are positive and hence are held very close to the cathode. Their high concentration interferes with the reduction of the ferric ions because of the mass law effect. The ferrous ions are redeposited as ferrous oxide forming a black scale. It seems reasonable to suspect that if CN^- were present they might form complex ions such as $\text{Fe}(\text{CN})_6^{---}$, which due to their negative charge would be drawn to the anode. It was hoped that these ions would be oxidized at the anode to CN^- and Fe^{+++} with the precipitation of Fe^{+++} as $\text{Fe}(\text{OH})_3$ but this did not seem to take place. If this had taken place the CN^- would have been regenerated and the process would have been cyclic. It seems that the

$\text{Fe}(\text{CN})_6^{4-}$ ions are oxidized only to $\text{Fe}(\text{CN})_6^{3-}$

This opinion is substantiated by the following facts. The sodium hydroxide, sodium cyanide solution after use gave a test for both ferricyanide and ferrocyanide. A solution of ferrocyanide,

made alkaline with sodium hydroxide and electrolyzed with platinum electrodes precipitated no $\text{Fe}(\text{OH})_3$ and gave a good test for ferricyanide afterward.

The solution was tested before electrolysis for ferricyanide and gave only a slight test.

Gas was evolved freely at both electrodes.

It was also found that a solution of ferricyanide would not reduce or remove rust effectively.

It seems reasonable then to suspect that the iron in the rust goes into solution as $\text{Fe}(\text{CN})_6^{4-}$ and is oxidized at the anode to $\text{Fe}(\text{CN})_6^{3-}$.

As a pickling process this would not be satisfactory because of the expense for the cyanide consumed.

It is possible tho that the salts could be recovered and sold as a byproduct. When sodium hydroxide

and sodium cyanide were used as an electrolyte gas was evolved freely at the anode. An effort was

made to find the nature of this gas. Some of the gas was caught in a test tube and gave a good

test for oxygen, however, the operators felt sure they detected the odor of cyanogen. This solution, like all the others, gave somewhat better results when hot.

Several other solutions were tried that contained ions that the operators thought might form negative complex ions in a manner similar to that outlined above. These will be enumerated and the results mentioned.

A 3 per cent oxalic acid solution was tried. This gave unsatisfactory results quite similar to those obtained with neutral sodium sulphate. About .5 per cent sodium hydroxide was added to the above solution with a slight improvement of results. The sodium hydroxide content was raised to 5 per cent and results somewhat similar to those with a 5 per cent solution of sodium hydroxide were obtained.

A 1 per cent solution of tartaric acid and a 5 per cent solution of sodium sulfate was tried. Unsatisfactory results similar to those obtained with a straight 5 per cent sodium sulfate solution were obtained.

A 10 per cent sulfuric acid and 2 per cent tar-

tartic acid solution was tried. The action was very similar to that of sulfuric acid alone.

A 5 per cent sodium hydroxide and a 2 per cent tartaric acid solution was tried. This gave better results than either of the two preceding solutions. The action seemed to be better than that of sodium hydroxide alone. However there seemed to be a tendency for the rust to be removed in spots. The current efficiency seemed to be rather poor as hydrogen was evolved from the first and action had to be continued for 10 or 12 minutes with a current density of about .3 amperes per square centimeter to get an average specimen clean. The specimen contained very little black deposit at the close of the treatment.

A 2 per cent citric acid and 5 per cent sodium sulfate solution was tried as well as a 2 per cent citric acid and 10 per cent sulfuric acid solution. Results very similar to the results with like solutions of tartaric acid were obtained.

A 2 per cent citric acid and 5 per cent sodium hydroxide solution was tried. This gave very good results. No hydrogen was evolved until after electrolysis had continued for some time if a low current density was used. The iron had more

or less of a dark appearance after treatment but there was no deposit. The metal was smooth when removed from the bath unless previously pitted by the rust. A $\frac{3}{4}$ inch L pipe fitting that had^a considerable layer of rust on it was cleaned with^a one ampere current in about 7 minutes. Gas was evolved at the anode continuously with all the citric and tartaric acid solutions. This was assumed to be oxygen. It seems very probable that the citrate ion concentration in this solution would remain constant and that the effect of the citrate ion would be cyclic, however that phase of the subject was not investigated because of the lack of time.

Solutions analogous to those prepared with citric and tartaric acids were prepared using sodium phosphate. No satisfactory results were obtained.

Since it has been reported* that a small per cent of formaldehyde aided in the chemical pickling of iron with sulfuric acid, some formaldehyde was added to a sulfuric acid bath, also to a sodium

* Griffin, R.C. (1920) The Solubility of Metals in Acids Containing Formaldehyde. J.I.E.C. 12:1159 - 60. Dec. 15, 1920.

sulfate bath, and an alkaline bath. The formaldehyde did not seem to give any assistance.

A solution of sodium sulphide, prepared by saturating a solution containing 96.6 grams of NaOH per liter with H_2S , was tried. A current density of about .1 amperes per square centimeter was used. Oxygen was liberated at the anode with apparently no effect to the specimen there. At the cathode hydrogen was liberated after the current had been running a short time. The rust on the cathode turned black. When the cathode was placed in dilute sulfuric acid a vigorous reaction set in with the liberation of hydrogen sulphide. The iron was left clean after being in the acid a few seconds. No current was passed. Apparently the iron had been reduced to the ferrous condition and reprecipitated on the cathode as ferrous sulphide.

More or less experimentation was carried on with borax solutions containing approximately 1 per cent of borax. A straight water solution of borax gave unsatisfactory results. One made acid with 2 per cent sulfuric acid also gave unsatisfactory results. However a solution made barely acid with sulfuric acid reduced the rust to a black

deposit similar to that obtained with sodium hydroxide.

An effort was made to secure titanium and vanadium salts as it was thought these might be reduced electrolytically and they in turn be oxidized chemically by the rust, since they are known to act in this way in certain other electrolytic reduction processes. It was not possible to obtain these salts. However a piece of vanadium steel was obtained and dissolved in acid. The residue was filtered off and fused with sodium hydroxide containing some sodium peroxide. It was assumed that this contained the vanadium in the form of sodium vanadate. A small portion of this mixture was added to a 10 per cent sulfuric acid solution but no improved qualities were noticed. The remainder of the mixture was added to a 5 per cent sodium hydroxide solution. This also showed no improved qualities.

To a 5 per cent solution of sodium hydroxide was added 1 per cent of chrome alum, $KCr(SO_4)_2$, hoping that it might react in the manner outlined for vanadium and titanium salts. The sodium hydroxide showed no improved qualities, however.

Some mercurous nitrate was added to a 5 per cent solution of sodium hydroxide. Mercury is

said to assist in the reduction of iron oxide in the Edison cell, perhaps by raising the hydrogen overvoltage. No improvement was noticed in the present instance however.

Anode Treatment.

A few experiments were made with the anode processes. It is evident that one of two classes of reactions may take place at the anode. Either a negative ion can be discharged or material may dissolve from the anode as positive ions.

It was in general found that in alkaline solutions, such as sodium hydroxide, sodium carbonate, or sodium sulfate with an excess of sodium hydroxide, it was almost impossible to get any reaction to take place at the anode other than the liberation of oxygen. One would suspect this as the large amount of OH^- ions present in such solutions would facilitate the discharge of these ions. Clean iron when treated in these solutions as anode showed very little change. In some cases there was evidence that some oxidation had taken place.

On the other hand with solutions of sodium chloride it was apparently impossible to liberate chlorine or oxygen from an iron anode. The iron

instead would go into solution, as ferrous ions as shown by the greenish color the solution assumed. By treating a sample first as cathode in sodium hydroxide and reducing the rust to a black scale, and then treating it as anode in a saturated sodium chloride solution with a high current density, a sample was obtained with an unusually bright, polished, metallic surface. With samples that had not been previously reduced, the action would take place only in spots eating holes into the sample. Even with samples that had been reduced there was a strong tendency to do this unless a high current density (1 to 4 amperes per square centimeter) was used. The more effective the reduction had been the lower the current density might be and still get effective results. The reason for this is quite evident for the iron that goes into solution is the metallic iron under any rust or scale that is on the specimen and as soon as a spot of free iron is exposed it is easier for iron to be dissolved there than elsewhere and the iron under a protecting coat of scale will not be attacked unless the current density is so high that part of the current of necessity passes thru the scale and dissolves the iron under it. The

treatment at the anode to give the specimen a bright luster after cathodic reduction requires only a fraction of a minute, if a high current density is used, as mentioned before. It was found that a saturated solution of sodium chloride worked much better than a more dilute solution.

Considerable experimentation was carried on with a mixture of sodium chloride and sodium hydroxide in the hope that a method might be evolved where by one sample might be reduced at the cathode at the same time another is being 'polished' at the anode. This did not prove very satisfactory tho, for the sodium chloride seemed to interfere with the cathode reaction somewhat and the hydroxide seemed to interfere somewhat with the anode treatment. This was probably due to the fact that a considerable part of the current would be carried by the hydroxyl ions and it would not be possible to get as concentrated solution of sodium chloride in the presence of sodium hydroxide as it would if the hydroxide were not present. Trouble was also encountered because of the fact that a high current density is best at the anode and a low current density at the cathode. This could, of course, be overcome by exposing a larger surface at the cathode, and it is possible

that with more experimentation a satisfactory process could be worked out along this line.

Neutral solutions of sodium sulfate and potassium nitrate were also tried. With a low current density in these solutions no oxygen was liberated and the iron went into solution. With a 5 per cent sodium sulfate solution it was found that a current density of about 1 ampere per square centimeter was about the maximum without the liberation of oxygen. With this current density, a specimen that did not have a very heavy scale left after reduction could be effectively cleaned. With a rather heavy scale tho it would not clean except in spots.

It is evident that any anode process has the same fundamental objection as the direct chemical pickling in acid, namely, good metal is dissolved from under the scale instead of the scale being dissolved off leaving the good metal unharmed. Anode treatment in saturated sodium chloride solution, however, gave the specimen a much higher luster than any other treatment tried.

CONCLUSION

1. Iron rust, such as appears on iron objects that have been exposed to the weather, can be reduced electrolytically.
2. This reduction takes place most effectively in alkaline solutions.
3. This reduction process apparently stops with some lower oxide of iron, and does not continue to metallic iron.
4. With all solutions, reduction was more effective at temperatures near the boiling point of the solution.
5. The nature of the material supporting the rust, and the nature of the rust deposit, itself, affects the ease of reduction.
6. Each of the following processes was fairly successful in the cleaning of rusty articles.
 - a. Reduction as cathode in hot 5 to 8 per cent sodium hydroxide solution followed by a short treatment as cathode in dilute sulfuric acid. This will give a clean metallic surface suitable for galvanizing.
 - b. By adding 2 to 3 per cent of NaCl to the hot sodium hydroxide solution a surface can be obtained with cathode treatment that is suitable for

pipe fittings. No tumbling would be necessary but there would probably be evolved small amounts of poisonous gas and the consumption of cyanide would probably be excessive.

- c. A hot solution of sodium hydroxide containing 1 to 2 per cent of sodium citrate gives as good or better results than the preceding treatment and there would be no possibility of poisonous gas. It is probable that the consumption of citrate would be very reasonable.
- d. Cathode treatment in sodium sulphide solution followed by immersion in sulfuric acid gives a metallic surface suitable for galvanizing. The hydrogen sulphide generated by the acid might be used in the preparation of more sodium sulphide.
- e. Anodic treatment in neutral saturated sodium chloride solution, preceded by reduction in solutions described under a, b, or c, gives a high metallic luster to articles.
- f. Before using any of the above processes extensively, it would be very advisable to make an extensive study of the effect of changes in temperature, concentration, current density, etc.

g. It is very probable that there are other electrolytes that would give better results than any of the above. The electrolytes used in electrolytic plating and refining processes are often complex in nature. Due to the short time allotted to this work no attempt was made to find the effect of mixing more than two substances in the electrolyte and then one of the constituents was usually some simple substance like sodium hydroxide or sulfuric acid. It is quite apparent that there is no end to the combinations that might be tried and these different combinations tried at various temperatures, concentrations, and current densities on various classes of materials. Hence no end of work might be done on the subject.

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