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REPORT ON

The Pickling of Steel Castings.

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ABSTRACT

The literature on pickling is reviewed and standard pickling practices and the use of inhibitors outlined. The behavior of cast steel in pickling is similar to rolled steel. The steel must be tested in the pickling solution in order to obtain true results. Pickling is responsible for a considerable loss in ductility of the steel. Sorbed atomic hydrogen is responsible for the embrittling effect. The magnitude of the internal stress in the steel or casting is important and determines the degree of embrittlement. The surface cracking of casting can result from pickling. Castings that do not crack during pickling will regain their ductility in air. The embrittlement is studied by tension, impact and internal friction testing. Because of the high internal stresses in steel castings it is recommended that pickling be discontinued and that sand blasting be substituted as a method of cleaning castings.

AUTHORIZATION

1. The studies on the pickling of steel castings were authorized by the Bureau of Engineering letter QP/Castings (5-18-Ds) of 20 May 1932.

OBJECT

2. The object of this report is to present the data obtained from a study to determine the effect of pickling on steel castings.

REVIEW OF PREVIOUS WORK

3. For many years attention has been directed to the embrittling of steel by acid, as encountered for example in the cleaning of surfaces prior to machining or the application of protective coatings. There has also been considerable discussion as to whether the cracks often found in pickled steel castings are caused, or merely uncovered, by the pickling operation. There is nothing in the literature which shows definitely the relative effects of the various pickling methods but the results of several series of experiments dealing with the problem have been published. One of the best of these was published by Johnson (1)* as early as 1875. The tests were carried out mostly on wrought iron wire with a few on steel wire. The wires were made brittle, as shown by the number of bends they would stand before breaking, by immersion in acid and by making them the cathode in acid, neutral and alkaline solutions. If the wires were made the anode they were unaffected even in acid solutions. If immersed inwater while still hot from bending, minute bubbles could be seen (with a microscope) to arise from the fracture. When the wires were left at 16°C (61°F) for three days, or heated to 200°C (392°F) for half a day, they regained their toughness. Johnson also found a loss in weight when pickled iron was annealed.

4. All this pointed to the theory of the occlusion of hydrogen in iron. Hydrogen was also found occluded when iron was made the cathode in an electrolytic cell and the same effects of brittleness and bubbling could then be detected. Tension tests were made on both annealed and bright iron after pickling "one hour in hydrochloric acid" and "twelve hours in very dilute hydrochloric acid," and compared with tests on wires similarly treated but then heated 12 to 48 hours to expel hydrogen. The former had lower tensile strength and elongation. Johnson also found that the presence of hydrogen in wire increased its electrical resistance. Diffusion of hydrogen in iron was shown by immersion of a wire in acid with half its length protected, diffusion taking place in iron to six times the extent it did in steel.

5. Cailletet (2) showed the extreme brittleness of electrolytic iron to be due to occlusion of hydrogen.

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*(1) Numerals refer to the bibliography included in the appendix.

6. Ledebur(3) quotes Hughes(4) who reported that brittleness was produced in iron after 30 minutes in dilute sulphuric acid, or after two minutes in the same acid if connected with zinc. The zinc protected the iron from attack by acid, but promoted the evolution of hydrogen at the surface of the iron, which pointed to the fact that the brittleness is due not to attack by acid but to hydrogen. Ledebur reports that brittleness is induced by immersion in 2.5% acid for 23 hours, 0.5% acid for 98 hours, or in contact with zinc in 2.5% acid for three hours. When tested immediately, there was considerable reduction in "bending quality" and in elongation in the tension test; but when held four days before testing, the values were found to be partially restored. Heating to cherry red nearly restored the original values. The embrittling effect produced by a vigorous electrolytic pickling was removed when the iron was allowed to lie for four weeks in a dry place. Brittleness was induced by 24 to 72 hours immersion in mine water containing acid or by two months rusting in the air, causing a reduction in the transverse strength of 1" (2.5 cm) square bars. Ledebur also determined the hydrogen content of pickled steels.

7. In 1889 Ledebur(5) gave evidence confirming his previous work and made further pickling experiments in which all pickling was done in contact with zinc in 3% sulphuric acid. Silicon in the steel seemed to reduce the liability to pickling brittleness, while carbon seemed to promote it.

8. Roberts-Austen(6) demonstrated that iron which has been made the cathode during electrolysis will exhibit the hydrogen points in a heating curve determination.

9. Heyn(7) found that iron heated above 730°C(1346°F) in hydrogen and quenched in water or mercury became brittle. Iron similarly heated in nitrogen and quenched was not brittle. The brittleness produced disappeared upon standing some weeks in the cold.

10. Burgess and Engle(8) found that unheated electrolytic iron dissolved in normal sulphuric acid almost twice as rapidly by weight as commercial zinc. After heating to 100°C(212°F) and cooling slowly, the rate of solution became the same as the least corroded form or iron tested, i.e., transfer iron.

11. Stromeyer(9) reports that contact with cold caustic soda of a concentration over 90° or 100° Twaddell not only causes mild steel to become brittle, but also tubes and plates crack and rivets fly off. This takes place even out of contact with the air where there is little corrosion. He states that this brittleness and corrosion occur only when the metal is in tension. Unstressed or compressed metal is not affected.

12. Longmuir(10) reports a very marked reduction in the toughness of rail steel as tested in alternating stress, when cleaned and pickled by various methods. Inexactness in reporting conditions of treatment impairs the value of the evidence, but he covers a wide range of treatments in various acids, re-heating, sand blasting and salt bath treatment.

13. Charpy and Bonnerot(11) observed that iron at ordinary temperatures acts as a membrane, permeable to nascent but not to molecular hydrogen. This was observed by experiment with hydrogen liberated from attack of acid on the iron membrane, and also by making the latter cathode solution. Osmosis occured only when the hydrogen was liberated directly upon the membrane. Pressures as high as 14 atmospheres were produced by such osmosis into a closed chamber.

14. Andrew(12) concluded from experiments upon iron and caustic soda that the embrittlement is due to the action of hydrogen in effecting a molecular re-arrangement.

15. Merica(13) and Parr(14) in considering boiler fractures made further studies on the effect of sodium hydroxide solutions at various temperatures on steel. There was considerable reduction of toughness in the alternating stress test. Parr concluded "that the embrittling effect of sodium hydroxide on steel is due to the evolution of hydrogen and the absorption by the steel of hydrogen in the nascent state".

16. Coulson(15) found that "hydrogen is absorbed rapidly by iron and steel when pickled either chemically or electrolytically as cathode in acid solutions thus causing brittleness, diminution of the tensile strength, elongation and reduction of area of the material" but that "iron and steel may be cleaned effectively and quickly by pickling electrolytically as anode, without impairing their strength, resiliency or other properties."

17. In this series of experiments the pickling bath consisted of a 27% solution of sulphuric acid kept at a temperature of 60°C (140°F). The electrolytic pickling time was 40 seconds. Steel springs were used for the test and all springs pickled chemically and as cathode electrolytically broke during the preliminary test which consisted of a continuous strain for twelve hours. The data, which was obtained by an alternating stress test, is given in Table I.

18. T.S.Fuller(16) also concluded that the absorption by the steel of atomic or nascent hydrogen liberated by pickling, or at the cathode in plating or electrolytic pickling, was the cause of the embrittlement of steel springs. Fuller also stated the embrittlement caused by plating could be prevented by first dipping the material in molten tin though in a later paper he shows that a layer tin tends to increase the rate of hydrogen penetration. The data obtained in the former experiments is given in Table II.

19. Thompson and Mahlman(17) investigated the relative efficiency or electrolytic and ordinary pickling but did not conduct any experiments to determine the embrittling effects of each method. They stated that electrolytic pickling was the more efficient method.

20. Watts and Fleckenstein(18) conducted a series of experiments to determine the cause of brittleness in electroplating and pickling. Watch springs were selected as the material for the tests, since, because of their thinness and temper they are particularly susceptible to brittleness. The test for brittleness consisted in bending the spring around a steel rod 1/4" in diameter. The untreated springs

withstood this test whether bent with or opposite to their natural curvature. Springs recorded as brittle broke when bent in the same direction as their curvature.

21. A spring was immersed in 30% sulphuric acid for 2 minutes and was very brittle. Springs were then used as cathode in several electrolytes some of which did not evolve hydrogen. As cyanide was believed to be responsible for the brittleness in plating by several observers some baths with free cyanide present were used. The data obtained, Table III, shows that in every case the presence of hydrogen caused brittleness while the material was not damaged if hydrogen was not present.

22. Treischel(19) found that when steel was pickled in a 3% solution of either hydrochloric or sulphuric acid the smount of hydrogen occluded in the steel was not sufficient to produce "blistering" when the steel was subsequently enameled. When, however, pickling was conducted in a 10% solution of either of these acids "blistering" subsequently occured.

23. Fuller(20) in a study of the penetration of iron by hydrogen found that the rate of penetration was greater for ordinary pickling than it was for electrolytic pickling as cathode. In the latter case the rate increased as the current was increased but not proportionately. In both cases the rate increased with temperature. Copper is not penetrated by hydrogen. Iron coated with tin is penetrated at a greater rate than untreated iron and zinc coated iron is penetrated at a rate less than that of untreated iron. The rate of penetration of nickel steel by hydrogen is roughly the same as that for iron.

24. In the discussion of this paper R. E. Zimmerman brought out the fact that hydrogen penetrated an unannealed steel much more rapidly than it did on annealed steel of the same composition.

25. Langdon and Grossman(21) conducted a rather complete study of the effects of pickling. The results obtained in this investigation may be summarized as follows. These effects were obtained by measuring the brittleness of plain carbon steel rods by the alternating stress method and of plates by the Erichsen penetration method.

Cleaning

(a) The strength of rods is practically unaffected by the removal of grease, either by means of organic solvents or by immersion in alkali.

(b) The removal of grease from plates causes a reduction of about 10% in the penetration values. That this change is probably due to a change in the surface condition rather than to an actual change in the physical properties of the steel, is indicated by the fact that the penetration value in certain instances approaches the original if the plates are regreased, especially if after regreasing they are slightly heated.

(c) Vigorous pumice brushing causes a reduction in strength of both rods and plates. This effect is obviously due to the scratching of the surface by the pumice.

(d) Electrolytic cleaning (as cathode) of rods or plates in the alkali cleaner does not produce any greater change than is caused by simple immersion in alkali.

Sand Blasting

(a) Sand blasting of steel rods in the "raw" state and also those which have been normalized, causes appreciable reduction in ability to withstand the alternating stress test. This effect is most marked with steel of relatively low or medium carbon content, e.g., up to 0.54%, for which the reduction is about 40%.

(b) Cold-rolled strip steel is only slightly reduced in ductility by sand blasting.

Pickling

(a) Pickling under "standard" conditions, i.e., 5 min. in 2 N sulphuric acid at 50°C (122°F) produces the following effects on rods:

(1) The stock as received is rendered increasingly brittle with increasing carbon content up to about 0.54% carbon. The brittleness produced in the high carbon steel is less marked.

(2) The brittleness produced in normalized steel rods decreases with increasing carbon content.

(3) The brittleness produced in hardened and tempered steel rods increases with increasing carbon content.

(4) These effects on rods were almost independent of size from 1/8" (3.2 mm.) to 3/8" (9.5 mm.) in diameter.

(b) The "standard" pickling produced the following effects upon cold-rolled stripsteel.

(1) The brittleness caused by pickling is greatest for steel that is "hardest", i.e., has received the greatest amount of cold work in its final stages of manufacture.

(2) Within the limits tested, the brittleness caused by pickling increases with the thickness of the strips.

(c) Increasing the temperature of the pickling bath from 0°C. (32°F) to 50°C. (122°F) causes increased brittleness, but above 50°C. (122°F) increasing the temperature has little effect.

(d) The brittleness increases with the time of immersion in the pickling bath. This increase is most marked up to 5 minutes immersion, after which the increase in brittleness is more gradual. Effects produced by long immersion are no doubt due in large part to solution of the metal, and consequently reduction in dimensions.

(e) Pickling in sodium acid sulphate (niter cake), hydrochloric acid, or hydrofluoric acid produces practically the same embrittling effects as in sulphuric acid of equivalent acid concentration.

(f) Nitric acid produces practically no brittleness in rods. It produces a slight reduction in penetration of strips, caused probably by the etching or roughening of the surface.

(g) Electrolytic pickling, whether the steel is made anode or cathode, or is made cathode and then anode, or if alternating current is used, causes about the same degree of brittleness as is produced by simple immersion in the same acid for an equal period of time. No doubt the effects due to immersion occur simultaneously with the electrolytic pickling, and may mask any minor effects of the latter. Electrolytic "pickling" as anode or cathode in a neutral sodium sulphate produced no brittleness, although hydrogen was evolved vigorously upon the cathode surface.

Treatment After Pickling

(a) Steel which has been rendered brittle by pickling becomes less brittle upon standing at ordinary temperature. With steel rods this recovery is nearly complete in three days. With steel plates the recovery is never quite complete, but reaches a maximum in about three days.

(b) In air, at higher temperatures, the maximum recovery takes place more rapidly, e.g., in about 2 hours at 100°C (212°F) and in 10 minutes at 150°C (302°F). Heating to 200°C (392°F) does not appreciably further increase the rate of recovery.

(c) When the embrittled steel is heated in water at 100° C (212°F), the maximum recovery occurs in from 2 to 5 minutes. The rate of recovery of rods is practically independent of size, up to 3/8" (9.5 mm).

(d) Brittleness produced by pickling in sodium acid sulphate, hydrochloric acid, or hydrofluoric acid, is removed under the same conditions as that produced by sulphuric acid. What slight brittleness is caused by pickling in nitric acid is not reduced by heating under any of the above conditions.

(e) In no case does strip steel give the original penetration values, even when the maximum restoration has occurred. The final value after pickling and heating is approximately the same as that obtained by nitric acid pickling. It is therefore believed that the effect of pickling consists of:

(1) A permanent effect, caused by the roughening of the surface.

(2) A temporary effect, due probably to occlusion of hydrogen.

(f) Treatment of embrittled steel rods with oxidizing agents, such as nitric acid or potassium dichromate solution, does not produce any measurable decrease in brittleness."

27. Williams and Homerberg(22) investigated the penetration of iron by hydrogen in electrolized hot caustic solutions. Their study of the penetration extended over a period of about a month. During this time the rate of penetration was determined at regular intervals, before the bar was loaded, while loaded below the yield point, at the yield point, and above the yield point.

28. The rate of penetration increased rapidly as the load was increased up to the yield point but stressing beyond the yield point did not appear to have any further effect upon the penetration.

29. Edwards(23) also studied the diffusion of hydrogen through iron and found that, at the same temperature, the rate of diffusion increases rapidly as the acidity is increased from 5% to 15% and very slowly as the acidity is further increased.

30. In a study of the effects of sulphuric and hydrochloric acids he found that for solutions of corresponding acidities the rate of penetration is greater for sulphuric acid than for hydrochloric. This holds for all temperatures and acidities.

31. Edwards states that the percentage of hydrogen that diffuses steadily decreases with temperature down to about 55°C (131°F), when it is only about 1/5 of the percentage which passes through at 96°C (205°F).

32. These two facts are interesting as Langdon and Grossman reported that there was no difference in the embrittling effect of hydrochloric and sulphuric acids. They also stated that the brittleness due to pickling increased with temperature up to about 50°C (122°F) but that an increase above this temperature had but little effect.

33. Edwards also conducted an experiment using single crystals of iron and found that the rate of diffusion was the same as that obtained in ordinary iron. This pointed out the fact that hydrogen passed through the iron and not through the grain boundaries as previous workers has believed. He also states that electrolytic pickling or the presence of suitable oxidizing reagents in the acids prevents hydrogen diffusion.

34. Pfeil(24) was the first investigator to determine the effects of pickling upon the tensile properties of iron. He divided the experimental work carried out during this study into three sections: (1) tests on iron in the normal finely crystalline condition, (2) tests on single crystals of iron and (3) tests on the boundry between two large crystals.

35. The tensile tests were carried out while the test pieces were still immersed in the acid (see Plate 1) as ferrous metals recover their normal properties on standing. The material used was 1/2" in diameter carbon steel rod which had been purified by prolonged

annealing in hydrogen at 750°C (1382°F) to remove carbon.

36. The test pieces were pickled electrolytically with a current density of 0.4 amperes per square inch of surface in an electrolyte of 10% sulphuric acid for one hour. Various concentrations of acid were used in the preliminary work but as no differences were observed the 10% solution was used throughout the remainder of the work. Current densities and pickling times greater than those used also failed to show any differences in the preliminary studies. The testing time was ten minutes.

37. Finely crystalline aggregates (Tables IV,V) tested during pickling at 25°C (77°F) showed a decrease in tensile strength of 9%, while the elongation was only one-sixth of that obtained in a normal test. The specimens broke suddenly as if made from a hard brittle material with a fracture similar to that obtained when metals are broken at temperatures near their melting point, i.e., a fracture that passes entirely between the crystals (intercrystalline). As the temperature is raised from 30° to 50° C (86° to 122°F.)(Table VI) the elongation increases and the fracture changes from intercrystalline to transcrystalline. The specimens showed many cracks at right angles to the length of the specimen. Near the fracture the cracks had opened up under the influence of the stress and the fracture itself occured in the position of the greatest crack.

38. From the results of the experiments on single crystals and on the boundaries between two large crystals, Pfeil concluded that hydrogen has a remarkable weakening effect on the intercrystalline boundary and that in addition to its effect on the boundaries, hydrogen decreases the cohesion across the cubic cleavage planes.

39. Pfiel also found that unless pickling was continued during the stressing (Table VII) the effect of the hydrogen was very slight. He pointed out that because of this the tensile test is of little value in investigating failures for which occluded hydrogen is thought responsible. As other investigators have shown that warming and cold work drives off occluded hydrogen, Pfeil attributes the failure of the tensile test to indicate the effects of hydrogen to the fact in the early stages of the tensile test the hydrogen is driven off and the normal properties restored.

40. H. Sutton (25,26) studied the embrittling effect of various methods of pickling and found that, in general, steel is embrittled by ordinary pickling in sulphuric, hydrochloric and to a slight extent in nitric acid. The degree of brittleness depended upon the composition and condition of the steel, as well as upon the conditions of pickling. The brittleness produced in a particular steel by pickling was greatest when the steel was in its hardest conditions and least when the steel was in its softest condition. Steel that was allowed to stand for several days at normal temperatures or immersed in boiling water for thirty minutes practically recovered its physical properties.

41. Sutton found that the addition of certain organic substances retarded the attack of the acid upon the steel. He found

no organic substances or colloids that prevented embrittlement although certain compounds, notably pyridine and quinoline, did decrease it appreciably.

42. Embrittlement was prevented by pickling electrolytically in neutral or alkaline solution under certain conditions but the de-scaling properties were very poor. In these solutions anodic pickling was generally found to be less injurious than cathodic pickling. Electrolytic pickling in 10% sulphuric acid was accompanied by severe embrittlement whether the steel was used as the anode of cathode. Cathode pickling appeared to be more effective for the removal of scale than standard pickling.

43. Schenechenbery(40) studied electrolytic pickling. He found that the pressure within a sealed steel tube, 1/4 inch thich when used as a cathode in an alkaline solution for several months, to be 2500 pounds per square inch. This increased pressure was due to diffusion by hydrogen. The high pressure caused by the accumulation of hydrogen at places where there are non-metallic impurities accounted for the formation of pickling blisters on sheet steel.

44. Dove(41) discusses the theory of scale formation. He shows how pickling influences the hardness of carbon steel sheets and that sheets hardened and tempered within certain ranges of temperature may develop surface hardness and perhaps crack on deformation during later operations after pickling.

45. Recently Slater(42) has completed an investigation on the effects of pickling on the properties of carbon steels and his observations are in substantial agreement with those of other investigations. In most of the experiments he used steel wires of different carbon contents and adopted the torsion test for studying the embrittling action. The test consisted of twisting a 8 inch length of wire between two headstocks, the number of twists through 360° to fracture being expressed numerically as a torsional value.

46. In the first experiment Slater studied the embrittling effect resulting from different immersion times of annealed wires in sulphuric acid. He also varied the strength of the acid and the pickling temperature. His results are listed in Table VIII. Embrittlement begins immediately the wires are placed in the pickling solution and the rate of embrittlement is especially rapid in the first few minutes. As the temperature and the concentration of the acid increase the initial rate of the embrittlement increases. However, the embrittlement is practically the same regardless of the acid concentration or temperature at the end of an hour. The carbon content of the wire sample does not appear to have any very appreciable effect on the rate of embrittlement. In all cases the wires become completely embrittled before the scale had been removed.

47. In the second experiment Slater studied the embrittling effect of hard-drawn wires pickled in 2 percent sulphuric acid at 20°C for varying times, (Table IX). The embrittlement of the hard drawn wires is mush more rapid than with the annealed wires, but in

this case, however, the torsional value is reduced more quickly in the steels of higher carbon content. The minimum torsional value obtained with the hard-drawn wire is considerably below that of the annealed wire.

48. A study was then made of the effect of pickling in Hydrochloric acid and in nitric acid, (Table X). With a 20 per cent hydrochloric acid pickle at 20°C the rate of embrittlement is approximately the same as that produced by a 5 per cent sulphuric acid solution at 20°C. Nitric acid effects a slightly more rapid deterioration.

49. A study of the action of inhibitors on the embrittlement of wires was undertaken. It can be seen from table XI that the rate of deterioration is much lessened by the addition of an inhibitor to the pickling solution. The time of immersion necessary for the complete removal of scale is slightly increased, but in every case the torsional value is quite appreciably above the minima resulting on pickling without an inhibitor. The effectiveness of the inhibitor decreases with increase in temperature of the pickle.

50. Along with the embrittlement studies Slater made recovery tests. He pickled wires in 2 per cent sulphuric acid for 20 minutes at 20°C, then allowed a time elapse and observed the recovery of the torsional values under the conditions as given in Table XII. The rate of recovery progressively increases with increase of temperature on heating in air, the maximum rate of recovery occurring immediately after removal from the pickle. Recovery on heating in water at 100°C is much more rapid than that obtained by heating in air at the same temperature.

51. Slater then proceeded to study the effect of pickling on the notched-bar impact value of carbon steel. Izod test pieces were pickled in 20 per cent sulphuric acid solution for 2 hours at 15°C and tested immediately (Table XIII). An increase in notched bar impact value occurred in each instance after pickling. This increase is somewhat variable and bears no relationship to the carbon content of the specimen.

52. Further test pieces were pickled electrolytically as cathode in 5 per cent sulphuric acid using a current of 0.5 amp. per specimen. (Table XIV). The results are most conflicting for with some steels there is a definite increase in impact value while with others there is an equally definite decrease. The change in impact value on electrolytic pickling appears to Slater to depend on some characteristic yet to be defined in each steel, and bears no relationship to the chemical composition of the metal. By allowing the impact specimens to remain exposed to the laboratory atmosphere for a few days, the original impact value was restored. A similar recovery could be effected by immersion in boiling water for 15 minutes.

53. Slater then studied the tensile properties of steel that had been pickled. His results are listed in Table XV. A slight increase in the ultimate strength occurred in specimens which had been pickled. The percentage reduction of area and the elongation are both

reduced. Steels of the higher carbon contents undergo the greatest modification in their properties. Slater also made hardness tests by Brinell. The steels were tested in the normalized and hardened condition after chemically and electrolytic pickling. With chemical pickling no change in hardness could be detected but by electrolytic pickling as cathode a small increase was obtained. The results are listed in Table XVI.

THE PHYSICAL CHEMISTRY OF PICKLING

54. Condition of Material to be Pickled.

(a) It has been shown by Pfeil(27) that iron or steel that is heated acquires a coating of scale. This scale consists of layers of oxide which decrease in oxygen content from the exposed surface down to the layer immodiately in contact with the metal. The nature of these layers and the extent of their development depends on the furnace atmosphere and the time and temperature of exposure. Winterbottom(28) noted that a scale coating formed in one day at 900°C consisted of three layers: an outer ferric-oxide layer forming about 2 per cent of the total thickness, and intermediate layer of magnetite comprising about 18 percent of the total thickness, and an inner layer of ferrous oxide amounting to approximately 80 per cent of the thickness. The over-all thickness of the scale was of the order of 0.16 inches.

(b) From a study of Pfeil's equilibrium diagram (Plate 2) of the iron-oxygen system, it is possible to obtain some idea of the constitution of the scale formed under the various temperature conditions. At temperatures below 575°C, the temperature of the Fe - Fe_3O_4 eutectoid separation, the scale can consist of only two phases, magnetite (Fe_3O_4) and ferric axide (Fe_2O_3). At higher temperatures the ferrous oxide (FeO) phase appears and as the temperature increases the scale thickness increases proportionately in the ferrous oxide content.

(c) Dunn(29) has shown that the formation of scale is a parabolic function of the time of scaling, and that the constant of the parabola, which determines its steepness, is an exponential function of the reciprocal of the absolute temperature. However, a complication arises in the theoretical explanations of the disposition and proportions of the scale layers in the form of cracking of the scale during its formation. This cracking allows for diffusion of oxygen from the crack and thus a departure is made from the parabolic law. The thickness-time graph in such circumstances consists of a series of parabolic segments approximating more nearly to a straight line.

(d) A deficiency of oxygen in the atmosphere producing scaling would result first in a reduction in the rate of scaling and progressively in the suppression of the outer oxygen rich layers, until eventually non-scaling conditions were reached.

(e) One other point in scale formation was brought out by Pfeil(31). He pointed out that the constitution of scale not only varied with the temperature at which it was produced, but was also affected by the rate of cooling which was carried out. In slow cooled material the inner scale layer dissolves in acid with a much greater rate than does a rapidly cooled material. The change in rate of solution with rate of cooling appears to be due to the eutectoid transformation - ferrous phase into iron and magnetite.

55. Theories Proposed.

(a) Several theories have been proposed to explain the removal of scale during pickling. The theory having the most popular following is that the acid dissolves the scale; however, the observed facts lead one to believe that the entire story has not been told as it is common knowledge that a scale sludge accumulates in pickle tanks in the course of working. Edwards(23), Chappel and Ely(39), and others have maintained that scale is negligibly attacked by the acid, but that the vigorous action on the underlying steel, to which access is gained by cracks and pores, leads to mechanical bursting-off of the scale layers. This outlook also lacks completeness, as no allowance is made for the case when inhibitors are used to reduce the action on the steel and at the same time not lessening the scale removal.

(b) It is Winterbottom's and Reeds'(30) opinion that the inner ferrous-oxide phase layer dissolves in pickle acid comparatively quickly, while the oxygen-rich phases, magnetite and ferric oxide are practically unattacked. Thus, at a scaling temperature of 900°C, about 80 per cent of the scale is dissolved and the remaining 20% falls from the piece and accumulates as a sludge in the pickling tanks.

(c) It is difficult to discover what occurs in the pickling of low temperature scales. Although these scales are thin, they require a much greater time to pickle than do the thicker ones formed at higher temperatures, a result that is not unexpected, since the FeO phase is absent according to the diagram.

(d) Hoor(32) explains the theory involved in the pickling of low temperature scales in a very satisfactory way. He shows the conditions that exist at a crack or pore in the scale. Here it can be expected that the cell would be set up in which the oxide scale

Scale : Acid : Metal

was cathodic towards the metal. Iron therefore would be dissolved anodically as $Fe^{\cdot\cdot}$, and scale would be reduced cathodically to ferrous oxide; the latter then dissolved in the acid, exposing fresh ferric oxide for cathode reduction. Thus, only ferrous iron would be found in solution, which Winterbottom and Reed(30) found to be experimentally correct. Since, however, the electrolytic action would be most pronounced near the scale-metal interface, where the internal resistance of the cell was smallest, the main solution of scale and metal would occur in these regions; thereby an undermining of the scale would set in, and it would eventually flake off.

56. <u>Kinetics of Pickling.</u>

(a) The chief variables that affect the time of pickling are the type and concentration of the acid, the temperature, the state of agitation, the concentration of iron salts, and the type and amount of the inhibitor.

(b) Winterbottom and Reed(30), by using a standard material, worked out the pickling times at various temperatures and concentrations of sulphuric and hydrochloric acid. Their results are given in Tables XVII and XVIII.

(c) It will be seen that above 30 gms per litre the pickling time varies in a practically linear manner with the concentration.

(d) In order to make their work complete, they studied the effects of progressive additions of ferrous sulphate in the case of sulphuric acid, and ferrous chloride in the case of hydrochloric acid on the pickling times (Table XIX).

(e) Winterbottom and Reed made the following conclusions concerning their experiments:

(1) The mechanism of scale removal is the same in the case of dilute sulphuric and hydrochloric acids, and by inference, the same in the case of any acid forming soluble ferrous salt.

(2) Provided that over-pickling is avoided, the acid consumption is directly dependent on the type and amount of ferrous-oxide phase. That is to say, the fundamental action in pickling is

$$\underset{\text{(solid)}}{FeO} + 2H = Fe^{\cdot\cdot} + H_2O$$

This is a heterogeneous reaction, and its rate should therefore be dependent on the hydrogen ion activity, the viscosity of the pickling acid, and the diffusion constant.

(3) The rate of pickling is directly proportional to the acid content at constant temperature, provided that the bulk of acid solution is sufficient to avoid appreciable alteration in concentration during pickling.

(4) The time necessary for removal of scale is dependent on:

(a) The temperature and time of formation of the scale.

(b) The hydrogen ion activity of the acid solution.

(c) The viscosity of the solution.

(d) The temperature.

(e) The iron salts.

(f) Agitation.

Of these, the temperature, both directly and also by its influence on (b) and (c) has by far the most important effect on the time of pickling a given material.

INHIBITORS

57. In general pickling inhibitors should be used, not only for a saving in acid that is likely to be made, but as an insurance against over-pickling and wastage of valuable material.

Physical Chemistry of Inhibitors

(a) Numerous substances do retard the action of free acid on steel and have therefore been suggested for use as inhibitors. Most of the commercial inhibitors are cyclic organic compounds containing at least one atom of nitrogen in the ring, as, for example, pyridine and quinoline. Many such cyclic organic bases show, to a considerable extent, a specific action in retarding the solution of the metal in the acid. This specific effect is probably due to the deposition of the inhibitor as a protective film on the metal or to some scientific action of the inhibitor in retarding the formation of free gaseous hydrogen.

(b) Only a few investigators have studied the mechanism of the action of inhibitors in minimuzing the corrosion of metals by dilute acids. Isgarishev and Bergman(33) have observed that certain colloids, for example, gum arabic and geletin, increase the apparent overvoltage of iron in contact with sulphuric acid. Siverts and Lueg(34) measured the apparent overvoltage of iron in contact with dilute sulphuric acid containing various heterocyclic nitrogen bases, but were unable to establish any general or quantitative relationship between the effect on overvoltage and the inhiniting efficiency. They suggested that the inhibiting action was due to the formation of an inactive film at the surface of the metal, but gave no data to support this hypothesis. Speller and Chappell(35) point out that many of the inhibitors are violent animal poisons and some are known to have a marked effect in certain catalytic processes. They further stated that the combination of these observations seems to justify placing the action of inhibitors in the general class known as catalysts. Inhibitors may be considered to act by forming some sort of film over the bare cathodic steel and this film acts to prevent the ready evolution of hydrogen.

(c) Chappell, Roetheli, and McCarthy(36) measured the effects of quinoline ethiodide, in various concentrations and under various conditions, upon the rate of evolution of hydrogen from iron and dilute acid and also upon the apparent over-voltage between iron and acid. They found that there was a general parallelism between the retardation of the evolution of hydrogen and the apparent overvoltage when the iron was made cathode in the acid solution. The effect of the inhibitor on the anodic overvoltage was slight and was considered insufficient to account for the inhibiting effect. These investigators conclused that when iron is placed in a dilute acid solution containing an inhibiting base, the inhibitor is set free at the locally cathodic areas, and the mechanism of inhibitive action is possibly due to the formation of a blanketing layer of discharged inhibitor substance absorbed on the cathodic areas.

Rhodes and Kuhn(37) studied the inhibiting powers of a large number of compounds, and concluded that in every case the addition of a specific inhibitor to the acid electrolyte increased the film resistance at the surface of the metal. They also pointed out that there is no quantitative relationship between the inhibiting efficiency of a given substance and its effect upon the true resistance at the interface. They also claimed that from their data it appeared that the absorption of the inhibitor upon the surface of the metal is a necessary condition for inhibiting action, but that the inhibiting action is not due solely to the effect of the absorbed film in increasing the electrical resistance between the metal and the electrolyte. The indications are that the protective action is due to some specific property of the absorbed film.

Inhibitors

(a) Chappell, Roetheli and McCarthy(36) studied a large number of inhibitors and their effect on the hydrogen evolution from steel. (Table XX)

(b) Rhodes and Kuhn(37) measured the inhibiting power of various cyclic organic compounds. In their experiments the rate of evolution of hydrogen was determined over a period of from 5 to 6 hours.. In the data, Table XXI, the inhibiting effect of the added substance is expressed as "percent inhibiting power". If A represents the rate of evolution of hydrogen when no inhibitor is present, the inhibiting power of that concentration of that inhibitor being calculated as 100 (A-B)/A.

(c) Speiler and Chappell(38) studied 13 inhibitors and the rate of hydrogen evolution. Their data is shown diagramatically in Plate 3.

(d) Chappell and Ely(39) studied about 25 inhibitors by the hydrogen evolution method and listed them (Table XXII) according to their inhibiting power. They concluded from their experiments with inhibitors that

(1) The amount of acid used in dissolving steel is a variable which can be controlled by an inhibitor;
(2) a small amount of acid is wasted in spent pickle;
(3) and the practical efficiency of a commercial inhibitor may be estimated from a simple hydrogen evolution test.

(e) Winterbottom and Reed(30) made a comparison of the effect of inhibitors on the pickling time of different strengths of sulphuric and hydrochloric acid solutions and from this figured the efficiencies of the inhibitors used. Their results are listed in Table XXIII. Their results showed that inhibitors increased the pickling times. The increase, however, was rather small.

(f) Concerning inhibitors, it can be said that they are helpful in preventing the acid from attacking the base metal and even though they increase the time of pickling they should be used in practice if the best procedure is desired.

BEST COMMERCIAL PICKLING PRACTICE

57. Based on the literature survey above, the following methods of pickling employ the best commercial methods. These processes should be technically controlled as to temperature and chemical requirements. Routine tests must be made if the results are to follow.

Hydrofluoric Acid Pickling.

58. Hydrofluoric acid is used to remove sand from the deep cored pockets of castings. The procedure as recommended by the Steel Founders Society of America is as follows:

Hydrofluoric acid	7% by volume
Hydrochloric acid	8.5% by volume
Water	84.5% by volume

59. The temperature should be 130°F for approximately one hour in order to attain the best results. However, good results are obtained when the solution is used at room temperature.

60. Before pickling, all loose sand should be removed, as otherwise acid would be wasted in dissolving sand that could be removed more economically by sand blasting.

61. After pickling, the castings should be washed with water and the placed in a sodium carbonate bath to neutralize the acid remaining.

62. As in sulphuric and hydrochloric pickling, an inhibitor should be used in order to minimize the acid attack on the steel.

63. Langdon and Grossman(20) showed that pickling in hydrofluoric acid produces practically the same embrittling effects as in sulphuric acid of equivalent concentration.

SULPHURIC ACID

Initial Concentration: A concentration of from 5 to 10 percent is most commonly commercially used. Suggest using a concentration of 50 grms of H_2SO_4 per litre (4.85%) by taking one part of volume of H_2SO_4 and 26 parts by volume of water (65 pounds per 100 gallon water). Density 1.062.

Temperature: Keep free-acid content up to 50 gms of H_2SO_4 per litre (4.85%, density 1.062) by additions of sulphuric acid as necessary, but on no account add more than a total of 250 lbs of sulphuric acid per 100 gallon of tank volume.

Finishing: Additions should be discontinued when the specific gravity of the liquor reaches 1.17. When the final addition has been made the activity of the liquor should be maintained as far as practicable by raising the temperature, and, if possible, the tank should be changed over to work as a preliminary rough pickle. When the activity has fallen below the point where the free-acid content is below 10 grms per litre, the liqour should be discarded. The discarded liquor should approach: 10 gms or less of H_2SO_4 per litre; 80 gms per litre of iron; and specific gravity 1.20.

Inhibitor: Inhibitors that are acceptable under the Navy Department Specification 51-I-2, March 1, 1930, will furnish good results.

Immersion Time: Immersion time is a variable depending on the size of the casting, the time and temperature of heat treatment, and the rate of cooling.

Neutralizing bath: The bath most commonly used is a 10 per cent sodium hydroxide solution at a temperature of 60 to 80°C.

Removal of Absorbed Hydrogen: Steel which is rendered brittle by pickling becomes less brittle upon standing at ordinary temperatures. The recovery is never quite complete, but sections of about 3/8 inch reach a maximum in about 3 days. In air at 100°C the recovery takes place more rapidly, about 3 percent of the previous time, while at 150°C the recovery is about 0.3 percent of the original time of 3 days. Heating in water at 100°C is the best practice and maximum recovery occurs in from 2 to 5 minutes on sections up to 3/8 inch.

HYDROCHLORIC ACID

Initial Concentration: A concentration of about 10 percent is most commonly used. Suggest using a concentration of 100 gms of Hcl per litre (9.7%) by taking one part of acid by volume per 2 parts (about) of water (530 lbs. per 100 gal. of water). Density 1.045.

Temperature: 30° to 40°C. Warm up initially by steam injection or by charging warm material from previous operation. Temperature will then be maintained by the heat of reaction.

Maintenance: Keep free-acid content between 50 and 100 gms of Hcl per litre by additions of acid as necessary, but on no account add more than a total of 720 pounds of acid per 100 gal. of tank volume. Additions should be discontinued when the specific gravity of the liquor reaches 1.20.

Finishing: The same remarks apply as for sulphuric acid, and the discarded liquors should approach: 10 gms per litre of Hcl or less; 120 gms per litre of iron; and specific gravity of 1.24.

Inhibitor: Same as for sulphuric acid.

Neutralizing Bath: Same as for sulphuric acid.

Removal of Absorbed Hydrogen: Same as for sulphuric acid.

EXPERIMENTAL METHODS

64. The studies to determine the effect of pickling on the impact strength of cast steel were conducted on cast steel bars 1" x 1" x 18". These bars were cast eight in a mold both with and without flanges. The bars without flanges should solidify with a minimum of internal strains while the bars with flanges, unable to contract because of the flange, should have considerable more internal strain. These bars were machined to 3/4" x 3/4" x 6", notched for the Charpy impact test, pickled and tested.

65. The pickling procedure in all experiments was similar to that used in commercial practice. The bath consisted of a 10 percent sulphuric acid solution kept at a constant temperature of 65°C (150°F) by means of a mercury thermostat which controlled two large incandescent heating bulbs immersed in the solution. The inhibitors used were Rodine and Quinoline ethiodide, a pure chemical inhibitor which has been found to be very efficient. After pickling the specimens were dipped in a 10 percent sodium hydroxide solution to neutralize the acid remaining on the specimens and then washed in hot water (75°C or 167°F) and dried.

66. In the study of elongated and pickled tensile specimens the test pieces were prepared from cast cupons. The standard 0.505 inch diameter test specimens were used. One half of the specimens were placed in a furnace at a temperature of 900°C (1650°F); ten minutes were allowed for the specimens to come up to heat. The specimens were kept at heat for 20 minutes and then furnace cooled.

67. Specimens were elongated 0.5, 1.0, 1.5 and 2.0 percent in a tensile machine, removed and pickled, and then tested. In elongating, 2.0 percent was chosen as maximum as a casting completely hindered in contraction would be equivalent to only 2.2 percent. Considerable time, about 3 hours, elapsed between the pickling and the testing.

68. In the study where the effects of testing in the pickling solution were determined the standard tensile specimens were used. A cup was attached to the specimen for holding the pickling solution as is shown in Plate 1. The specimen was put in place in the tensile machine and then the acid was poured around the specimen. When chemically pickling, the solution was kept at 65°C by electrically heating the glass container by means of a nichrome coil around the glass container. In electrolytic pickling a platinum wire helix was used first at the cathode and then as the anode. The electrolytic pickling was carried on at room temperature.

69. After the specimen had pickled a predetermined time, which was usually an hour, since Slater(42) and Pheil(31) had shown that an hour was sufficient for maximum embrittlement, the specimen was tested to failure in the acid.

70. In studying the recovery from embrittlement the specimens were pickled for one hour then washed in water and tested in air at room temperature after allowing them to stand in air at room temperature for the predetermined time.

71. It was thought advisable to conduct some experiments on castings to show the effect of pickling on different shapes. Two small castings somewhat similar in design were chosen for this purpose. One, the Hall pattern, shown on Plate 5, is designed in such a manner that the small member used in testing is in compression upon solidifying. In the N.R.L. design the center member, used in testing, is in tension upon solidifying. The direction of the forces caused by solidification are shown by the arrows. The castings were poured in green sand so that any stress present would be due to solidification alone.

72. Both types of castings were pickled in a bath of 10 percent sulphuric acid, maintained at a temperature of 65°C (150°F) for 45 minutes. After pickling the castings were washed in cold water and then, as the stresses were not sufficient to crack the castings, the small member of the Hall pattern and the center member of the N.R.L. design were cut off and tested in a tensile machine. The test pieces were cut off as rapidly as possible and tested immediately in order to prevent as much recovery of embrittlement as possible. Cold water, rather than hot water, was used as a wash for the same reason. The average time required to wash, cut off and test a specimen was approximately 12 minutes.

73. The small member of one of the Hall castings was cut in two and the amount of contraction measured. This amounted to 0.021 inches.

74. The center member of one of the N.R.L. castings was also cut and the resulting expansion measured. This amounted to 0.023 inches. The casting was then placed in the testing machine and compressed to the original dimensions. The load required was 11,360 pounds per square inch. The actual stress in the casting was probably of this order although this method of obtaining the stress is not accurate.

75. The results and conclusions of other investigators have pointed out that all acids commonly used in pickling cause a weakening at the grain boundaries of pickled steel. Since this is the case pickling should have an effect on the internal friction of steel as measured on the apparatus designed and reported on by Dr. R. H. Canfield of this Laboratory. (Report No. M-1029, 28 Feb.1934). Therefore a cold rolled steel specimen of a medium carbon content was selected and tested while pickling. This specimen had previously been twisted through an angle of 180° but as considerable time had elapsed since it was twisted the aging effect was considered to be negligible.

76. In order to carry out the pickling operation the bottom of the hollow specimen was closed by a rubber stopper. A platinum wire, to be used as the anode, was run through the center of the specimen. After a set of readings had been taken to obtain the curve of the unpickled specimen 10 percent sulphuric acid was placed in the center of the specimen. It was then pickled electrolytically as the cathode with a current density of 0.4 amperes per square inch. Readings were taken periodically during the pickling operation.

77. The specimen was pickled for two hours and then the acid was removed and the specimen washed with distilled water to remove all traces of acid. Readings were taken at intervals to determine the rate of recovery after pickling.

78. The method of testing was the usual procedure except for the pickling operation and the fact that the machine was kept running at a low amplitude (2 cm) between readings. The results of this test are shown on Plates 7 and 8.

79. The results of this test were so encouraging that some specimens were machined out of cast steel for another series of tests. The precedure was modified slightly by placing a glass cup similar to that shown on Plate 1 around the specimen. The acid was placed in this cup and the specimens pickled cathodically using a platinum helix as the anode.

80. Tests were made on specimens in the unannealed and annealed conditions. One of the annealed specimens was twisted through an angle of 0.4 degree, by means of helical springs attached to the pendulum on the machine, in order to demonstrate the effect of stress on the pickling action. The results of these tests are shown on Plates 9 to 12, inclusive.

DISCUSSION OF RESULTS

81. Although the effects of pickling on steel have been studied by many investigators all of the experimental work has been confined to cold rolled steel in the forms of wire, strip, or rods. Since no data are available on cast steel in either the "as cast" or heat treated conditions it was deemed advisable to conduct several experiments on this material in order to determine whether or not pickling was responsible for or merely uncovered the cracks which are often found in pickled castings.

82. It has been previously pointed out by various investigators that pickling is responsible for an embrittlement effect caused by atomic hydrogen. Experiments were planned to study this embrittling effect, its extent, and amount in cast steel.

Effect of Pickling on Experimental Castings:

(a) The small pickled castings showed definitely that the important stress in embrittlement by hydrogen is tension. The results of the tests on the pickled Hall castings showed that the pickling had no great effect on the member in compression as there was no drop in tensile strength and practically no change in ductility.

(b) The tests on the N.R.L. design using the member in tension showed that this stress was very important. Even though the specimens were pulled in air after the interval of 10 to 12 minutes required to saw off the specimen and set it up in the tensile machine there was a decided drop in physical properties.

	Tensile Strength Lbs.per sq.in.	Elongation %	R.A. %
"As Cast" specimen	67,700	17	23
Pickled specimen	60.950	7.5	13

The Effect of Pickling on the Impect Strength of Cast Steel:

(a) In was thought that cast steel would be subject to considerable change of impact strength by pickling, and that the general effect produced would be of an embrittling nature. It was also reasoned that steel cast with high internal stress would show a greater degree of embrittlement than a stress-free steel. Tests were carried out according to the conditions of Table XIV.

(b) The results were somewhat surprising. In part they showed the same feature of toughening as Slater(42) found in his experiments on hot rolled rods. This feature of toughening was apparent on only the free contracting series. In the hindered contracting series an embrittlement action was noted. It would appear, therefore, that perhaps the condition of the steel is very important in determining its reaction after pickling. By this it is not inferred that the amount of internal stress is the controlling factor as it can be seen that in the case of the annealed specimens one set became embrittled while the other obtained a certain degree of toughening.

(c) The impact test is of a dynamic nature and does not involve a time factor which is often of considerable magnitude as is found in the tensile, bend, or torsion tests. It is true that dynamic tests will give some measure of the properties of the interstitial solid solution initially formed and perhaps this accounts for the varied results obtained.

(d) Considerably more testing must be done however to prove this point. It was not especially desirable to continue experimentation along this line as the test did not strictly represent conditions found in practice, as pickled castings failed usually in tension and not by the application of an impact force.

The Effect of Pickling on Previously Elongated Tensile Specimens:

(a) Since all castings have internal casting strains of some magnitude it was decided that by elongating tensile specimens prior to pickling, an idea as to the relative stress condition necessary for marked embrittlement would be obtained. The test results are listed in Table XXIV and shown in Plate 4.

(b) It will be noticed that the magnitude of embrittlement remained the same regardless of the amount of elongation. In fact, specimens that were pickled without elongation showed an embrittlement action equal to that of the elongated specimens.

(c) Changes were found to exist in the yield point, the elongation and the reduction of area. The tests were made approximately three hours after the pickling operation.

(d) The series of tests checked in general the work of other investigators in that tensile testing following pickling showed a slight reduction of ductility. The tests also pointed out that the internal stress obtained by elongating specimens 2 percent was not sufficient to cause a marked embrittling effect.

Effect of Pickling on the Tensile Properties of Cast Steel When the Testing is carried on in the Pickle.

(a) Pfeil(31) has shown that the embrittlement effect is much more pronounced when testing is carried on in the pickling solution. As castings which become cracked undoubtedly fail during pickling, such a test would give the amount of stress necessary to cause failure.

(b) The results obtained from the study of testing in the pickling solution are set forth in Table XXVI. The ductility has dropped off considerably. There are no differences in the physical properties obtained when the specimens are pickling either under stress or free of stress, even though the stress used is of a magnitude, approximately one-half of the tensile strength. The time element of pickling is important if full embrittlement is desired. This is in line with the work of Slater(42). When the specimen is removed from the pickling bath and tested in air the ductility has increased and the specimen is already on its way to recovery.

(c) The important thing that this study points out is that the internal stress must be extremely high before failure takes place.

Effect of Time in Air on the Rate of Recovery from Embrittlement:

(a) It was noticed in the preceding experiment that the ductility increased considerably as soon as the specimen was taken out of the acid. The rate at which this recovery takes place was of interest and the results as set forth in Table XXVII and Plate 7 show several interesting points. A 7% decrease in tensile strength, a 60% decrease in elongation and a 64% decrease in reduction of area were obtained by testing in the pickling solution. The recovery takes place at a very rapid rate during the first few minutes. Previous investigators have shown that in time the material recovers nearly all its ductile properties.

(b) From these results two things become apparent. First that the embrittling effects produced by pickling are not permanent in cast steel, and second, the physical properties of a material undergoing pickling are very much reduced.

(c) In Plate 6, a comparison can be made between annealed specimen (A) and a specimen that was tested in the pickling solution (B). The embrittling effect in (B) is shown by a lack of reduction of area as compared with (A). The specimens tested in the pickling solution also exhibit many small cracks. These cracks develop about the time the ultimate tensile strength was reached, just a short time before the specimen broke. As will be noticed these small cracks are numerous and account for nearly all of the elongation obtained. The break is very typical of an embrittled material.

(d) The specimen (C) offers a very interesting example. This specimen was pickled in the acid. The acid was removed with a pipette and a water wash substituted which likewise was removed. Because of haste a very small amount of very dilute acid remained in the bottom of the cup and around the fillet of the specimen. Upon testing, the specimen broke in that portion which was subject to the attack of the very dilute acid, which points out that the very slight pickling effect was sufficient to select the breaking location. The hydrogen penetration through this area had not stopped and consequently the physical properties were at a minimum whereas the remainder of the specimen was on its way to recovery from embrittlement.

(e) Since other investigators have studied at great length the effects of electrolytic pickling it was thought advisable to compare this method with the chemical pickling methods. In Table XXVIII the results of this study are compared. The chemical pickling is the more drastic although there is very little difference between it and the cathodic pickling. The effect of anodic pickling is not as pronounced though the specimens were very badly pitted. This however might have been prevented somewhat if an inhibitor had been added.

(f) Considerable has been said about the action of inhibitors and the results of other investigators have been presented. Therefore, it was not considered advantageous to go into lengthy testing with various inhibitors. The important feature that was brought out in the study of inhibitors (Table XXIX) is that they are responsible for a decrease in the degree of embrittlement. This decrease in the amount of embrittlement is very small. The reason the inhibitor is beneficial in preventing the embrittlement from attaining its full value probably lies in the fact that it reduces tha acid attack on the steel and consequently there is not as much hydrogen formed to penetrate the specimen. It does not prevent embrittlement as certain commercial concerns have suggested.

<u>The Effect of Pickling on the Internal Friction of Steel</u>:

(a) The change in internal friction caused by pickling draws attention to several interesting facts. Although it is as yet impossible to state just what actually causes this change, data previously obtained on this machine with various other samples would lead one to believe that the change is caused by a weakening at the grain boundry, or possibly, a change in the lattice itself. Previous investigators, notably Pheil(24), have come to the conclusion that the weakening effect of pickling is to be found at the grain boundaries or in the octahedral planes of the crystal.

(b) The changes in internal friction occurring when a medium carbon cold-rolled steel is pickled in 10 percent sulphuric acid are shown on Plate 8. It will be noted that the change is very rapid at the beginning of the test and decreases as the pickling time increases. That is, the increase in internal friction obtained by pickling in the first 10 minutes is greater than that which takes place between one and two hours.

(c) The recovery from embrittlement (Plate 9) occurs in almost the same way in that the rate of recovery decreases as the time in air increases. In this case the normal curve of the unpickled specimen is again obtained upon standing in air for two hours.

(d) The "as cast" steel specimen (Plate 10) shows an increase in internal friction upon pickling similarly to the cold rolled specimen although the effect is not so great. This is probably due to the fact that the cold-rolled specimen had previously been twisted through an angle of 180 degrees and, therefore, was in a more stressed condition.

(e) The annealed specimen, which was obtained not only from the same heat but from the same test block, shows (Plate 11) even less change in internal friction upon pickling.

(f) These results agree very well with those obtained by previous workers and in the tensile tests mentioned above. That is, the degree of hydrogen embrittlement appears to be a function of the amount of stress present in the pickled object. This appears to be quite reasonable as it is logical to assume that the amount of embrittlement is proportional to the amount of hydrogen present. Williams and Homerberg(22) have shown that the amount of hydrogen penetrating a specimen increases as the load increases up to the yield point. Above the yield point an increase in the load does not increase the amount of hydrogen penetration.

(g) In order to show this fact more conclusively this same annealed specimen was tested under acid and twisted through an angle of 0.4 degrees by helical springs attached to the vibrating pendulum. The stress induced in the specimen by such a small amount of twist, approximately 7000 pounds per square inch, is sufficient to cause considerable increase in the internal friction upon pickling (Plate 12). It should also be noted that after pickling for thirty minutes there is no increase in the internal friction (embrittlement) with this specimen.

(h) The recovery from pickling embrittleness was also studied with this specimen (Plate 13). It will be noted that although the sample does recover to some extent the recovery is not complete even after standing eight days in air.

CONCLUSIONS

83. It has been shown from the preceding data that pickling is responsible for an embrittling effect. This brittleness is brought about by an absorption of atomic hydrogen by the steel.

84. A careful search of the literature indicates that there is no conclusive evidence yet available regarding the manner in which the atoms of absorbed hydrogen are distributed through the mess of solid iron. There appears to be considerable conflicting evidence as to the existence of metallic hydrides, however it has been shown by several observers (43) that an increase in volume and a change in electrical conductivity occur in most metals when absorption takes place. With copper, palladium and platinum, a positive expansion of the space lattice has been measured. It is also known that absorption forces can cause spontaneous pulverisation especially in the softer metals. It is likewise apparent that the absorbed hydrogen can eventually collect in the form of local concentration areas, which have the power of disrupting the space lattices to form a discontinuity.

85. Slater(42) believes that the absorption evidence suggests that the hydrogen atom is initially held interstically in the space lattice and that absorption of further quantities of hydrogen may result in the attainment of a second stage in which hydrogen agglomerates at local areas such as grain boundaries and non-metallic inclusions. Then if a relatively showly applied stress and deformation, such as those occurring in the tensile, bend, or torsional tests, is applied it will result in the breakdown of the initial interstitial solid solution, with subsequent agglometation of hydrogen to produce a series of local stress concentrations or even disruptions.

86. Pickling is responsible for low ductility and for a slight loss of tensile strength. It is exceedingly difficult to measure the yield point when specimens are tested in the pickling bath so no data is presented as to the effect of pickling on the yield point. Specimens that are pickled and tested in air show a greater yield point, or at least the same yield point, than those which have had no pickling treatment.

87. Pickling does cause cracking in castings. The actual process is not known. It is known however that the cracking depends on certain things which are, a casting of a high internal stress and the action of the pickling solution.

88. There appears to be no record of castings failing to complete destruction by pickling. What is usually encountered is a series of surface cracking which may or may not penetrate to considerable depth. It is not known how these cracks begin to form as it is difficult to see how a reduction in ductility could cause cracking unless there was some bending movement. If the yield point is measurably depressed and the stress high the slight yielding of the casting would be sufficient for crack formation. Once a beginning is made the crack development is merely the result of the centralization of stresses. When these stresses are relieved the cracking stops.

89. Since cracking resulting from pickling is found entirely on the surface of a casting perhaps the surface imperfections which are present in all castings are sufficient for excessive stress concentration and crack development.

90. The work of previous investigators and the data obtained at this laboratory bring out the fact that internal stress is one of the most important contributors to embrittlement in steel. If it were possible to obtain a piece of steel in the unstressed condition it is highly probable that it would exhibit no embrittlement upon pickling.

91. All of the data collected points to the fact that the greater the internal stress the greater the degree of embrittlement will be. This is probably shown best by the data obtained on the Canfield internal friction machine. The annealed specimen was embrittled less than the "as cast" specimen. A slight twist of the annealed specimen increased the brittleness markedly.

92. It should be noted that even though the annealed specimen had received a full anneal, embrittlement was still to be found. This points

out the fact that castings that require pickling must receive a full anneal prior to this operation. As many so-called "commercial anneals" are not full anneals and are in fact, in many cases, merely a normalizing treatment there is real danger of cracked castings resulting from pickling.

93. The embrittling effect due to pickling is mainly a temporary effect. The steel will usually recover and have almost its original physical properties if allowed to stand in air about three days or is boiler in water for an hour. It will never recover all of its physical properties, however. The portions that are permanently lost are probably due to a roughening of the surface which causes a concentration of stresses at the minute holes and cracks etches out. Therefore, any casting which has not been cracked during the pickling operation has probably not suffered a great deal as far as physical properties are concerned.

94. Due to this rather rapid recovery from embrittlement tensile tests of portions of cracked castings will give no indication of hydrogen embrittlement. Tensile tests will not show the true embrittling effect unless the specimen is submerged in acid during the tests. The time lost in cutting out a portion of the casting and machining it to size and the heat generated during cutting and machining are usually sufficient to remove any occluded hydrogen and embrittlement.

RECOMMENDATIONS

95. It is recommended that pickling of steel castings be discontinued and that sand blasting or tumbling be substituted as a method of cleaning castings.

96. If it is necessary to pickle for cleaning when sand blasting will not clean intricate openings it is recommended that the casting be given a full and complete annealing prior to pickling so that the high internal stresses may be somewhat eliminated.

97. If pickling is necessary, it is recommended that a good commercial inhibitor be used and that the pickling operation be carried out under careful control, in accordance with pages 16 and 17.

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TABLE I

(Data obtained by Coulson)

Life Tests on Steel Springs

Load 16 pounds	No of oscillations
Original state	12,000,000
Sand blasted	11,500,000
Pickled chemically	Broke in preliminary test
Pickled as Cathode	Broke in preliminary test
Pickled as Anode	12,000,000

Tensile and Ductility Tests on Different Materials

Material	Diameter	Pickling	Lbs./sq.in.	R.A.	Elong.2"
Spring		none	254,000	51	
Steel	0.0785	chemically	247,000	3	
Wire		cathode	247,000	3	
		anode	252,000	51	
Spring		none	228,000	47	
Steel	0.205	cathode	224,000	3	2
Wire		anode	221,000	49	10
		none	169,000	22	5
Drill	0.25	cathode	162,000	7	2.5
Rod		anode	163,000	25	6.6
Hot-rolled		cathode	69,000	22	29
Bessemer	0.236	anode	68,000	63	35
Cold-rolled		none	106,000	50	
Steel	0.25	Chemically	100,000	40	
		cathode	103,000	35	
		anode	102,000	50	

TABLE II

(Data obtained by Fuller)

Treatment	Breaking strength* in pounds
Untreated	421
Copper plated	103
Pickled in 20% H_2SO_4	
3 minutes	198
1 hour	29
Pickled, Sn dipped	36
Pickled, Sn dipped, Cu plated	28
Sn dipped, Cu plated	326
Sand blasted, Sn dipped, Cu plated	351

*Averages of several tests.

TABLE III

(Data obtained by Watts and Fleckenstein)

Expt.	Electrolyte	Time	Amps.	Amps.per sq.dm.	Results
1	30% H_2SO_4	5 min	0.05	2.5	very brittle
2	N K_2SO_4	5 min	0.05	2.5	brittle
3	N H Cl	3 min	0.06	3	very brittle
4	N H Cl	3 min.	0.06	3	brittle but less than 3
5	NaOH(15.5g/ 100 cc	5 min	0.04	0.26	not brittle
6	Na OH(15.5g/ 100 cc	15 min	0.04	0.26	brittle, bluing removed.

	Metal Deposited	Bath	Hydrogen evolution	Deposit	Time Min	Brittle-ness	Amps	Amps/ sq.dm.
7	Cu	Cyanide,free Cy.	yes	fair	20	brittle	0.002	0.21
8	Cu	Alk. tartrate	No	poor	60	not brittle	0.002	0.16
9	Cd	Cyanide	No	good	39	not brittle	0.05	2.6
10	Cd	Cyanide and free Cy	Yes	fair	40	brittle	0.02	0.18
11	Cd	Fluoborate acid	Yes	good	30	brittle	0.05	0.31
12	Cd	Fluoborate faintly acid	No	good	10	brittle	0.10	4.2
13	Cu	Cyanide, free Cy	No	good	12	not brittle	0.12	1.1
14	Zn	Sulphate plus Cl	No	poor	40	not brittle	0.004	0.46
15	Zn	Sulphate plus Cl faintly acid	No	poor	40	Not brittle	0.004	0.74
		From hot baths, temp. 82-85°C						
16	Ag	Cyanide, free Cy.	No	good	5	Not brittle	0.082	2.0
17	Cu	Cyanide	No	poor	7	not brittle	0.11	0.54
18	Cu	Cyanide, free Cy.	No	bright	4	not brittle	0.11	1.0
19	Cu	Cyanide, free Cy.	Yes	bright	5	brittle	0.11	0.5

TABLE IV

(Date obtained by Pfeil).

Finely Crystalline Aggregate Tested in the Normal Manner

No. of Test	Tensile Strength	Elongation
	tons per sq.in.	percent on 1 inch
1	18.15	62.0
2	18.30	63.5
3	18.42	62.5
4	18.50	62.0
	Average 18.34	Average 62.5

TABLE V

(Data obtained by Pfeil)

Finely Crystalline Aggregate tested during Pickling at 25°C.

No of Test	Tensile Strength	Elongation	Remarks
	tons per sq.in.	percent on 1 inch	
5	16.10	8.0	Intercry- stalline fractures
6	16.72	10.0	
7	16.80	11.0	
8	17.14	13.5	
Average	16.69	Average 10.6	

TABLE VI

(Data obtained by Pfeil)

Finely Crystalline Aggregate Tested during Pickling at temps. from 30°C to 50°C.

No. of Test	Temp. of Test C°	Tensile strength tons per sq.in.	Elongation percent on 1"	Remarks
9	30	17.54	22.5	Intercrystalline fractures with cracks and a tendency to local contraction.
10	35	17.62	25.5	
11	35	17.85	26.5	
12	40	17.80	42.0	Transcrystalline fractures with cracks and local contraction.
13	45	17.93	49.0	
14	50	17.53	44.0	
	Average	17.71	Average 34.9	

TABLE VII

(Data obtained by Pfeil)

No. of test	Time elapsed since pickling	Tensile strength tons per sq.in.	Elongation percent on 1"	Remarks
17	-	18.17	63.0	A few cracks
18	15 seconds	18.44	60.5)	Normal fractures
19	3-1/2 minutes	18.30	66.5)	
20	20 minutes	18.59	62.0)	

TABLE VIII (Annealed Wire)

(Data obtained by Slater)

Steel % C.	Pickle	Nil	2-1/2	5	10	20	60	Time to clean minutes
		Time of Immersion - Minutes						
	20% H_2SO_4 at 20°C	32	18	14	12	11.5	11	40
0.60	20% H_2SO_4 at 60°C	32	16	13	12	11	11	10
	5% H_2SO_4 at 20°C	32	21	18	16	13	12	60
	5% " " 60°C	32	16	14	12	12	11	20
	5% " " 90°C	32	15	13	11	11	11	10
	20% H_2SO_4 at 20°C	15	11	8	6	5.5	5	40
	20% " " 60°C	15	8	6	5	5	5	10
0.77	5% " " 20°C	15	12	11	10	7.5	6	60
	5% " " 60°C	15	8.5	7.5	6	5	5	20
	5% " " 90°C	15	8	6	5	5	5	10
	20% H_2SO_4 at 20°C	7.5	6	5.5	5	4	4	15
	20% " " 60°C	7.5	5	4	4	4	4	7
0.89	5% " " 20°C	7.5	6	5	5	5	4.5	40
	5% " " 60°C	7.5	5.5	5	4	4	4	10
	5% " " 90°C	7.5	5	4	4	4	4	6
	20% H_2SO_4 at 20°C	8.5	6	5.5	5	5	5	15
	20% " " 60°C	8.5	5.5	5	5	5	5	7
0.96	5% " " 20°C	8.5	7	6	6	5.5	5	35
	5% " " 60°C	8.5	5.5	5	5	5	5	10
	5% " " 90°C	8.5	5.5	5	5	5	5	6

TABLE IX

(Data obtained from Slater)

Hard Drawn Wire

Steel % C.	Pickle	Gage SWG	Time of Immersion - Minutes Nil	2-1/2	5	10	20	60
0.60	20% H_2SO_4 at 20°C	6-1/2	13	9	5	3	2	1.5
		10	22	15	10	9	5	2
		12	33	25	20	14	8	5
		18	72	59	45	36	25	23

TABLE X

(Data obtained from Slater)

Annealed Wire

Steel % C	Pickle	Nil	Time of Immersion - Minutes 2-1/2	5	10	20	60	Time to clean minutes
0.60	20% HCL at 20°C	32	20	17	16	15	13	60
	5% HNo_3 at 20°C	32	22	19	17.5	15	11	60
	20% HNo_3 at 20°C	32	20	16	15	9	9	60
0.60	5% H_2SO_4 at 20°C	32	21	18	16	13	12	60
	20% H_2SO_4 at 20°C	32	18	14	12	11.5	11	40

TABLE XI

(Data obtained from Slater)

Annealed Wire

Steel % C.	Pickle	Inhibitor	Time of Immersion - Minutes Nil	2-1/2	5	10	20	60	Time to clean minutes
0.60	5% H_2SO_4 at 20°C	2% Flour	32	25	22	21	19	17	65
	5% " " 60°C	2% "	32	20	18	17	17	16	25
	5% " " 90°C	2% "	32	17	15	14	13	13	15
	5% H_2SO_4 at 20°C	none	32	21	18	16	13	12	60
	5% " " 60°C	"	32	16	14	12	12	11	20
	5% " " 90°C	"	32	15	13	11	11	11	10

TABLE XII

(Data obtained from Slater)

Exposure during Recovery	Time Elapsed	Torsional Value .60 carbon	Torsional Value .96 carbon
Laboratory atmosphere $16^{o} - 20^{o}C$	Nil	12	5
	1 hour	17	6
	3 hours	22	6.5
	24 "	25	6.5
	72 "	28.5	7.5
	168 "	32	8.5
	Original	32	8.5
Air oven at $50^{o}C$	1 Hour	20	6
	3 Hours	25	6
	24 "	30	7
	48 "	32	8
Air oven at $100^{o}C$	5 minutes	17	6
	20 minutes	25	7.5
	60 minutes	31.5	8.5
Boiling water	10 minutes	32	8.5

TABLE XIII

(Data obtained from Slater)

Steel Carbon %	Before pickling	After pickling
0.21	20	24
0.31	14.8	16
0.41	10.8	13.2
0.50	5.3	5.5
0.61	6.0	6.5
0.71	2.9	3.2
0.89	2.4	2.8
1.00	2.3	3.3
1.10	1.6	2.0

TABLE XIV

(Data obtained from Slater)

Steel Carbon %	Notched Bar Impact Value Ft.Lbs. Not Pickled	After 1/2 hr.	After 3 hrs.	After 17 hrs.
0.21	20	26	25	25.3
0.31	14.8	20.5	16	13.9
0.41	10.8	8.7	10.9	11.4
0.50	5.3	4.7	3.9	3.9
0.61	6.0	4.3	3.8	3.4
0.71	2.9	4.7	2.1	3.3
0.80	2.5	4.1	3.0	3.3
0.89	2.4	2.4	2.2	2.4
1.00	2.3	3.3	2.7	1.8
1.10	1.6	1.6	1.4	1.6

TABLE XV

(Data obtained from Slater)

Steel Carbon %	Treatment	Tensile Str. Tons per Sq.in.	Elongation in 2 in. %	Reduction of Area %
	Not pickled	33.96	35	59.5
0.31	Pickled chemically in 20% H_2SO_4 at 20°C for 2 hours.	34.03	34	55.6
	Pickled as cathode for 1/2 hour.	34.2	35	58.2
	Pickled as cathode for 3 hours.	35.15	32	41.7
1.00	Not pickled	69.8	7	16.4
	Pickled as cathode for 1/2 hour.	69.9	6	6.67

TABLE XVI

(Data obtained from Slater)

Steel Carbon %		Brinell Hardness Before Pickling	After 10 min.	After 30 min.	After no further increase	Total increase %
	Normalized	163	165	167	167	6
0.20	Hardened and tempered	251	255	262	269	7
0.50	Normalized	207	215	215	220	7
	Hardened and tempered	302	321	331	331	10
1.10	Normalized	241	255	255	255	6
	Hardened and tempered	352	365	375	375	6.5

TABLE XVII

Times for Pickling Standard Material with H_2SO_4 at Various Temperatures and Concentrations.

(Data obtained from Winterbottom and Reed)

H_2SO_4 gms litre*	%	Minutes 25°C	35°C	50°C	60°C	80°C
10	1.0	440	251	99	73	48
30	2.96	210	87	46	29	14.5
50	4.85	165	79	36	22.5	10
80	7.6	125	58	27	19	8

Volume of pickle liquor 50cc

*Material 1-1/4 in. of 5/8 in. x 16 s.w.g. conduit.
Area scale 28.5 sq.cm.; thickness of scale 0.015 mm; weight of scale, average 0.27 gms, or 0.01 gms. per sq.cm. Average acid consumption: 0.35 gms. of H_2SO_4.

TABLE XVIII

Times for Pickling Standard Material with Hcl at Various Temperatures and Concentrations.

(Data obtained from Winterbottom and Reed)

H_2SO_4 gms/litre*	%	Minutes 25°C	35°C	50°C	60°C	80°C
10	1.0	255	86	48	37	27
30	2.97	45	25	13	9	5
50	4.9	33	18	8	5.5	3.5
80	7.7	18	12.5	–	4	2.5

Volume of pickle liquor: 50 cc
Material: As described under Table XVII
Average acid consumption: 0.24 gms of Hcl.

*It should be noted that the figure for gms per litre is the same as for lbs. per 100 gal.

TABLE XIX

Effect of Iron Content on Pickling Time for Hydrochloric and Sulphuric Acids.

(Data obtained from Winterbottom and Reed)

Temperature °C	No Iron	Iron 10 gm/1	Iron 20 gm/1	Iron 40 gm/1
	MINUTES			
Hydrochloric Acid 30 gms per litre.				
25	45	57	57	56
35	25	31	33	37
50	13	14	15	15
Sulphuric Acid 30 gms per litre.				
35	87	106	121	131
50	46	50	55	60
60	29	34	37	41

TABLE XX

Inhibiting Power of Compounds Studied by Chappel, Roetheli and McCarthy.

Temperature 60°C
Acid, normal sulphuric

Inhibitor concentration 0.70 grams per litre.
Electrolytic pickling, current density 9.1 milliamperes per sq.cm.

Substance	Hydrogen Evolved cc/min./sq.cm.
None	0.091
Sodium cyanide	0.064
Picric Acid	0.061
Bismarck brown	0.029
Sodium arsenate	0.020
Quinoline ethiodide	0.020

TABLE XXI

Inhibiting Power of Compounds
Studied by Rhodes and Kuhn

Compound	Inhibiting Power 10 Millimols per Litre	In Percent 100 Millimols per Litre
Loluidine	7.3	-
Triethanolamine	10.5	41.3
Aniline	14.5	-
Pyridine	19.0	41.3
Picoline	23.2	48.4
Piperidine	28.7	-
Lutidine	29.5	57.9
Colidine	36.6	78.6
8 - Hydroxyquinoline	48.6	98.4
Quinoline	49.4	84.6
Phenylquinoline	53.4	97.6
2 - Methylquinole (quinoldine)	53.9	-
Crude quinoldine*	82.3	-
6 Methylquinoline	59.7	93.2
2.4 - Dimethylquinoline	61.7	99.0
Pyrrole	63.5	94.4
Acridine	82.4	-
Diquinolyl	86.5	-
Diquinolylmethane	88.8	-
Dimethyldiquinolyl	89.5	-
B - Naphthoquinoline	91.2	95.9
Methylacridine	91.8	-
3,6 - Diaminoacridine	95.4	
Phenylacridine	97.5	
3,6 Dimethyl- 2,7 diaminoacridine ethyl chloride	99.7	
3,6 - Dimethyl - 2,7 diethyldiamicoacridine hydrochloride	98.8	
	Saturated Solution.	
Benzidine	14.2	
A - Naphthylamine	32.0	
Phenyldinaphthacridine	87.7	
A,B - Dinaphthacridine	90.4	
Fluorenenaphthacridine	90.8	
B,B - Dinaphthacridine	92.8	
A,A - Dinaphthacridine	92.9	
Diphenanthracridine	96.6	
	Special Experiments with Impure Inhibitors	
	c.c. per litre	Percent
Commercial restrainer	0.05	33.5
" "	0.10	44.2
Kerosene sludge	10.00	3.7
Lubricating sludge	10.00	84.0

*In the experiments made with crude quinoldine it was assumed that the average molecular weight of this material was the same as that of pure quinoldine, and the solutions were prepared on this basis. It will be observed that the crude material showed appreciably higher inhibiting power than did the purified quinoldone. The impurity in the crude produce is apparently a very efficient inhibitor.

TABLE XXII

Inhibiting Power of Compounds
Studied by Chappell & Ely

Description of Inhibitor	Conc. of Bath %	H Evolution cc/sq.cm/hr	Inhibiting Power in %
None	–	30	–
Sulphonated oil in acid	0.1	27	10
Nitrogen base oil from gas works.	0.1	21	30
Paper waste, liquor	0.1	20	33.3
Paper waste, solid	0.1	19	36.7
Sulphonated oil in acid	0.1	17	43.3
Synthetic chemical in acid	0.1	14	53.4
Sulphonated animal matter	0.1	11	63.4
Paper waste	0.1	9.5	68.4
Synthetic chemical in acid	0.1	8.7	71.0
Paper waste	0.1	8.0	73.4
Low grade wheat flour	0.2	4.0	86.7
Nitrogen bases in acids	0.1	3.5	88.4
Synthetic chemical	0.1	2.0	93.4
Synthetic chemical	0.1	1.8	94.0
Coal tar, nitrogen bases in acid	0.1	1.5	95.0
Synthetic chemical	0.1	1.12	96.4
Sulphonated oil	0.1	0.31	99.1
Sulphonated oil	0.05	0.35	99.2
Synthetic chemical	0.04	0.36	99.2
Synthetic chemical	0.03	0.32	99.1
Synthetic chemical	0.02	2.04	93.3
Synthetic chemical	0.01	6.28	78.5

TABLE XXIII

Comparison of Pickling Times for H_2SO_4 Pickles at 60°C with and without Inhibitor
(From Winterbottom and Reed)

H_2SO_4 gms/l	None Minutes	Inhibitor A	B	C	D	Glue size 0.05% Minutes
		Minutes				
30	29	34	34	34	34	34
50	22.5	22	22	22	22	22
80	19	22	20	20	21	21

Comparing Pickling Times for HCl Pickles at 35°C with and without Inhibitor.

30	25	36	32	37	32	36
50	18	22	25	26	20	25
80	12.5	14	16	15	12	16

Inhibitor Efficiencies.

Inhibitor	HCl 50 gm/l at 25°C: Rate of solution gm/sq.cm/hr	Percentage Inhibition	:	H_2SO_4 50 gm/l at 55°C: Rate of Solution gm/sq.cm/hr	Percentage Inhibition
None	70	0	:	480	0
A	3.5	95	:	8.1	98
B	4.5	94	:	11.9	97
C	3.9	95	:	19.6	96
D	5.6	92	:	6.0	99
Glue size	4.2	94	:	29.0	94

TABLE XXIV

The Effect of Pickling on the Impact Strength of Cast Steel.

Free Contracting Bars.

Condition	Pickling Treatment	Impact Foot pounds
As cast	None	23.5
As cast	10% H_2SO at 65°C for 1/2 hour	47.5
Annealed	None	85.0
Annealed	10% H_2SO_4 at 65°C for 1/2 hour	100.0
	Hindered Contracting Bars. (Bars with flanges)	
As cast	None	38.5
As cast	10% H_2SO_4 at 65°C for 1/2 hour.	28.0
Annealed	None	165.0
Annealed	10% H_2SO_4 at 65°C for 1/2 hour.	103.0

TABLE XXV

Physical Properties of Elongation and Pickled Tensile Specimens
"As Cast" Specimens.

Treatment	Yield* Point lbs/sq.in.	Tensile* Strength lbs/sq.in.	Elongation %	Red. Area %
No elongation, not pickled	35,666	70,333	21.8	31.1
No elongation, pickled	36,800	70,333	17.6	24.7
Elongated 0.5%, pickled	37,366	70,233	19.6	26.8
Elongated 1.0%, pickled	38,600	69,366	16.5	21.5
Elongated 1.5%, pickled	40,050	70,866	19.0	23.8
Elongated 2.0%, pickled	41,566	70,833	18.4	23.9
Annealed Specimens				
No elongation, not pickled	47,800	71,300	26.9	46.2
No elongation, pickled	51,366	71,000	21.8	28.9
Elongated 0.5%, pickled	47,466	71,800	22.9	30.4
Elongated 1.0%, pickled	47,233	71,400	21.0	28.0
Elongated 1.5%, pickled	47,933	71,666	21.0	26.3
Elongated 2.0%, pickled	47,666	72,533	21.2	26.7

*Averages of three readings.

Carbon 0.23%
Manganese 0.76%
Silicon 0.31 %

TABLE XXVI

Effect of Testing in the Pickling Solution.

Treatment	Tensile Strength lbs./sq.in.	Elongation %	Reduction of Area %
Annealed	71,300	26.9	46.2
Pickled 1 hr. at 65°C in 10% H_2SO_4 under tension of 34,000 lbs. per sq.in. and tested in the acid.	71,000	15.5	16.4
Pickled 1 hr. at 65°C in 10% H_2SO_4 and tested in the acid.	70,250	15.3	16.3
Tested in 10% H_2SO_4 at 65°C Testing time 8 minutes	69,850	17.2	20.7
Pickled 1 hr. at 65°C in 10% H_2SO_4 under tension of 34,000 lbs. per sq.in. Removed acid and tested. Testing time 10 minutes.	71,700	21.0	25.5

Carbon	0.23%
Manganese	0.76%
Silicon	0.31%

TABLE XXVII

Effect of Time in Air on the Rate of Recovery from Embrittlement.

Treatment	Time Elapsed in air after pickling.*	Tensile Strength lbs./sq.in.	Elongation %	Reduction of Area %
Annealed	--	70,000	30.5	42.5
Tested in 10% H_2SO_4 at 65°C-1 hr.	nil	65,625	12.0	15.7
Pickled 1 hr. - 10% H_2SO_4 at 65°C	1 min. 20 sec.	68,450	16.0	17.8
" " "	8 min.	68,700	21.0	22.0
" " "	25 "	68,950	21.5	22.5
" " "	50 "	69,050	22.0	25.0
" " "	150 "	68,600	22.0	25.5
" " "	24 hours	69,100	23.0	26.0

*Includes the time the specimen stood in air at room temperature plus the testing time.

TABLE XXVIII

Comparison of Electrolytic and Chemical Pickling.

Treatment	% H_2SO_4	Tensile Strength lbs./sq.in.	Elongation %	Reduction of Area %
Pickled 1 hr. as Cathode	10	66,400	14.5	16.0
Pickled 1 hr. as Anode	10	66,600	19.0	25.0
Pickled 1 hr. Chemically at 65°C.	10	65,625	12.0	15.7

Specimens tested in acid.

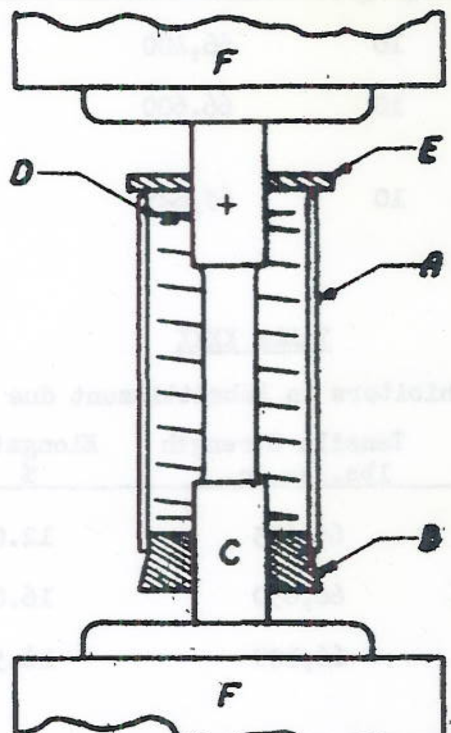
TABLE XXIX

Effect of Inhibitors in Embrittlement due to Pickling.

Inhibitor	Tensile Strength lbs./sq.in.	Elongation %	Reduction of Area %
None	65,625	12.0	15.7
Quinoline Ethiodide 0.01%	66,850	16.0	19.0
Rodine 10%	66,100	16.5	19.5

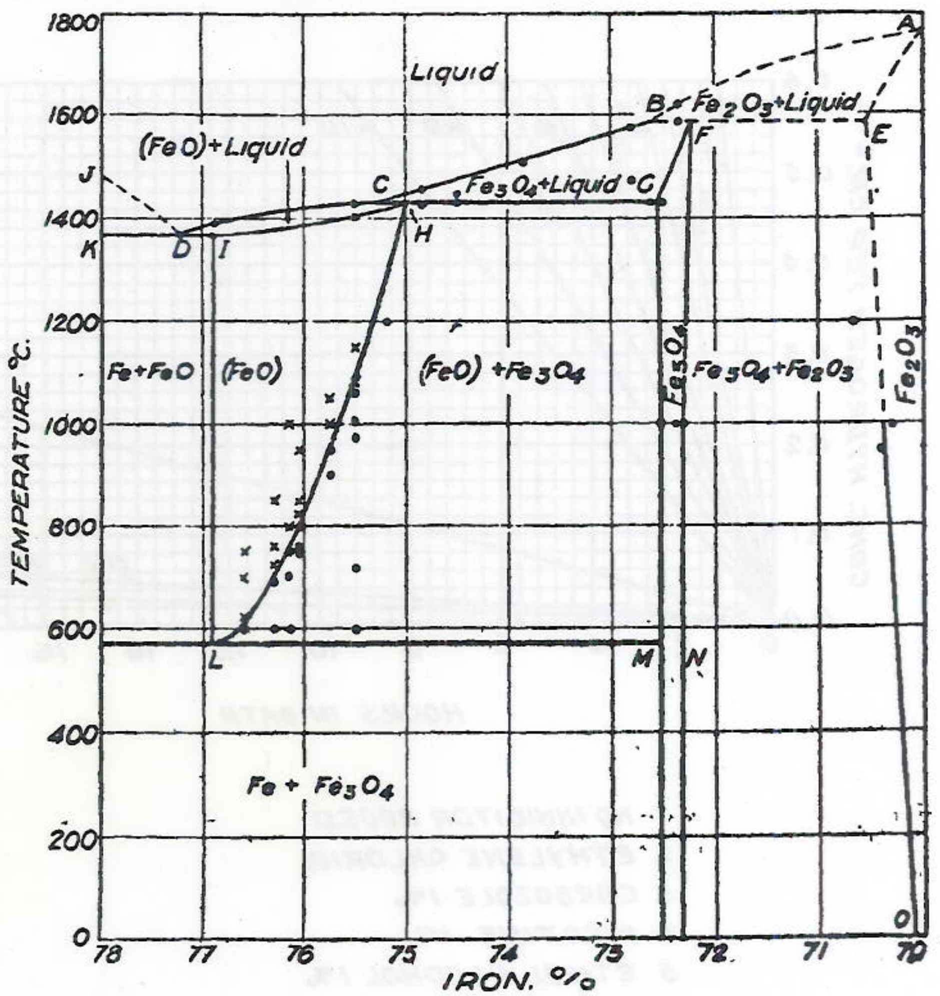
All samples pickled 1 hr. at 65°C in 10% H_2SO_4 and tested in acid.

METHOD FOR PICKLING UNDER TENSION



A- GLASS TUBE
B- RUBBER STOPPER
C- TEST SPECIMEN
D- PLATINUM COIL USED AS ANODE
IN ELECTROLYTIC PICKLING
E- SHIELD TO PROTECT TENSILE
MACHINE FROM ACID SPRAY
F- JAWS OF TENSILE MACHINE

PLATE I

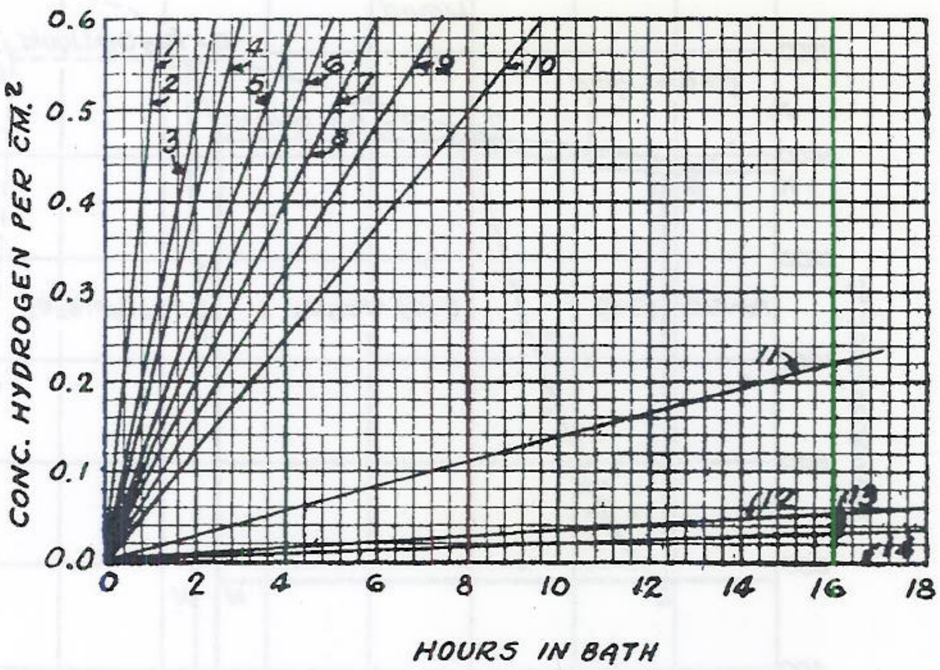


Equilibrium Diagram of the Iron-Oxygen System from 70 to 78 per cent. Iron (Pfeil).

PLATE 2

INHIBITORS

DATA OBTAINED BY SPELLER AND CHAPPELL



1 NO INHIBITOR ADDED
2 ETHYLENE CHLORIDE
3 CARBOZOLE 1%
4 NICOTINE 1%
5 ETHYL ALCOHOL 1%
6 ANILINE
7 PARAMETHYLAMINOPHENYL SULPHATE 1%
8 ETHYL IODIDE 1%
9 GLUE 0.5%
10 PYRIDINE 1%
11 QUINOLINE 1%
12 ACID EXTRACT OF COAL TAR 1%
13 QUINOLINE ETHIODIDE 0.01%
14 QUINOLINE ETHIODIDE 0.10%

PLATE 3

PHYSICAL PROPERTIES OF ELONGATED
PICKLED CAST STEEL

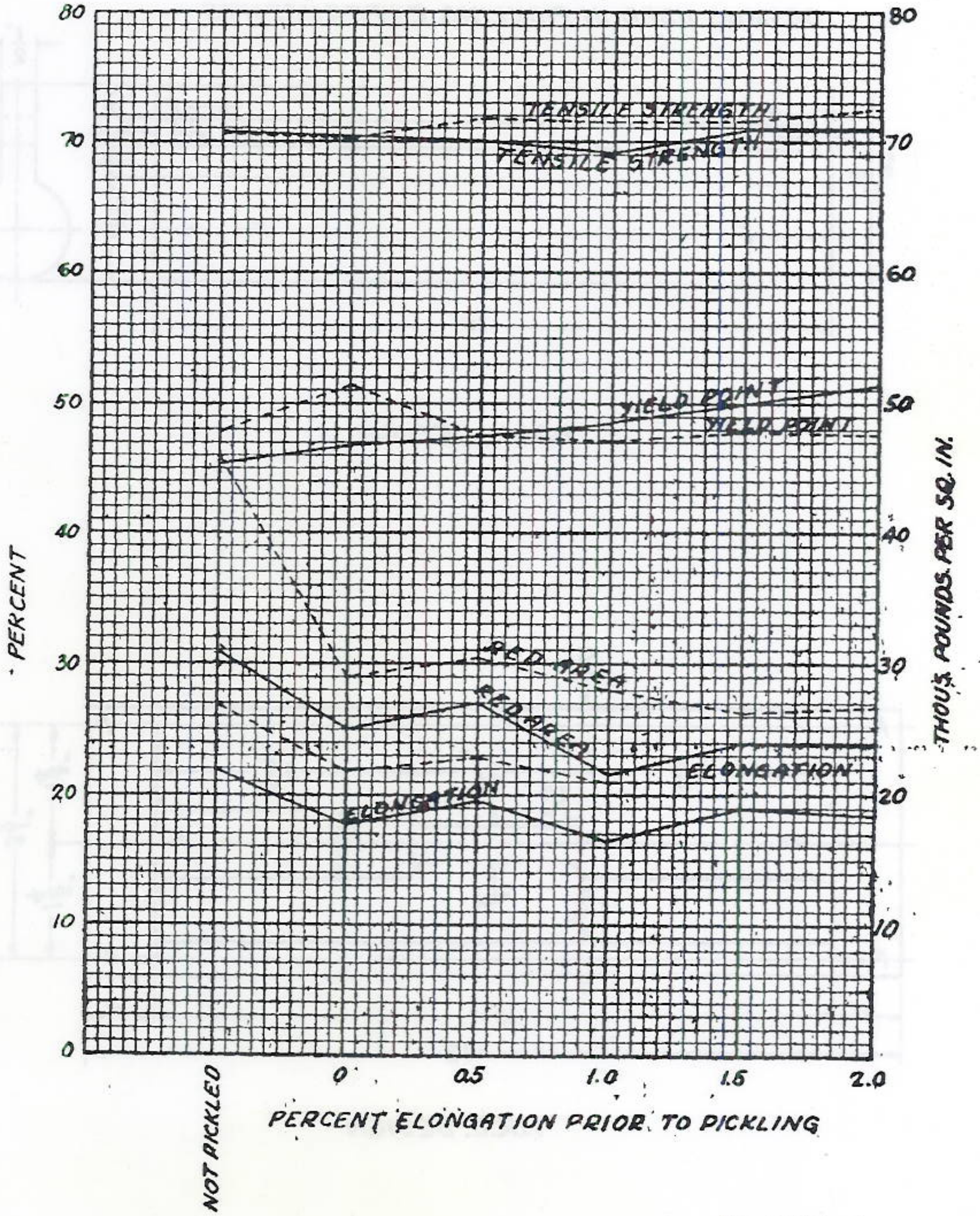
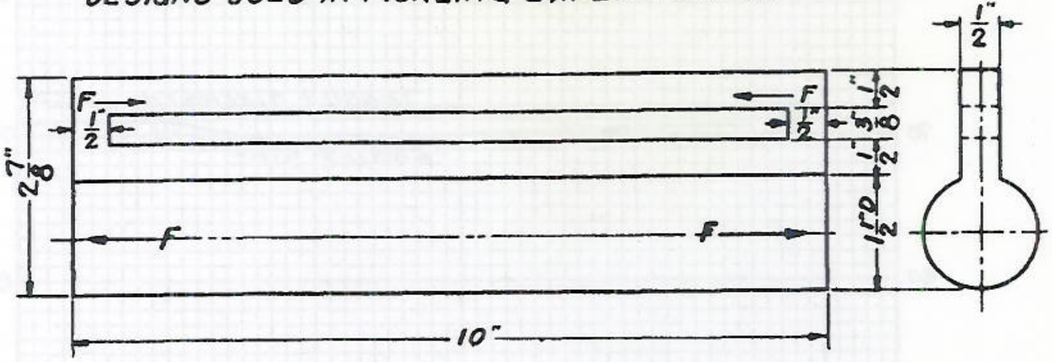
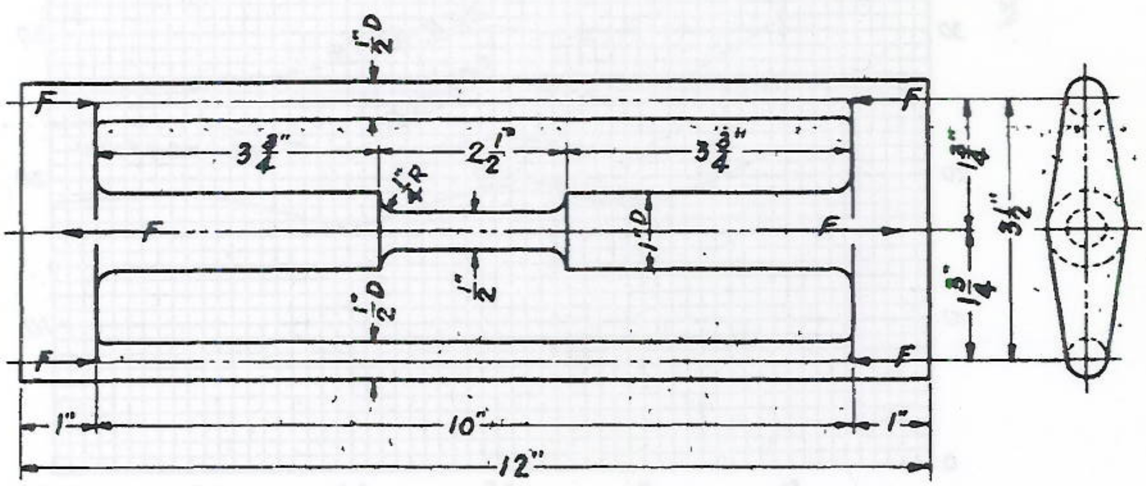


PLATE 4

DESIGNS USED IN PICKLING EXPERIMENTS



HALL DESIGN



N.R.L. DESIGN

PLATE 5

C

B

A

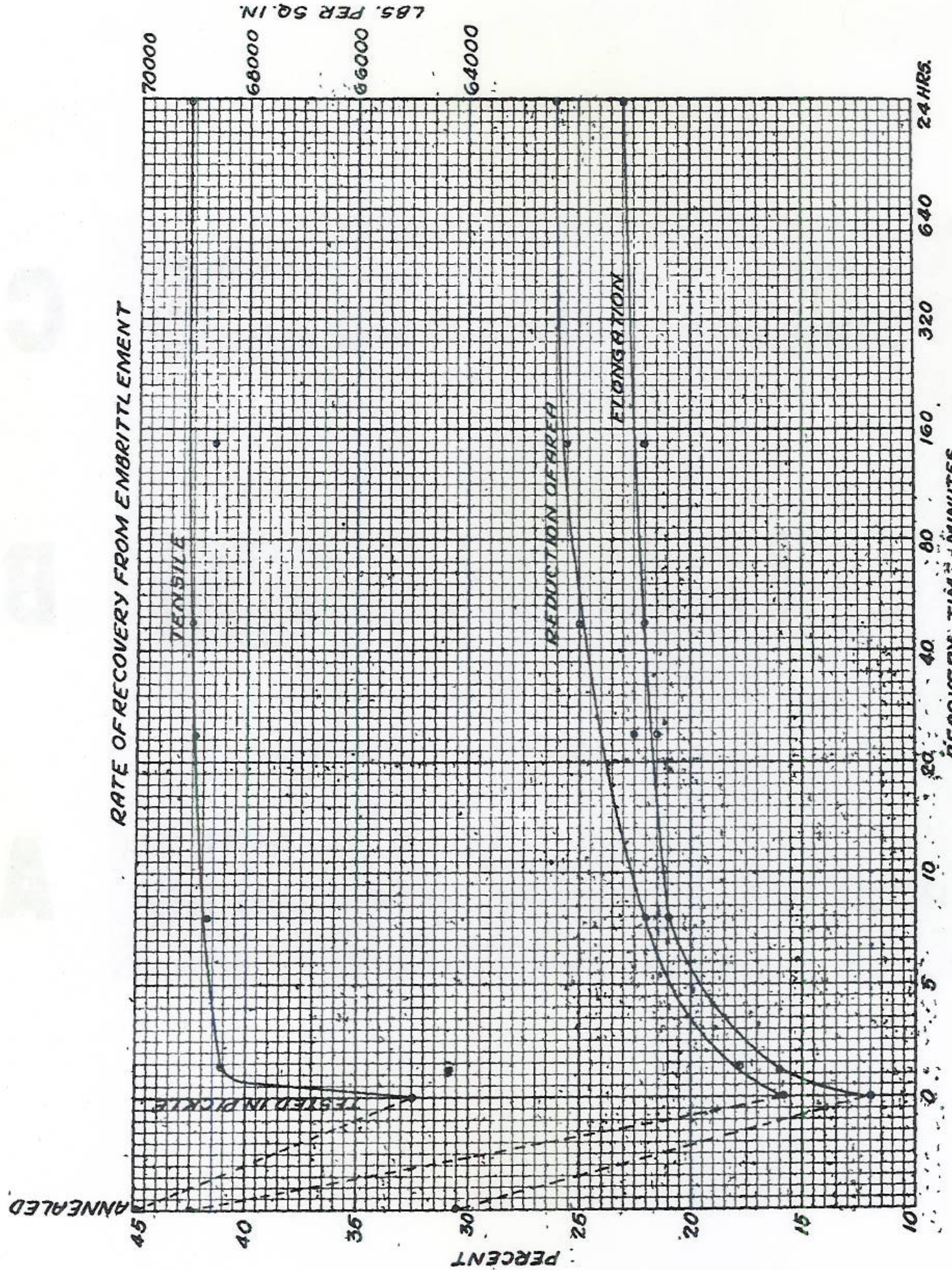
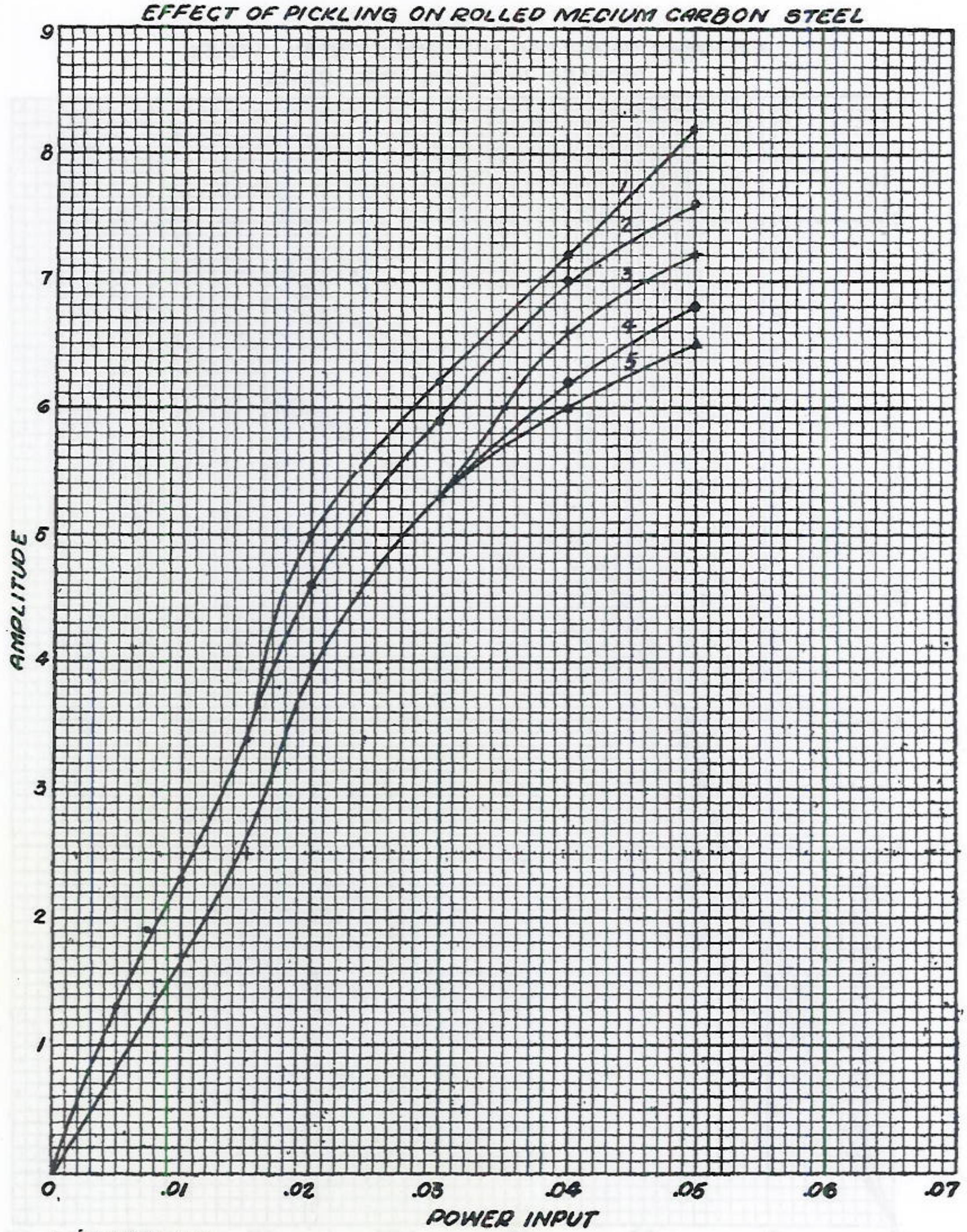

RATE OF RECOVERY FROM EMBRITTLEMENT
LBS. PER SQ. IN.
70000
68000
66000
64000
TENSILE
REDUCTION OF AREA
ELONGATION
TESTED IN PICKLE
ANNEALED
45
40
35
30
25
20
15
10
PERCENT
0
5
10
20
40
80
160
320
640
24 HRS.
RECOVERY TIME - MINUTES

PLATE 7

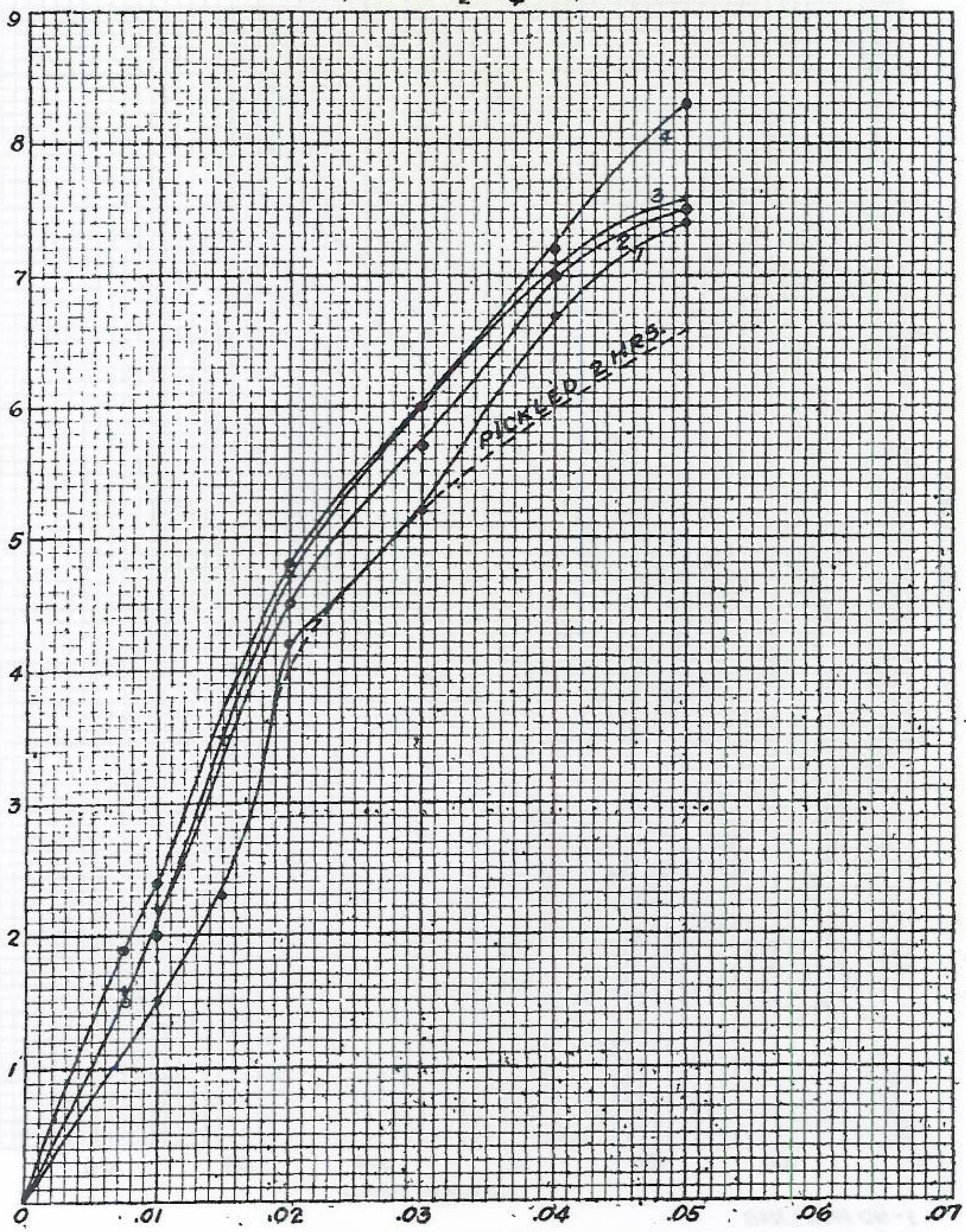
EFFECT OF PICKLING ON ROLLED MEDIUM CARBON STEEL



1-NO PICKLING
2-PICKLED CATHODICALLY IN 10% H_2SO_4 FOR 10 MIN.
3- " " " " " " 30 "
4- " " " " " " 60 "
5- " " " " " " 120 "

PLATE 8

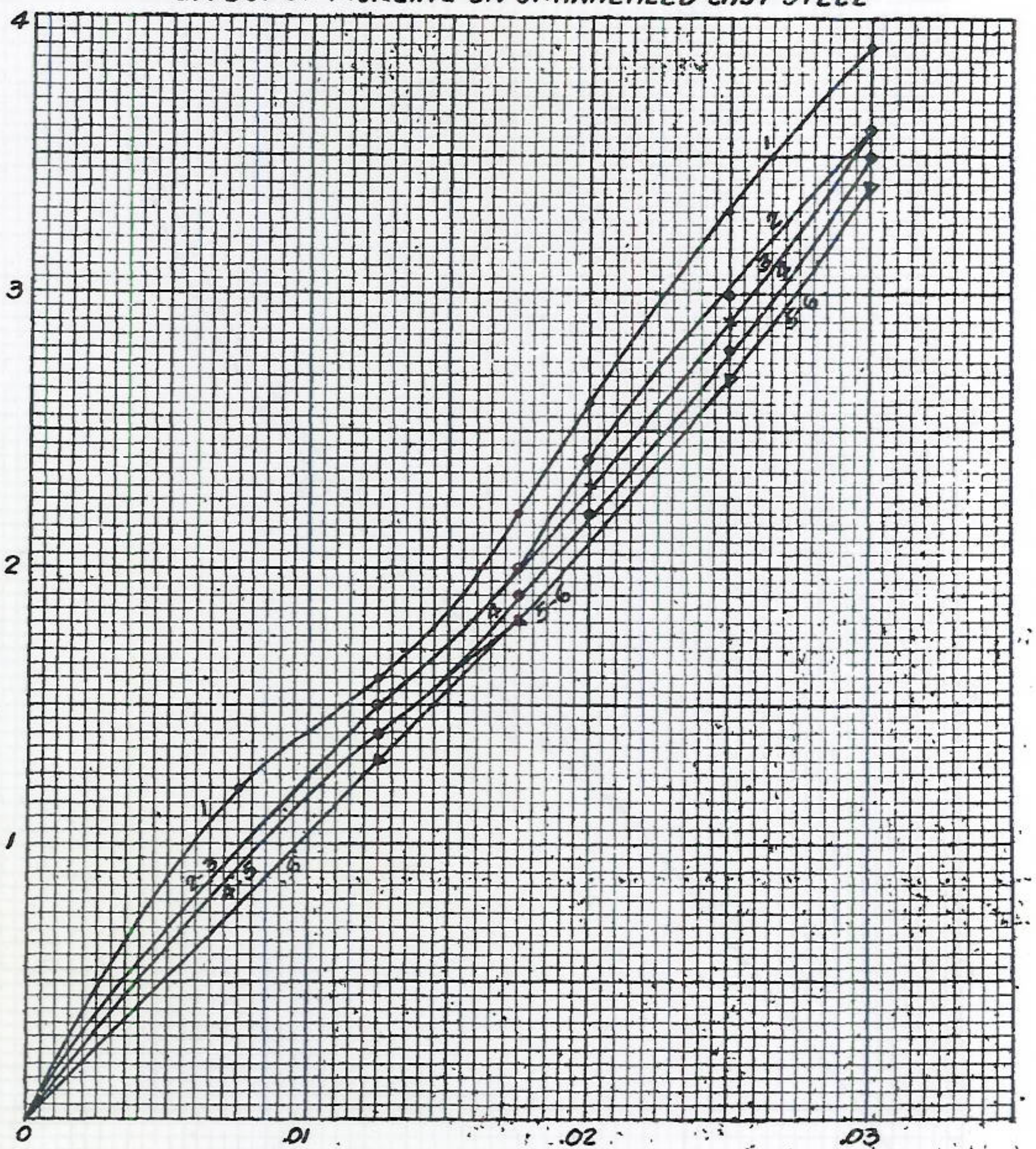
RECOVERY OF ROLLED MEDIUM CARBON STEEL
PICKLED IN H_2SO_4 FOR 2 HRS.



1- 20 MIN. AFTER REMOVAL OF PICKLING SOLUTION
2- 40 " " " " " "
3- 80 " " " " " "
4-160 " " " " " "

PLATE 9

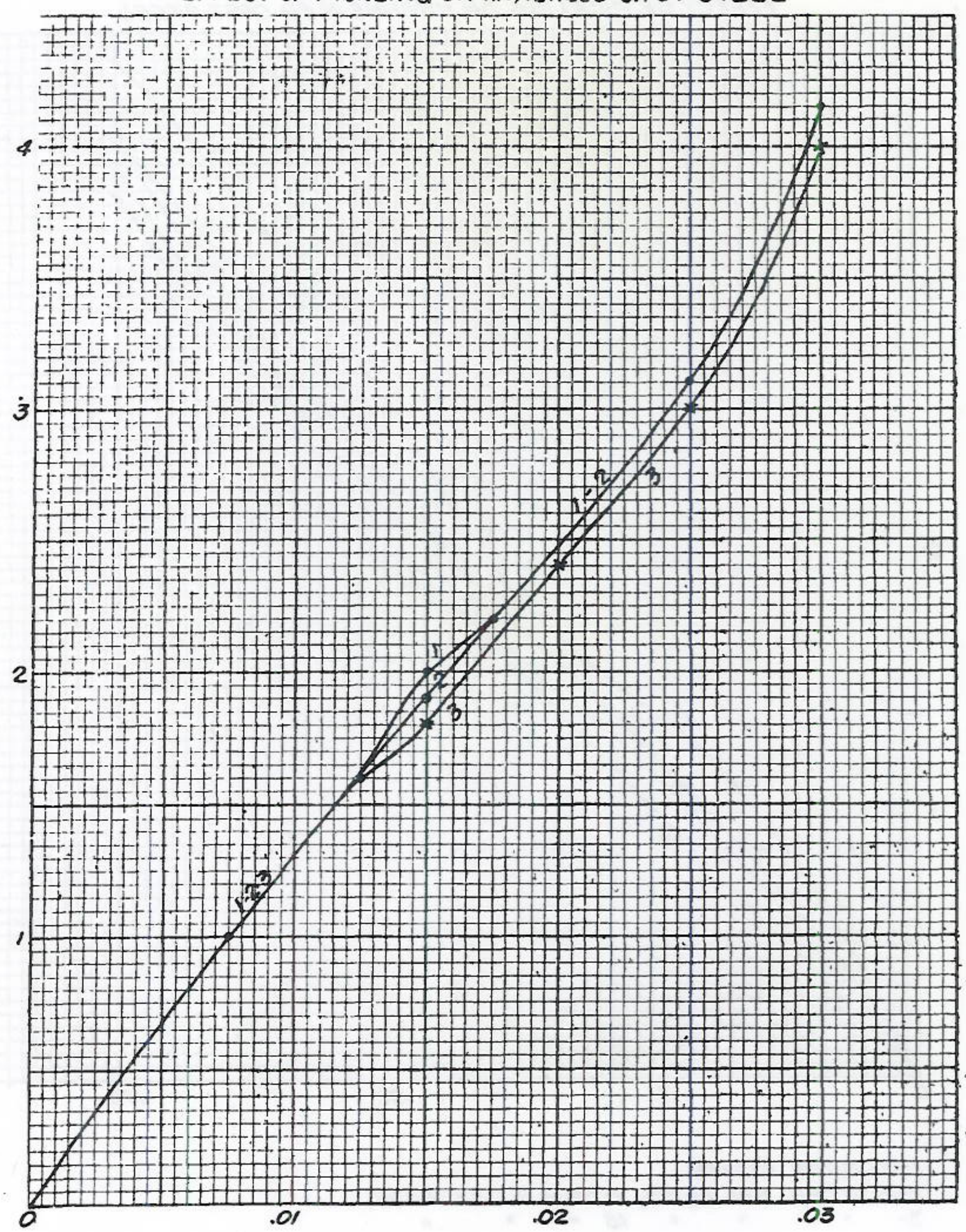
EFFECT OF PICKLING ON UNANNEALED CAST STEEL



1-ORIGINAL CURVE
2-PICKLED 10% H_2SO_4 5 MIN. AS CATHODE
3- " " " 15 " " "
4- " " " 30 " " "
5- " " " 1 HR. " "
6- " " " 2 HRS. " "

PLATE 10

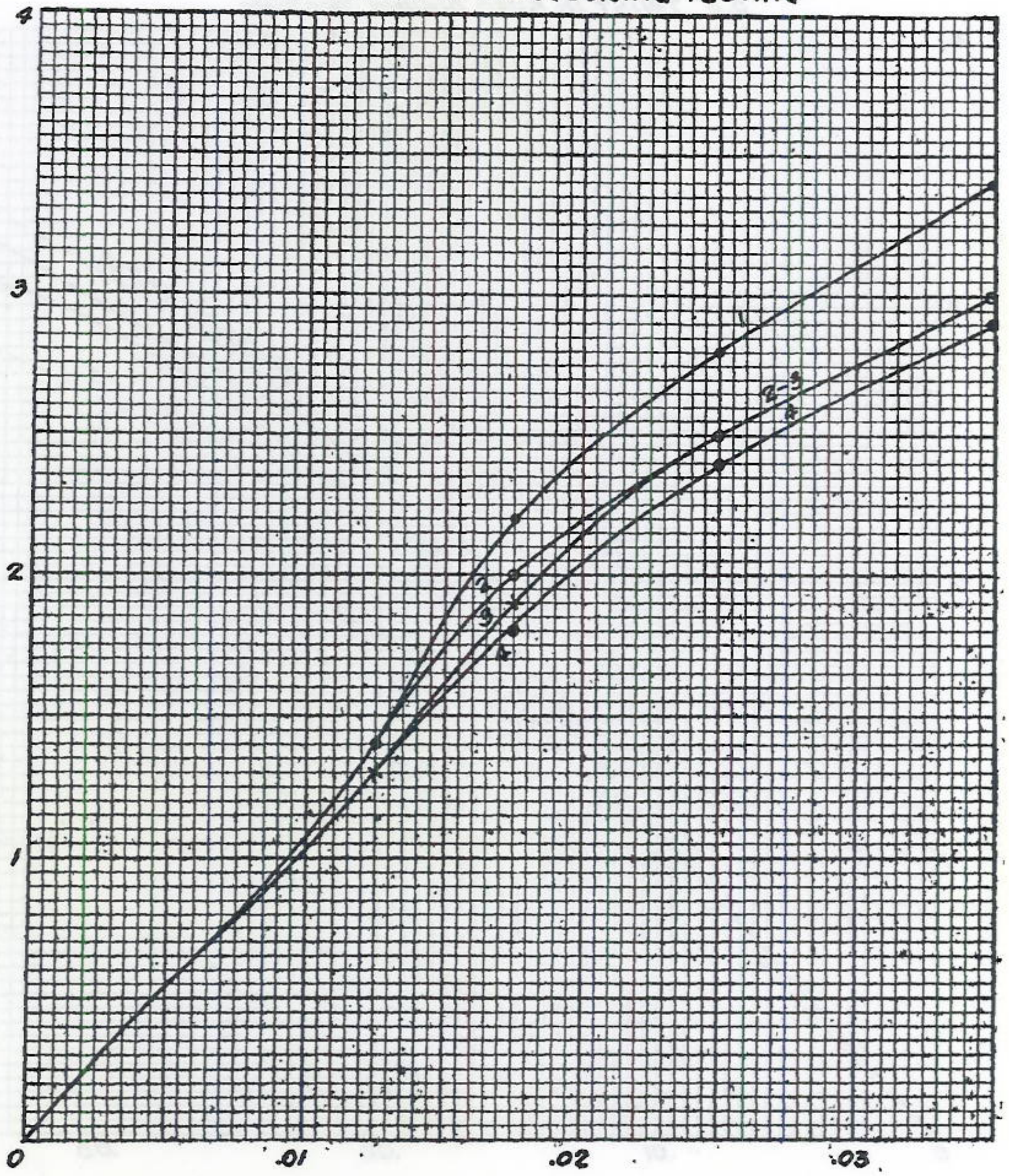
EFFECT OF PICKLING ON ANNEALED CAST STEEL



1 - ORIGINAL CURVE - ALSO PICKLED 5 MIN.
2 - PICKLED AS CATHODE IN 10% H_2SO_4 FOR 15 MIN.
3 - " " " " " " " 30 " .

PLATE 11

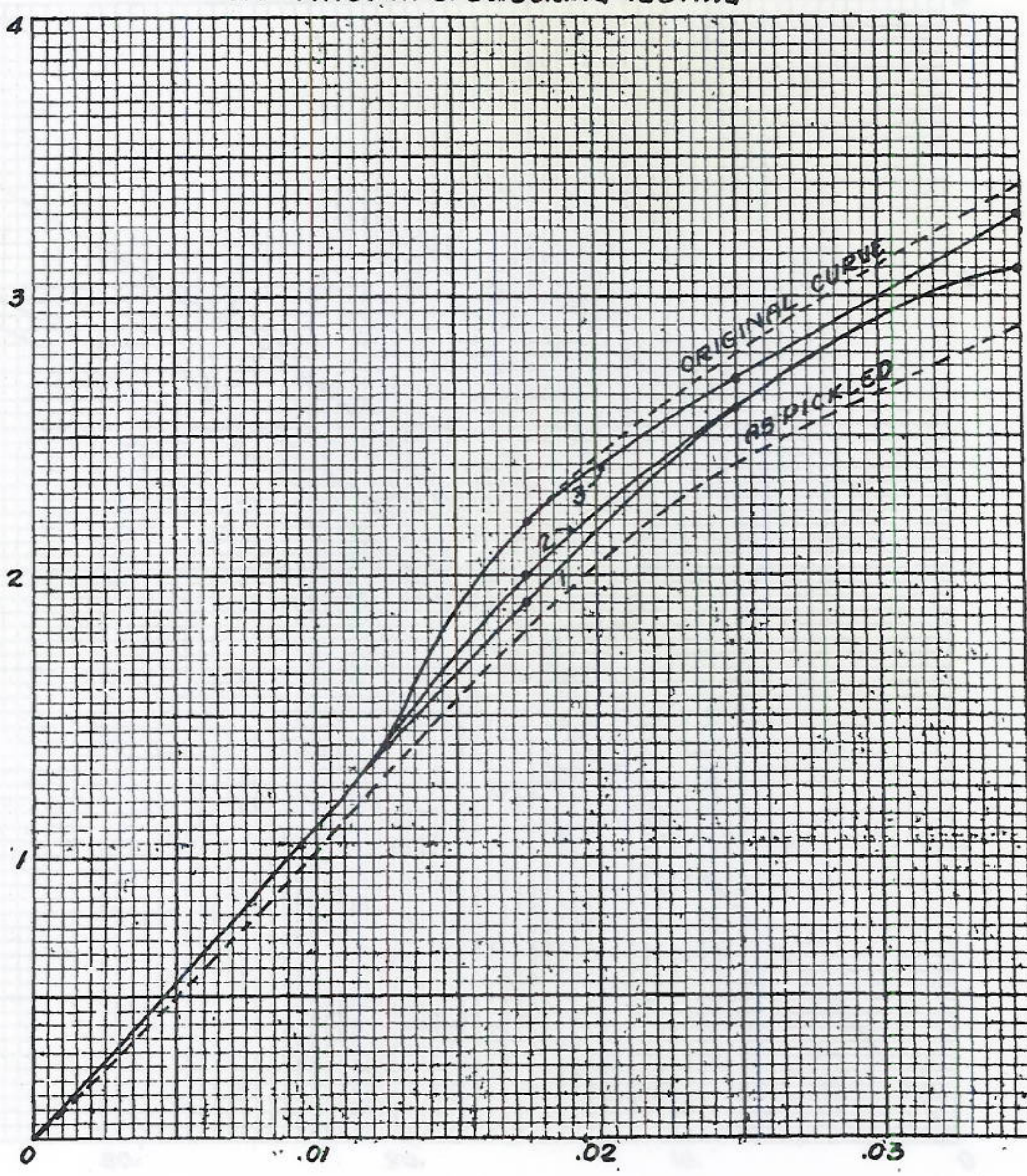
EFFECT OF PICKLING ON ANNEALED CAST STEEL
0.4° TWIST IN SPEC. DURING TESTING



1-ORIGINAL CURVE
2-PICKLED AS CATHODE IN 10% H_2SO_4 FOR 5 MIN.
3- " " " " " " " 15 "
4- " " " " " " " 30, 60, AND 120 MIN.

PLATE 12

RECOVERY OF ANNEALED CAST STEEL AFTER PICKLING IN H_2SO_4 FOR 2 HRS.
0.4° TWIST IN SPEC. DURING TESTING



1-5 AND 15 MIN. AFTER REMOVAL OF SOLUTION.
2-2 HOURS AFTER REMOVAL OF PICKLING SOLUTION
3-8 DAYS " " " "

PLATE 13