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THE EMBRITTLING ACTION OF SODIUM HYDROXIDE ON SOFT STEEL

BY
S. W. PARR

BULLETIN No. 94

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ENGINEERING EXPERIMENT STATION

Bulletin No. 94 January, 1917

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BY

S. W. PARR
Professor of Applied Chemistry

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THE EMBRITTLING ACTION OF SODIUM HYDROXIDE ON SOFT STEEL

I. THE EMBRITTLEMENT OF STEEL BY CAUSTIC SODA

1. *Introduction.*—Early in the year 1912 a certain boiler distress which had occurred at the University of Illinois brought to a focus the more or less controverted point as to whether the method of construction of the boilers in question, the material used, or chemical action was at fault. After numerous conferences with the representatives of the Babcock and Wilcox Company and the presentation by them of a mass of facts and opinions relating to similar difficulties elsewhere, it was agreed that there was sufficient evidence at hand practically to preclude the theory of faulty material, and that the subject was important enough to deserve the attention of a special committee to formulate a method of procedure for carrying out an extended investigation of the difficulty.

In consequence a committee was appointed by the Director of the Engineering Experiment Station as indicated by the following letter:

URBANA, ILLINOIS,
January 28, 1913.

PROFESSOR C. R. RICHARDS, Chairman; PROFESSOR E. J. BERG, PROFESSOR A. N. TALBOT, PROFESSOR J. M. WHITE, PROFESSOR S. W. PARR, PROFESSOR H. F. MOORE:

GENTLEMEN:—

At a meeting of the Station Staff held January 27 a statement was submitted by the Director outlining a problem in boiler maintenance which had been formally referred to the Station. The question raised concerns the cracking of plates in boilers which has been observed in a considerable number of instances in three different localities in the Mississippi valley. In all the cases reported the boilers were fed with artesian well water.

The undersigned reported that in the process of developing the question there had been some correspondence and that several of those interested in the matter at the University had two meetings with Mr. I. Harter, Jr., of the Babcock and Wilcox Company. At my request Professor Richards has formulated a statement, dated January 23, 1913, covering the investigation that should be made, which statement supplemented by briefs submitted by Professor Talbot and Professor Parr were presented in full at the meeting of the Station Staff. It was unanimously agreed that you should be appointed a Committee to have charge of the proposed investigation, and the purpose of this letter is formally to notify you of your appointment upon such a Committee. I assume that the facts involved are already known to you and that the initiative in the further development of the problem will rest with the Chairman of the Committee.

May I add an expression of my belief that the problem which has been outlined is one of unusual importance and that its solution will justify the bestowal of generous attention upon the part of each member of the Committee.

Very truly yours,

W. F. M. GOSS,
DIRECTOR OF THE ENGINEERING EXPERIMENT STATION.

As a result of the conference of this committee it was agreed that certain of the more evident phases of the topic were of a chemical character and that these should be taken up by the department of chemistry. Dr. William Hirschkind of the division of Industrial Chemistry was detailed under the direction of Professor S. W. Parr to begin the work. His first report under date of April 15th, 1913, was supplemented by a more complete report covering all the phases of his investigation up to June 15th, 1913.

Following Dr. Hirschkind, the work was taken up again in March of the next year by Dr. Paul D. Merica and continued until July, 1914.

Before presenting the results of these investigations some of the preliminary facts are discussed which have led up to the work and to some extent have controlled or indicated the line of chemical investigation to be followed.

2. *A New Type of Water Supply.*—The water works at Urbana, Illinois, installed in 1884, has its source of supply in a gravel and sand stratum about 165 feet below the surface. This plant has the distinction of being the first to bring this particular type of water into service.

The character of the water is unique in that it is almost free from sulphates and has from sixty to seventy parts per million of free sodium carbonate. Chemical analysis shows it to contain the seemingly incompatible mixture of approximately four hundred parts per million of the carbonates of calcium, magnesium iron, and the sixty to seventy parts of free sodium carbonate first mentioned. It should be remembered, however, that in the natural water these properties are all present in the "half-bound" or bicarbonate form and, hence, are soluble. The water, therefore, not only has no permanent hardness but is designated as having "negative hardness" in that it is self-purging and forms no scale whatever within the boiler.

In the year 1895, and following, a series of studies was in progress in the division of Industrial Chemistry at the University of Illinois which sought to follow the changes and interactions going on in the water within a steam boiler, under the existing conditions of temperature and pressure, for the purpose of arriving at an understanding of the processes involved in the formation of scale, the treatment which would be indicated for its removal, the causes of corrosion, and other factors. Two interesting facts developed which were not fully appreciated at the time.

First, because of the opportunity placed at our disposal for studying the water-supplies of certain railroads, especially the Illinois Central, the Big Four between Indianapolis and Peoria, and the Chicago and Alton, a rather extended zone for this particular type of water was indicated and fairly definitely outlined.*

Second. In waters of this type, after a few days of use in stationary boilers where the blow-off is naturally only partial and periodic, the sodium bicarbonate, $Na_2H_2(CO_3)_2$, of the raw water did not stop in its process of decomposition by heat

$$2(NaHCO_3) = Na_2CO_3 + CO_2 + H_2O$$

but went further; part of the sodium carbonate hydrolyzed and became sodium hydroxide according to the reaction:

$$Na_2CO_3 + H_2O = NaHCO_3 + NaOH$$

The residual water within the boiler became an active reagent for the precipitation of scale-forming material the moment it came in contact with the fresh incoming water, thus indicating why such waters are self purging and develop no scale whatever within the boiler. Further significance which might attach to the presence of caustic soda in the boilers did not appear at that time.

Within the last few years a series of phenomena has developed which seems to have a direct interest in connection with the data of former years.

In addition to the distribution of such waters as described in the article referred to in the Journal of the American Chemical Society, the Illinois State Water Survey has found waters of this type to be

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*Journal Am. Chem. Soc., vol. 28, p. 640, 1906.

much more widely distributed than formerly when the main supplies came from shallow wells. The local area may be roughly indicated* by drawing a line from a point somewhere between Paxton and Gilman on the Illinois Central Railroad, proceeding westward to include Normal, thence southward through the center of Bloomington somewhere between the C. & A. Junction and the pumping station of the Big Four at the foot of Center Street, thence south and east to include Bement, Tolono, Philo, on to Veedersburg, Indiana, and thence westward again to include Hoopeston and Paxton, the starting point.

COMPOSITION OF ALKALINE WATERS IN THE URBANA–CHAMPAIGN DISTRICT, SHOWING THE HYPOTHETICAL COMBINATIONS IN GRAINS PER UNITED STATES GALLON[1]

Location	Urbana	Hoopeston	Paxton	Normal	Bloomington	Bement	Tolono
Depth of Well (in Feet)	160	350	120	180	174	150	146
Supply	U. of I.	City	City	City	Big 4	City	City
Potassium Carbonate	.....	.09	.....	.....	.....	.....	.....
Potassium Nitrate	.05	.....	.....	.....	.....	.04	.....
Potassium Chloride	.24	.12	.....	.89	.....	1.78	.32
Potassium Sulphate	.18	.08	.....	.....	.....	.....	.....
Sodium Nitrate	.....	.....	.07	.....	.02	.....	.....
Sodium Chloride	.....	.....	.26	.16	.77	1.98	.33
Sodium Sulphate	.....	.....	.39	.18	3.60	.37	.27
Sodium Carbonate	5.09	3.96	6.56	12.06	8.15	4.53	12.61
Ammonium Carbonate	.71	.09	.....	.60	.....	.32	1.59
Magnesium Carbonate	6.40	5.95	6.98	4.70	9.01	7.63	7.33
Calcium Carbonate	8.40	7.60	10.71	7.30	13.07	9.02	12.93
Iron Carbonate	.21	.19	.....	.12	.01	.26	.22
Alumina	.05	.14	.....	.05	.....	.01	.23
Silica	1.47	.81	1.30	.81	.....	.79	1.34
Bases	.00	.01	.....	.15	.....	.11	.06
Undetermined	.....	.....	.....	.....	1.57	.....	.....
Total	22.80	19.04	26.27	27.02	36.20	26.82	37.23

[1] Data from the Illinois State Water Survey.

According to Bulletin No. 4 of the State Water Survey, pp. 28 and 29, another marked area is found in the Fox River Valley in the northern part of the state which includes Kane and Henry counties and the region about DeKalb.

3. *Boiler Difficulties.*—It so happens that coincident with the development of these areas, certain characteristic boiler troubles have appeared which have given no little concern to boiler users and makers alike. The details of boiler inspection reports show a decided increase of boiler faulting in areas where the water supplied to the boilers is

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*Journal Am. Chem. Soc., vol. 28, p. 640, 1906.

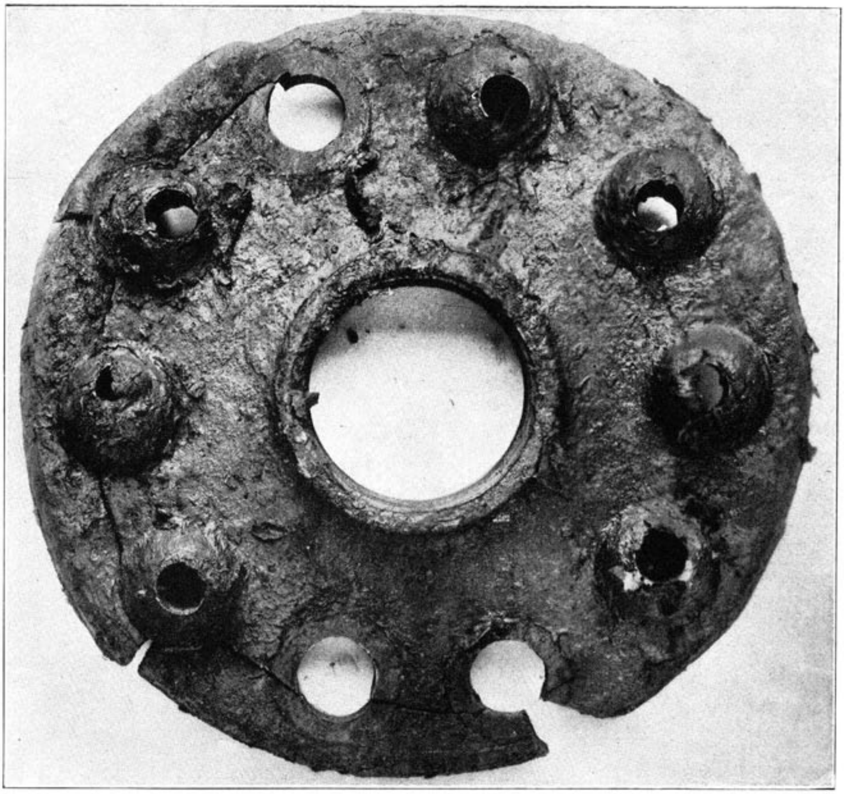

FIG. 1. A BLOW-OFF FLANGE OF A 260 H. P. STERLING BOILER

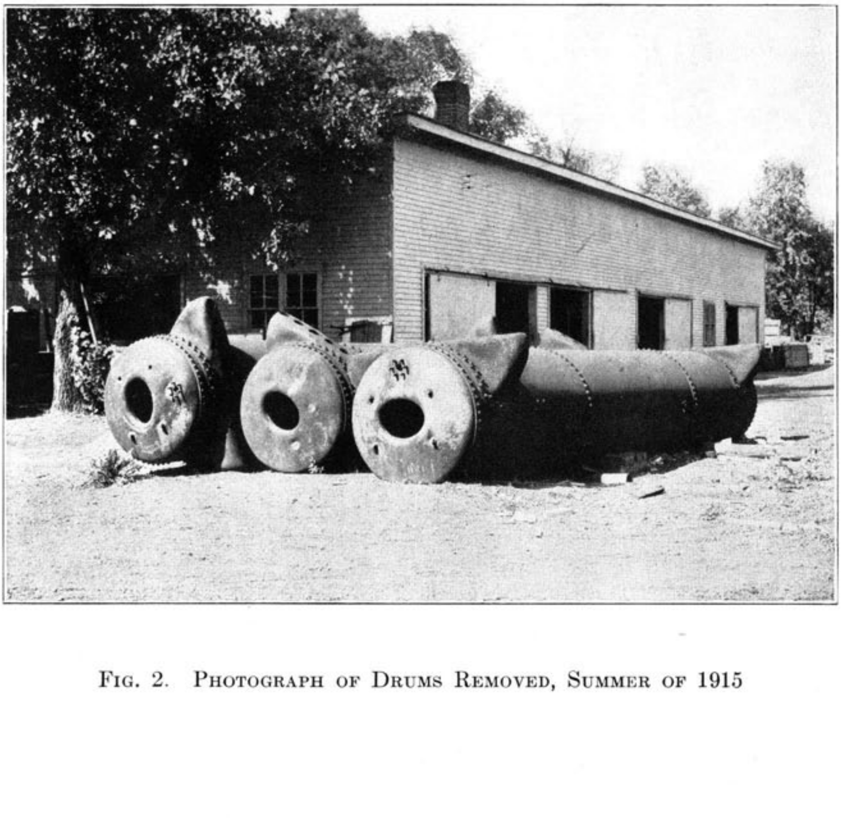

FIG. 2. PHOTOGRAPH OF DRUMS REMOVED, SUMMER OF 1915

of the character described. Without going into the various items, it is sufficient for purposes of this discussion to note that the number of boiler explosions occurring in the last twenty years and seemingly referable to the same cause, whatever that may be, have numbered twelve in the northern area above outlined and eleven in the southern.

The boiler distress is described as showing first in the form of fine cracks which develop and may proceed from the rivet holes to the surrounding plate, or from rivet hole to rivet hole, or from rivet holes to the edge of the plate where there is no tensile stress whatever. The development of these cracks occurs always below the water-line, and in the University of Illinois boilers, always in conjunction with a leak or other condition which promotes a concentration of the soluble material to the saturation point. Some of the characteristics of these cracks are shown in the accompanying illustration (Fig. 1) of a blow-off flange of a 260 H. P. Sterling boiler. Leakage had developed about this flange to an extent which made it desirable to remove the flange for refitting. The first attempt to drive out a rivet revealed the condition which is shown in its full development in the picture. Attention is called to the fact that the leakage area is confined to the outer edge of the flange; no leakage occurred at the center. Cracking is in evidence from rivet hole to rivet hole in every case and similarly every rivet hole has a crack extending outward to the edge of the flange.

4. *Purpose of these Studies.*—The purpose of this investigation has been to determine the embrittling effect of certain chemicals when brought into contact with iron and steel in such a manner as to set up a chemical reaction. It is not an attempt to explain the cause for boiler failures in these areas. Though it may throw some light upon one of the factors in the case which may be the predominating factor, emphasis should be laid upon the fact that much more remains to be done before a complete and adequate explanation can be offered. For example, the first twelve or fifteen years of use of this water in the University boilers was without noticeable effect on the boiler plates. In 1915 four drums in a new equipment of two 500 H.P. B & W boilers, which had been in use only three years, were so badly cracked that it was necessary to remove them. The old plant which was used for heating, however, operated only at less than 100 pounds pressure, and the use of the boilers was intermittent. In the new plant carrying both the heating and the power load of the University the service has been continuous, shutting down only for repairs. A constant

heavy overload has been maintained and the pressure carried at approximately 140 pounds.

Temperature, concentration, and continuity may, therefore, be important factors. Moreover, the soluble salts remaining in the water from these two particular districts, at least, consist almost entirely of sodium carbonate and hydroxide with only a minimum of sulphate and chloride present. The inhibitive effect or perhaps simply the diluting effect of larger percentages of sulphates and chlorides may be a determining feature.

It is evident, therefore, that many factors enter into the problem, and it has seemed wise to confine our attention to one factor only with the definite understanding that the immediate objective has been a contribution to our knowledge of the embrittling process and the conditions under which it may be brought about.

The first report presented herewith (Chapter II) is that of Dr. Hirschkind, and since he has compiled a valuable list of the more important references, this part of his paper is given entire in Appendix B, together with additions of more recent date.

It will be noticed that Dr. Hirschkind's line of investigation consisted, in the main, of a study of the change in potential of iron which had been subjected to the action of nascent hydrogen. The first pressures used were normal; hence the temperatures were generally confined to from 100 degrees to 120 degrees Centigrade.

In Dr. Merica's work (Chapters III, IV, and V) the action of caustic solutions was extended to include reactions under pressure and, consequently, at higher temperatures. Other effects than potential modifications were studied, as, for instance, the inhibiting effect of certain reagents.

5. *Summary.*—Certain conditions may be summarized as indicating the direction taken in carrying on the experimental work. These may be briefly enumerated. The peculiar cracking or faulting of boiler plates under consideration occurred:

a. Below the water line.

b. In connection with leakage at seams and rivet holes.

c. Accompanied by an exterior accumulation of incrustation of strongly alkaline character.

d. Where the water employed contained a very considerable amount of caustic soda (NaOH).

The experiments, as a result of this general agreement in the conditions, were directed toward determining the effect of caustic soda upon steel or the indirect effect of hydrogen resulting from such action. In general there seemed to be sufficient data for concluding that—

a. Caustic soda of sufficient strength attacks iron with the generation of hydrogen. Indicating the reaction with the hydroxyl ion only, we would have $3Fe + 4OH = Fe_3O_4 + 4H$.

b. Hydrogen in the nascent state, whether generated by alkali or acid, enters into the texture of the iron in a way to modify its physical properties.

c. The hydrogen effect, at least in its first application, is transient, and after a period of rest or freedom from the hydrogen action, the iron reverts to its normal condition.

d. Sodium carbonate is without action on iron; there is, therefore, no generation of hydrogen. The hydrolysis of sodium carbonate is directly dependent upon the temperature maintained, the withdrawal of the vapor of CO_2, and the admission through the feed water of carbonated water. It is evident, therefore, that the chemical activity would vary with the ratio of hydrolization or the degree of concentration of the sodium hydroxide.

e. Certain accompanying salts, as the chromates, have an inhibitive effect. Other salts, as sulphates, have at least the effect of acting as diluents. The limits of concentration for maintaining a condition which would be below the danger point have not been studied, but are features of the case which are of the utmost importance. A continuation of experiments along the lines suggested is in progress.

II. THE EFFECT OF CAUSTIC SODA ON IRON

6. *Introduction.*—The studies made up to the present time, which are given in outline in Appendix B, have proceeded on the assumption that hydrogen in the ionic form does not exist in metals. T. W. Richards in his investigations denies this assumption because

of the difficulty of demonstrating the presence of ions in metals. According to our present views concerning electricity, such a difficulty does not now exist. We have only to make the assumption that molecular hydrogen changes neither the potential nor the structure of the iron. Hydrogen ions, however, whether generated electrolytically or chemically, increase the potential of the iron and cause the so-called hydrogen brittleness.

Molecular hydrogen can be absorbed in large amounts by porous or finely divided iron; it does not change the electro-motive force.[*] On the other hand, iron treated with electrolytic hydrogen or with acids, that is, with hydrogen ions, becomes remarkably active and brittle.[†]

The experiment of Heyn,[‡] in which iron becomes active and brittle when heated in a hydrogen atmosphere above 750 degrees and rapidly cooled down, has not found a satisfactory explanation so far, but according to our theory it may be explained without difficulty. At 750 degrees the iron begins to send out electrons which ionize the surrounding gas; in this case hydrogen ions are formed which, taken up by the iron, cause activity and brittleness.

The normal water as used in the University boilers contains no caustic soda and far too little sodium carbonate to have any action whatever on the boiler plates. However, by hydrolysis and by concentration in certain localized places a point may readily be reached where chemical action occurs with the liberation of hydrogen.

7. *Experimental Work.*—The first series of experiments was directed toward the measuring of the iron potential in a solution. The difficulty in this process lies in finding a solution which does not change the iron to either the active or the passive side. The best solution would be a normal solution of $FeSO_4$, such as was used by Richards and Behr, but the preparation and handling of such a solution so as to avoid all oxidation is very difficult. The simpler method as employed by Grave was, therefore, adopted; that is, the potential was measured in a 1/10 normal solution of KOH. This solution converts the iron slowly into the passive state. From the rate of change, however, we can determine the original state of the iron piece.

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[*] Zeitschrift für physikalische Chemie, Stoñchiometrie, und Verwondtschaftlehre, vol. 58, p. 301, 1907.

[†] Proceedings Royal Society, vol. 23, p. 186, 1875.

[‡] Stahl und Eisen, vol. 20, p. 837, 1900.

The iron used was steel wire which had been annealed to eliminate the effect of the previous stress. A long piece of wire was cut into uniform lengths of six inches, heated in a tube of Jena glass to 700 degrees, and slowly cooled. The surface of these wires was covered with an oxide layer, which was carefully removed before testing.

The method used for measuring the electromotive force was the Poggendorf compensation method with a Deprez D'Arsonval galvanometer as a zero instrument. The standard cell was of the Weston type. The normal element was Ostwald's Calomel normal electrode. Between the 1/10 normal KOH solution and the normal KCl solution of the normal electrode, was a saturated solution of KCl.

Two pieces of annealed steel wire were dipped in a solution of 1/10 normal KOH. The potential against the Calomel electrode and the change of the potential with the time was measured.

Sample No. 1			Sample No. 2	
Potential immediately after dipping into the solution				
0.32 Volt			0.34 Volt	
After 5 min.	0.3000		0.3035	
		0.0085		0.0140
After 5 min.	0.2915		0.2895	
		0.00931		0.0085
After 10 min.	0.2822		0.2810	
		0.0044		0.0097
After 10 min.	0.2778		0.2713	
		0.0198		0.0113
After 30 min.	0.2500		0.2600	

These figures show that the potential at the beginning is about 0.3 volts and drops in one hour to 0.2600 volts. This is very different from the potential of a piece of the same steel wire which is made active before measuring. The easiest way to convert a piece of iron into the active state is by cathodic polarization. Another method was

Sample No. 1		Sample No. 2
Immediately after dipping in our solution.		
0.573 Volt		**0.600 Volt**
After 5 min.	**0.560 Volt**	**0.574 Volt**
After 1 hour	**0.537 Volt**	**0.480 Volt**

tried in this experiment: Pieces of steel wire of exactly the same kind as described were treated for a few minutes with dilute sulphuric acid; that is, with a concentrated solution of hydrogen ions. Then they were carefully washed to remove the rest of the acid, and the electromotive force measured in 1/10 normal KOH.

The different electromotive behavior of these pieces when compared with the original is evident. It shows distinctly that the hydrogen ion taken up increases the potential very materially; furthermore, the rate of change is much smaller.

Now if iron or steel treated with caustic soda of a certain concentration also takes up hydrogen ions, the potential must be increased and the breaking strain lowered. In order to test this, experiments were carried on as follows:

Steel wires three inches long annealed in the manner described were treated in boiling caustic soda solution of different concentration. The caustic soda attacks even Jena glass so strongly that the tubes were seriously affected by the heating. Therefore, two Jena glass tubes fitting into each other were used. The inside tubes contained the steel wire and the caustic solution and were drawn out a little to prevent evaporation. The evaporation and the effect on the outside tubes could not be entirely prevented, but were greatly reduced. For our experiments four caustic soda solutions of different strengths were used, 10, 25, 50 and 70 per cent. Each tube contained two pieces of annealed steel wire three inches long.

The tubes were heated in an air bath to from 110 to 120 degrees for one week. Afterwards the tubes were opened and the wires taken out and carefully washed with water. The wires in the 10 per cent NaOH solution did not show any change on the surface, but the wires in the stronger solution became rough, and dark colored, and contained on the surface adherent particles of solid caustic which were hard to remove.

The elongation and breaking strain of the original and of the treated pieces were determined through the courtesy of Prof. H. F. Moore. The results are given in Table 1.

The treated pieces show a slow increase in the elongation and a very distinct lowering in the breaking strain. Between the pieces in the various concentrated solutions there is only a small difference. If the lowering of the breaking strain is due to the hydrogen taken up, then the treated pieces must show a different potential in a solution.

TABLE 1
BREAKING STRAIN AS AFFECTED BY DIFFERENT STRENGTHS OF CAUSTIC SODA SOLUTIONS

SPECIMEN	Diameter	Length		Ultimate	Elongation in Entire Length Per Cent	Unit Stress at Ultimate lb. per sq. inch
		Before	After			
Pieces of steel	0.104	2.95	3.68	510	24.75	60000
	0.104	2.93	3.65	510	24.60	60000
Wire annealed	0.104	2.94	3.66	520	24.50	61200
	0.104	2.95	3.73	510	26.40	60000
Untreated	0.104	2.50	2.94	510		60000
No. 1 Steel wires treated in 70 per cent NaOH	0.104	2.96	3.74	470	26.30	55400
	0.104	2.97	3.72	470	25.50	55400
No. 2 Wires treated in 50 per cent NaOH	0.104	2.96	3.75	480	26.70	56600
	0.104	2.98	3.74	470	25.50	55400
No. 3 Wires treated in 25 per cent NaOH	0.104	2.95	3.80	485	28.80	57100
	0.104	2.94	3.70	475	25.90	56000
No. 4 Wires treated in 10 per cent NaOH	0.104	2.97	3.74	480	25.90	56600
	0.104	2.91	3.55	480	22.00	56600

In this way the electromotive force of the different treated and untreated pieces was determined.

The pieces of steel wire were carefully cleaned with sandpaper and fixed with paraffin in small glass tubes so that only a small part of the wire with the broken end came into the solution. In order to have a good contact a little mercury was admitted into the glass tubing which was closed with paraffin against the liquid. The method of measuring was exactly the same as in the preliminary experiments.

The results are given in Tables 2 and 3. The first series was measured about two days after the wires were taken out of the solution, the second about five days after. The figures show undoubtedly that the treated pieces have a considerably higher potential than the untreated.

The potentials in the second table are not quite as high as those in the first, probably because of a loss of hydrogen resulting from the exposure to the open air for a few days.

In order to test the action of caustic soda upon iron under stress another series of experiments was carried on as follows:

Four pieces of steel wire three inches long and four pieces six inches long having one bend in the middle were boiled in caustic soda solutions of the same concentration as in the experiments described.

TABLE 2

VARIATION IN POTENTIAL DUE TO TREATMENT IN CAUSTIC SODA SOLUTIONS OF VARYING STRENGTHS. MEASURED TWO DAYS AFTER TAKING OUT OF SOLUTION

SPECIMEN	Time	Potential in Volts	Time	Potential in Volts	Time	Potential in Volts	Time	Potential in Volts	Time	Potential in Volts	Time	Potential in Volts	Time	Potential in Volts
Untreated wire.	4.08	0.370	4.13	0.332	4.19	0.300	4.30	0.287	4.45	0.275	5.05	0.255	Next Day	0.174
No. 1. Treated in 70 per cent NaOH.......	4.09	0.428	4.14	0.401	4.20	0.380	4.31	0.359	4.46	0.331	5.06	0.301	Next Day	0.186
No. 2. Treated in 50 per cent NaOH.......	4.10	0.437	4.15	0.407	4.21	0.391	4.32	0.346	4.47	0.351	5.07	0.332	Next Day	0.242
No. 3. Treated in 25 per cent NaOH.......	4.11	0.405	4.16	0.381	4.22	0.366	4.33	0.346	4.48	0.322	5.08	0.303	Next Day	0.215
No. 4. Treated in 10 per cent NaOH.......	4.12	0.399	4.17	0.378	4.23	0.359	4.34	0.344	4.49	0.327	5.09	0.308	Next Day	0.188

TABLE 3

VARIATION IN POTENTIAL DUE TO TREATMENT IN CAUSTIC SODA SOLUTIONS OF VARYING STRENGTHS. MEASURED FIVE DAYS AFTER TAKING OUT OF SOLUTION

SPECIMEN	Time	Potential in Volts	Time	Potential in Volts	Time	Potential in Volts	Time	Potential in Volts	Time	Potential in Volts	Time	Potential in Volts
Untreated .	11.11	0.376	11.16	0.343	11.21	0.329	12.00	0.285	2.50	0.240	Next Day	0.217
No. 1	11.12	0.419	11.17	0.400	11.22	0.349	12.01	0.338	2.51	0.279	Next Day	0.220
No. 2	11.13	0.400	11.18	0.379	11.23	0.369	12.02	0.321	2.52	0.277	Next Day	0.220
No. 3	11.14	0.389	11.19	0.376	11.24	0.356	12.03	0.323	2.53	0.274	Next Day	0.236
No. 4	11.15	0.376	11.20	0.358	11.25	0.346	12.04	0.280	2.54	0.234	Next Day	0.184

TABLE 4

MODIFICATION OF THE ULTIMATE STRENGTH OF IRON AFTER TREATMENT UNDER STRESS WITH CAUSTIC SODA SOLUTIONS OF VARYING STRENGTHS

THREE-INCH LENGTHS

SPECIMEN	Diameter	Length		Ultimate	Elongation in Entire Length Per Cent	Unit Stress at Ultimate, Lbs. per Sq. Inch
		Before	After			
Untreated..................	1.04	3.05	3.75	935	22.0	110000
Pieces......................	1.04	3.00	3.70	770	23.3	90700
No. 1. 70 per cent NaOH..	1.04	3.01	3.75	610	24.6	71800
No. 2. 50 per cent NaOH..	1.04	2.96	3.74	558	26.4	65700
No. 3. 25 per cent NaOH..	1.04	2.93	3.65	560	24.6	66000
No. 4. 10 per cent NaOH..	1.04	2.86	3.63	570	26.9	67000

TABLE 5

MODIFICATIONS OF THE ULTIMATE STRENGTH OF IRON AFTER TREATMENT UNDER STRESS WITH CAUSTIC SODA SOLUTIONS OF VARYING STRENGTHS. SIX-INCH LENGTHS

SPECIMEN	Diameter	Length		Ultimate	Elongation in Entire Length Per Cent	Unit Stress at Ultimate, Lbs. per Sq. Inch
		Before	After			
Untreated................	....	....	....	....	....	.....
Pieces one bend...........	1.04	6.09	6.86	710	12.65	83000
No. 1. Spoiled............	....	....	....	....	....	.....
No. 2. 50 per cent NaOH..	1.04	5.96	6.80	480	14.10	56500
No. 3. 25 per cent NaOH..	1.04	5.97	6.80	490	13.90	57700
No. 4. 10 per cent NaOH..	1.04	5.94	6.76	490	13.80	57700

The heating was done in an air bath of from 100 to 110 degrees for one week. Afterwards the breaking strain was determined. The results are shown in Tables 4 and 5.

The pieces show after treatment a small increase in the elongation, just as in the first series of experiments. The ultimate stress diminishes with the treatment, especially in the pieces which were bent before insertion in the electrolyte.

In studying the effect of hydrogen ions on iron under stress the electromotive force of the bent pieces after treatment was not determined. The potential of the straight pieces was first determined immediately after they were taken out of the solution and again two days later after testing in the machine. The results are given in Tables 6 and 7. In the measurements of Table 7, the broken end of the tested pieces was dipped into the solution, as in the tests the results of which are given in Tables 2 and 3; in both series 6 and 7 the pieces used were carefully cleaned with sandpaper.

These experiments show again that the treated pieces have a distinctly more active potential than the untreated ones. The results

TABLE 6

EFFECT OF POTENTIAL OF STRAIGHT TREATED PIECES IMMEDIATELY AFTER TAKING OUT OF THE SOLUTION

SPECIMEN	Time Min.	Volts	Time Min.	Volts	Time Min.	Volts
No. 4 10 Per Cent NaOH ...	0	0.4000	10	0.379	30	0.370
No. 3 25 Per Cent NaOH ...	0	0.470	10	0.466	30	0.453
No. 2 50 Per Cent NaOH ...	0	0.541	10	0.540	30	0.540
No. 1 70 Per Cent NaOH ...	0	0.520	10	0.510	30	0.5

given in Table 5, where the bent pieces show a much greater lowering of the breaking strain, require more investigation before conclusions may be drawn from them.

TABLE 7

EFFECT OF POTENTIAL OF STRAIGHT TREATED PIECES AFTER DETERMINING THE BREAKING STRAIN. BROKEN END DIPPING INTO SOLUTION

SPECIMEN	Time Min.	Volts	Time Min.	Volts	Time Min.	Volts	Time Min.	Volts	Time Min.	Volts
No. 4 10 Per Cent NaOH..	0	0.422	10	0.3852	40	0.3565	3 hrs.	0.315	......	.....
No. 3 25 Per Cent NaOH..	0	0.451	10	0.4300	......	....	......	....	......	.....
No. 2 50 Per Cent NaOH..	0	0.457	10	0.434	10	0.432	40 min.	0.391	3 hrs.	0.338
No. 1 70 Per Cent NaOH..	0	0.400	10	0.370	10	0.356	40 min.	0.323	3 hrs.	0.296

As a result of our investigations, we are justified in making the following statements:

1. Pieces of steel wire, heated to from 100 to 120 degrees in caustic soda solution of a higher concentration than 10 per cent in a sealed tube, show a small increase in their elongation and a considerable lowering of the breaking stress.

2. At the same time the potential of these wires changes distinctly to the active side, which fact cannot very well be explained otherwise than by the taking up of hydrogen.

3. The electromotive test of any kind of iron and steel may give very important information, and it may be worth while to work out the details of this specific application to a greater extent.

III. THE EMBRITTLING ACTION OF SODIUM HYDROXIDE ON SOFT STEEL

8. *Chemical Reactions Involved.*—It is well known * that at ordinary temperatures iron is passive or non-reactive to sodium hydroxide solutions having concentrations in the range of approximately 1/10 N to 2 N sodium hydroxide. If, however, the concentration of the hydroxide is increased, the passivity vanishes and a reaction of the sort described in the following may take place. This is shown by the electrolytic potential of iron toward solutions of sodium hydroxide or potassium hydroxide. A curve, Fig. 3, reproduced from Heyn and Bauer's work,† shows the Emf at ordinary temperatures of iron to

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*Heyn and Bauer. Mitteilungen aus den Kgl.Material-prufungsamt, 1908.
†Stahl und Eisen, 1908.

solutions of varying hydroxide concentration. It is seen that an anodic reaction of the type

$$\mathrm{Fe} + \mathrm{xOH} = \mathrm{FeO_x} + \mathrm{xH}$$

becomes possible at hydroxide concentrations of about 5N–1ON. At higher temperatures the reaction between sodium hydroxide and iron is more rapid; Krassa[*] has shown that hydrogen gas is generated by the action of N sodium hydroxide on steel at from 150 to 200 degrees C. We may expect, therefore, to obtain hydrogen at temperatures above the ordinary by the action on steel of sodium hydroxide of higher concentrations.

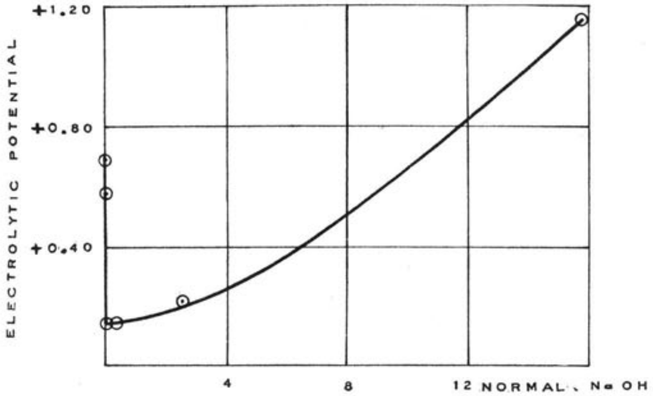

Fig. 3. The Electrolytic Potential of Iron Toward Sodium Hydroxide Solution

(According to Heyn and Bauer)

Abscissas....Concentration of NaOH in mols per liter
Ordinates....Emf of Fe/NaOH/normal calomel electrode

9. *The Effect of Nascent Hydrogen upon the Physical Properties of Steel.*—The researches of Ledebur[†] into the so-called "pickling brittleness" have shown that very marked brittleness is produced in steel by treatment with dilute acid or by making it the cathode in an electrolytic cell. In both cases "nascent" hydrogen is generated on the surface of the steel and reacts with it, in some way not yet clear, to produce a material which is less tough than the original steel. The analogy of the two cases is now apparent, and it is not surprising

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[*] Zeitschrift für Elektrochemie, p. 490. 1909.

[†] Stahl und Eisen, p. 681, 1887; p. 745, 1889.

to find that the action of sodium hydroxide on steel at higher temperatures, at which this reaction first proceeds with appreciable velocity, produces a brittleness comparable with the "pickling brittleness" and due to the same cause.

In Ledebur's study of this type of brittleness he found that it was not possible to show by the static tensile or compression test the deterioration which took place upon generating nascent hydrogen on steel. The various quantities measured, including elongation and reduction of area, remained practically unchanged. Some slight change was detected by a transverse static test, but when an alternating fatigue or impact test was used the deterioration was at once very definitely indicated; reductions in toughness of from 25 to 75 per cent were noted. In this investigation, therefore, it was decided not to rely upon a tensile test alone, but to include some form of impact and alternating stress test. This decision proved to be a wise one.

There is some reference in the literature to the effect that sodium hydroxide has a "destructive effect" on mild steel,* but detail data of the experiments are not at hand. Similarly an article has recently appeared by Andrews † on the same subject, in which, however, the description of his method of testing is not made clear. He states that a thin strip of soft steel became very "brittle" and "crystalline" after immersion for one week in sodium hydroxide at 100 degrees C., and he advances a theory to account for it. Further reference will be made to this article later.

Before describing the testing apparatus used, it may be well to give the reasons why small specimens were chosen for the tests. The chemical part of the problem requires a small specimen, since whatever effect the chemical may have on the material will be localized more or less at the surface, and in order to make the test sensitive it is necessary to have the ratio of the area of the section to the periphery small. This is done, doubtless, at the cost of accuracy, but for the reason stated it did not seem advisable to use standard dimensions either in the tensile test or in the impact bending test.

IV. DESCRIPTION OF THE TESTS, TESTING APPARATUS, AND MATERIAL TESTED

10. *The Tensile Test.*—The tensile tests were carried out on a 10,000 pound Olsen Machine; the same speed was used for all tests.

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*Stromeyer Manchester Steam Users' Association, 1910.

†Transactions Faraday Society, March, 1914.

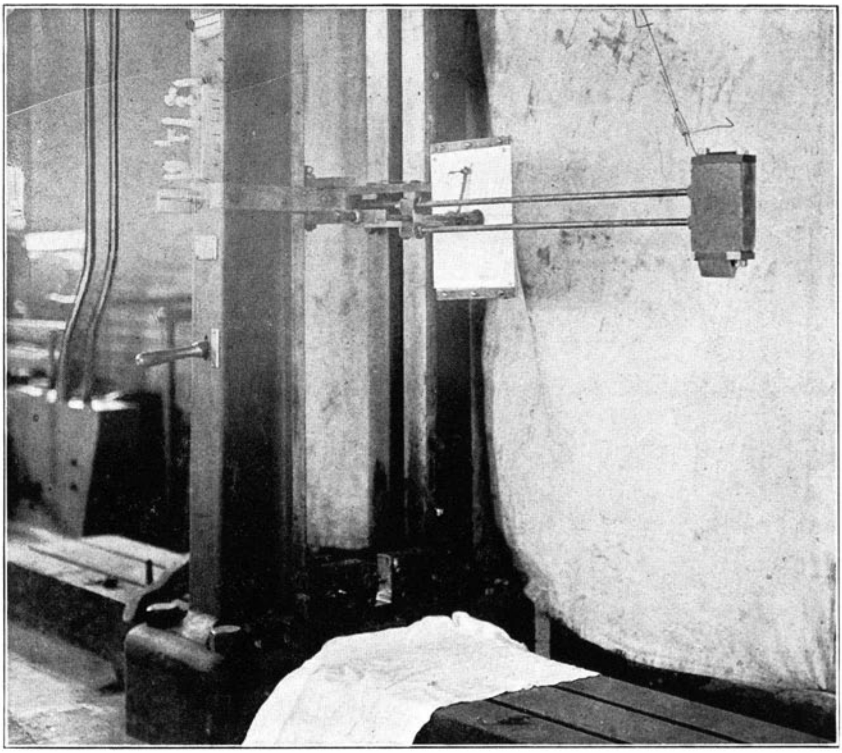

FIG. 4. IMPACT TESTING MACHINE

An automatic recording device was attached, and all the constants were read from the stress-strain diagram. It was considered possible that the form of this curve or the area under it might indicate any change in the quality of the material. The specimens were 2¼ inches long, and were turned down in the middle to a diameter of 0.150 inches for a length of 1¼ inches; thus a shoulder was left by which they were supported in the machine. This was considered better than threading the heads, as the thread would have been rendered useless by the corrosion due to the sodium hydroxide. It was intended to study the ultimate strength, the yield point, the elongation, and the area under the curve during the various treatments.

11. *The Impact Test.*—As there was no impact testing machine at hand which was small enough for these investigations, and time was an important factor, it was decided to build a special apparatus for the tests. Fortunately base and supports were already at hand in the form of a large drop testing machine, and it was only necessary to construct the pendulum, fasten it to the upright guides of the drop testing machine by means of wooden clamps, and bolt an anvil in place. An illustration of this machine as set up is presented as Fig. 4. The pendulum, consisting of a 1½ in. by 4 in. by 6 in. steel block held by two half-inch bars, was supported in conical bearings from the side bars clamped to the fall-hammer guides. Its weight was 16.5 pounds (7.48 kg.). The striking face, which was hardened, had an angle of 45 degrees and was rounded with a radius of about ⅛ inch. The anvil was a 2-inch steel block securely clamped to the base of the fall-hammer; it had an opening two inches wide with hardened anvil faces, rounded with a radius of about 3/16 inch. The recording device was simply a pencil attached to the rotating axis of the pendulum which traced the record on a card tacked to a board secured at right angles to this axis. The height of fall of the center of inertia of the pendulum was taken at 24.6 inches (624 M). The round specimens, 4½ inches long, were notched with a right angle tool in the lathe, and the material for about ½ inch on either side of the notch turned down

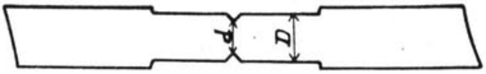

FIG. 5. FORM OF IMPACT TESTING SPECIMEN

to a definitely uniform diameter. The diameter at the bottom of the notch will hereafter be designated as *d*, the diameter of the specimen next to the notch as *D*. (For sketch showing shape of the specimens see Fig. 5.)

In the earlier tests the following procedure was adopted: The specimens were turned to the value of *D* and to within about 0.015 inch of the value of *d* as determined upon for the test. After the sodium hydroxide treatment, in which corrosion always took place, the notch was cut to the final value *d*, nothing further being done to the specimen at *D*. Since, however, the specimen at this point was corroded down to a value of *D*, which was 0.002 to 0.004 inch less than the original dimension, values of the specific impact work (work measured relative to the area at bottom of notch) were obtained which were actually higher after the sodium hydroxide treatment than before, since the tests on the untreated material had been made on uncorroded specimens with the original value of *D*. Reference to Fig. 6 will show the effect of variation of *D* for a constant value of *d*

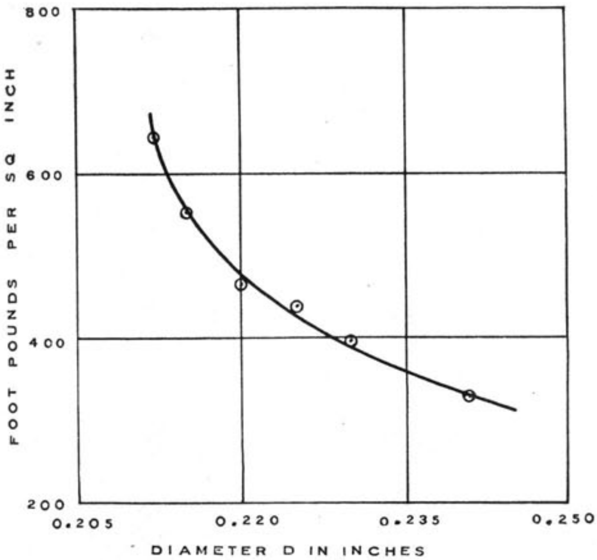

FIG. 6. EFFECT OF VARIATIONS IN THE DIAMETER *D* OF THE SPECIMEN (*d* CONSTANT) UPON THE SPECIFIC IMPACT WORK

Abscissas. . . . *D* in inches
Ordinates. . . . Specific impact work in foot pounds per square inch

on the specific impact work. Fig. 6 also shows how great is the effect of variation of the value of D on the results obtained on the same material. After this had been noted in the experiment the procedure was adopted of turning down both at d and at D to the desired values *after* the treatment, thus securing the same conditions in all the tests. It may be mentioned that the same point was taken into consideration when the specimens were prepared for the repeated bending test, and the same order of operation observed.

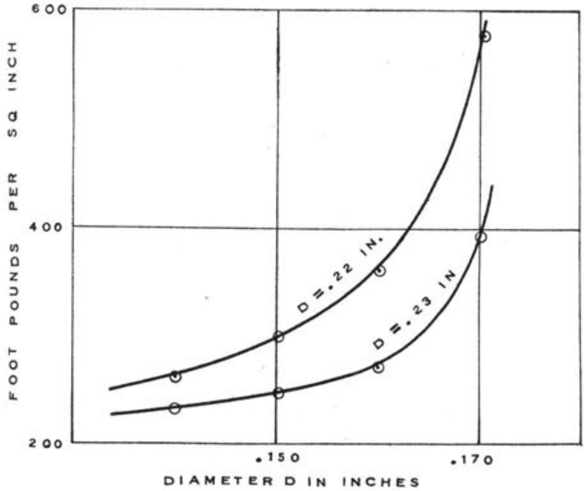

FIG. 7. EFFECT OF VARIATIONS IN THE DIAMETER d AT BOTTOM OF NOTCH (D CONSTANT) UPON THE SPECIFIC IMPACT WORK

Abscissas.... d in inches
Ordinates.... Specific impact work in foot pounds per square inch

In tests run with any impact machine on notched specimens, there is some question as to the accuracy of the tests or accuracy of agreement, because there are two sources of error which are difficult to separate: (a) that which may be due to the machine, and (b) that due to the notching of the specimen. The latter is the more troublesome and difficult to avoid. With this machine an accuracy of agreement of values for the specific impact work of 10 to 15 per cent was generally obtained on specimens notched at the same time and under the same conditions. Variations of more than this were, however, observed when these conditions were not fulfilled.

Attention may be called to some of the results which were obtained with this machine in the early period of work on the dependence of the specific work of rupture on the diameters *D* and *d*. The curves showing these results are given in Figs. 6 and 7, in which the diameters, either *D* or *d*, are plotted in inches as abscissas, and the specific impact work in foot-lbs. per square inch, as ordinates. From a consideration of these curves it was decided to take for *d* the value 0.140 inches at which the variation of *W*, the specific impact work, with *d* was not so rapid.

12. *The Alternate Bending Test.*—A simple test of bending a thin wire back and forth in a vise gave to Ledebur the best indication of brittleness induced by pickling in acid. It was desired to apply, if possible, some more refined form of test to the present problem.

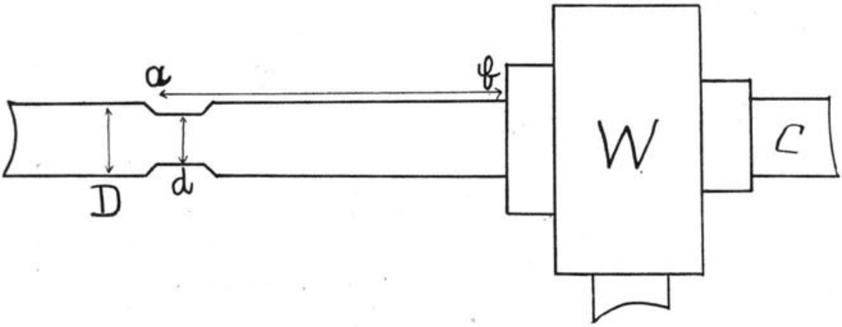

FIG. 8. ALTERNATE BENDING TEST SPECIMEN

Heyn has improved Ledebur's test by notching the specimen, and modern investigations on the "fatigue" of metals have brought out and developed many machines which apply a repeated bending stress. The one which seemed most suited to the present purpose was the White-Souther type. Although there was a White-Souther machine in the laboratory, it was considered best to use the arrangement of which an illustration is presented as Fig. 9. At one end the specimen is supported in a draw-chuck in a small lathe, and at the other in a bushing and ball-race, fitted in a frame. Through a universal joint this frame carries a spring balance by which the applied force is measured.

The shape of the specimen is shown by Fig. 8, the ball-race frame being indicated at *W*. The notch is cut with a right angle tool. As

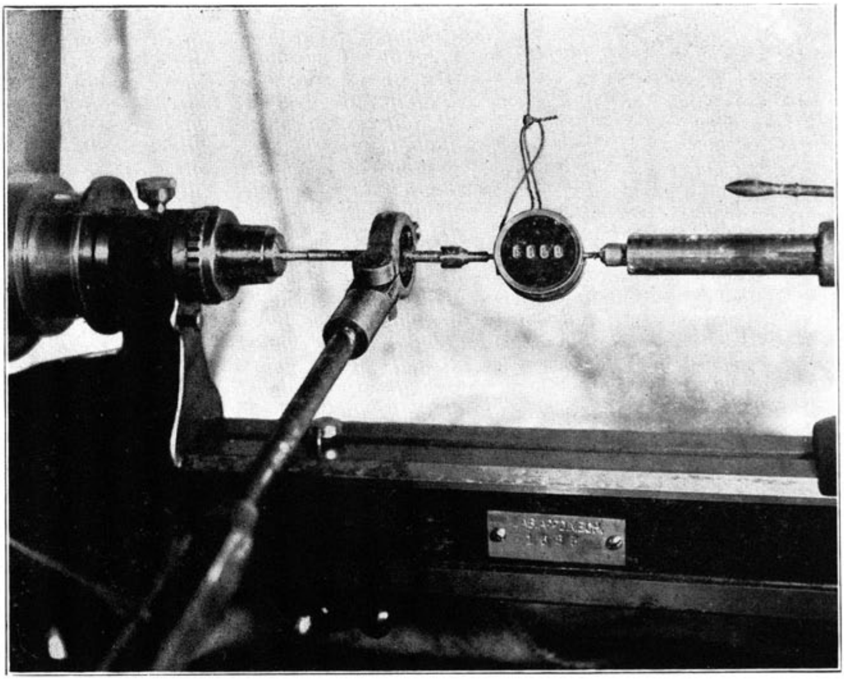

Fig. 9. Alternate Bending Testing Machine

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the fiber stresses in the notch depend on the dimensions of the specimen, in order to have comparable values it is only necessary to maintain as constants the force applied at *W*, and the lever arm of the force as measured from *a*, the end of the notch where the specimen breaks, to *b*, at which the force is applied. A rotation counter which registers the number of alternations required to rupture is attached to the free end of the specimen at *C*. The force and the lever arm were so chosen that about 300 alternations sufficed to rupture the

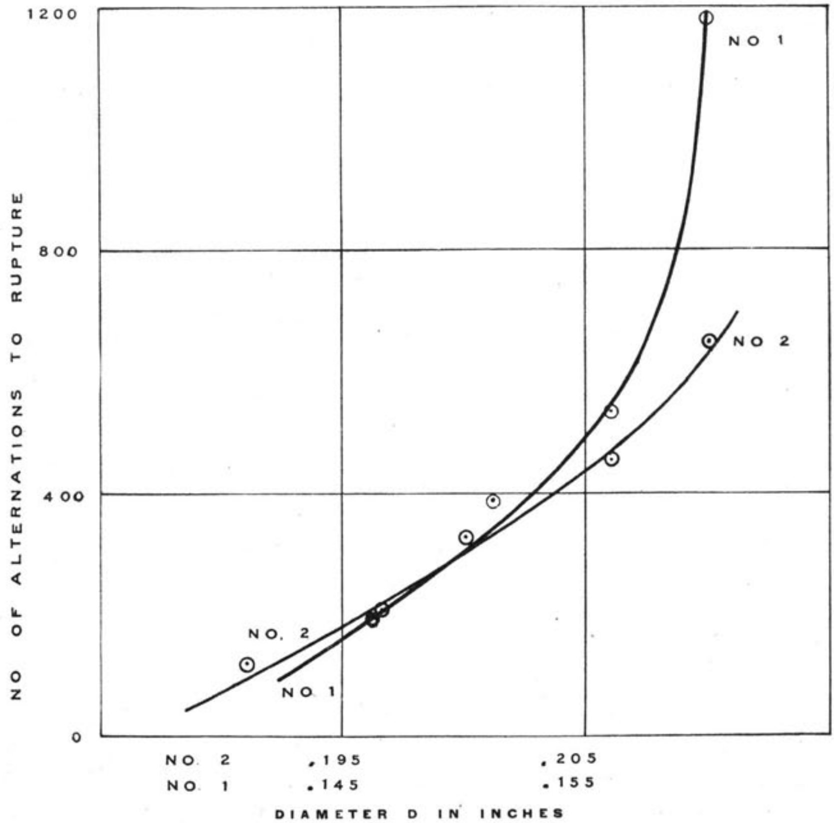

FIG. 10. THE ALTERNATE BENDING TEST. EFFECT OF VARIATIONS OF *d* (*D* AND *M*, THE BENDING MOMENT CONSTANT) ON THE NUMBER OF ALTERNATIONS TO RUPTURE

Abscissas. . . . *d* in inches
Ordinates. . . . Number of alternations to rupture

specimen. All the tests were run at the speed of about 120 revolutions a minute.

It is recognized that present knowledge of the theory of repeated stress does not permit as definite conclusions from this test as from the tensile or even from the impact test. Nevertheless, this repeated bending test with a small number of revolutions has undoubtedly been successful in indicating brittleness in many cases where the tensile test failed, as for example, in the cases of phosphorus brittleness,* of pickling brittleness,† and of overheated steel.‡

As to the consistency of results, here again it was found that much depended upon the method of preparing the specimen. Reference to the curves in Fig. 10 shows that it was necessary to turn the specimen accurately. These curves were obtained in a series of tests on the untreated material by using a constant bending moment at a and a constant value for D, and by varying the diameter at the bottom of the notch d. Two ranges of values for d are shown, the values of the bending moment being constant. It is seen that for the lower value of d the rate of variation of the number of alternations to rupture (ordinates) is much greater than for the higher value. It was decided, therefore, to use the higher value for d (0.195) in the actual tests. In any series of tests on the same material under the same treatment, a maximum variation from the mean of about 5 to 10 per cent was usually found, although occasional variation of 50 to even 75 per cent would be found. Such exceptions were likely due to a lack of homogeneity in the material.

13. *Treatment of the Specimens with Sodium Hydroxide.*—It was decided to study the action of sodium hydroxide on steel at three temperatures, 100, 180 and 280 degrees C, and to use, for the most part, a concentration of 13.6 N sodium hydroxide or 38 per cent. In a few cases as noted in the tables a different concentration and different substances were used.

The treatment of the specimens at the lower temperature (100 degrees), even with the concentrated alkali, offered no difficulties, since it could be done in Jena glass tubes, and by putting a small funnel in the top of the tube the loss by evaporation could be minimized. At the higher temperatures, however, the glass would have

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*Kommers, Proc. Int. Soc. Test. Mat., 1912.

†Stahl und Eisen, p. 681, 1887; p. 745, 1889.

‡Heyn, Handbuch der Materialienkunde, 1912.

been destroyed in a very short time, and some other material had to be sought, therefore, as a containing vessel for the solutions. Iron pipe was regarded as the simplest thing to use, but it was found impossible, even with the exercise of great care in cutting threads and with the use of asbestos and lead gaskets, to cap both ends securely enough to prevent the solution from evaporating completely in a short time. This is interesting in view of the fact that water can be held very easily under the same conditions, and it throws some light on the persistence of leakage at boiler seams when alkali is present. The next procedure after the solution and specimens had been put in was to weld up the tubes with the oxyacetylene torch. This was done by immersing the pipe during the welding in cold water to a point slightly above the level of the solution inside. It is again interesting to note that some of the welded pipes containing sodium hydroxide which were pressure tight upon the completion of the weld, after being heated for some days, developed leaks due to the action of the alkali. In general, however, this method of treatment was satisfactory.

The 100 degree temperature was obtained by means of a steam bath. The two higher temperatures were obtained by means of electrically heated air-baths which were constructed for this purpose by winding a 15-inch length of asbestos covered 6-inch iron pipe with nichrome wire, smearing it with a mixture of talcum and water glass, and putting it in a box of sand. In series with each of these two air-baths was a regulating resistance.

14. *Description of Steel Used.*—Owing to the short time allotted to this work, it was possible to carry out tests on only one material. This was ¼-inch open-hearth wire obtained from the Kokomo Steel and Wire Company, and had the following composition:

C	0.18 per cent
P	0.024 per cent
S	0.045 per cent
Mn	0.42 per cent

Two batches of five hundred feet each were annealed in a large gas furnace in the forge laboratory of the University, and, unless otherwise mentioned, it was this material which was used in all the work.

It is to be noted that this steel is of a composition such as is specified for boiler plate. The significance of this will be seen in the following discussion.

To summarize, the specimens were prepared by turning down each to within about 0.015 inch of the diameter required in the tests, and were placed in a pipe which contained four or five of the samples for both the impact and bending tests and two for the tensile strength determinations. The solution was added, and the pipe sealed and put in the furnace for the required period. It was then removed, opened, and the specimens turned down to the correct dimensions and tested. Care was taken in this final turning not to heat the specimens, since it was thought that such a re-heating might affect the results. The results of the impact and of the repeated bending tests as presented in Table 8 are the averages of four or five tests; the values for tensile strength are the averages of two results.

TABLE 8
SERIES 1 OF TESTS SHOWING EFFECT OF ALKALI TREATMENT ON PHYSICAL PROPERTIES OF STEEL EXPRESSED IN PERCENTAGES OF THE CORRESPONDING VALUES FOR UNTREATED MATERIAL

SOLUTION	Time of Treatment in Days	Temperature of Treatment Degrees C	Tensile Test				Alternate Bending Test. No. of Alternations to Rupture*	Impact Test Specific Impact Work*	Hydrogen Evolution
			Yield Point Lbs. per Sq. In.*	Ultimate Tensile Strength Lbs. per Sq. In.*	Elongation in 1¼ Inches Per Cent*	Area under Stress-Strain Curve* Per Cent			
13.6 N NaOH..	17	100	116.0	102.0	100.0	112.0	85	92	......
	30	100	101.0	102.0	83.0	92.0	110	108	......
	10	180	110.0	100.5	98.0	110.0	64	...	Strong
	15	180	100.8	102.0	97.4	107.0	69	...	Strong
	15	180	103.0	98.5	82.0	88.0	82	...	Strong
	19	180	80.0	97.0	88.0	92.5	82	100	Strong
	23	180	....	....	....	....	88	100	Slight
	24	180	....	....	....	....	90	88	Strong
	12	180	....	....	....	....	....	...	Strong
	5	280	100.6	98.6	104.0	113.0	79	...	......
	8	280	97.6	95.6	67.0	70.0	56	...	Strong
	10	280	99.6	100.1	97.0	110.0	57	83	Strong
	13	280	98.5	96.0	87.0	92.0	80	102	Strong
	15	280	89.0	94.4	98.0	104.0	75	104	None
	15	280	97.6	101.0	90.6	91.0	73	92	Slight
	15	280	....	....	....	....	79	104	Strong
	16	280	107.0	97.0	97.0	104.0	77	94	Strong
	15	...	....	....	....	....	...	...	Slight
13.6 N NaOH + $Na_2Cr_2O_7$..	17	180	102.0	104.0	104.0	117.0	126	106	None
	19	180	116.0	105.0	101.0	116.0	105	102	None
	19	180	....	....	....	....	....	...	Yes
	17	280	96.5	101.0	87.0	94.5	119	86	None
	19	280	96.5	96.0	94.0	101.0	93	107	Slight
	20	280	....	....	....	....	....	...	None
Na_2CO_3......	23	180	....	....	....	....	104	109	Some
	..	280	....	....	....	....	....	...	Some
	16	280	101.0	100.0	91.0	97.0	131	104	None
	24	280	....	....	....	....	....	...	None
Boiler Scale....	19	180	106.0	101.0	94.0	104.0	91	94	......
	23	180	....	....	....	....	90	103	Strong
	19	280	....	....	....	....	....	...	Slight
	19	280	....	....	....	....	....	...	None

*The results are expressed in terms of percentages of the values on original untreated material.

V. RESULTS OF THE PHYSICAL TESTS

Table 8 presents the results of the first series of tests; all values are expressed for convenience in terms of percentages of the corresponding values for untreated material. Column 9 indicates the amount of hydrogen set free during the action of the solution as evidenced by the amount of pressure developed. The material in the untreated state had a yield point at about 37,700 pounds, an ultimate strength of 55,900 pounds, and an elongation of 31 per cent on 1½ inches. The area under the stress-strain curve was 1,190 foot-pounds per cubic inch. The specific impact work in the bending test when a deep notch ($d = 0.150$ inch) was used was 248 foot-pounds per square inch (5.36 m–kg. per sq. cm.). No value can be given for the repeated bending test which would have any absolute significance, because of the difficulty of calculating the fiber stresses in the notch.

The results of the tensile test do not show any effect of the sodium hydroxide on the yield point or on the ultimate strength. The impression is gained from a study of the elongation that its value is reduced slightly by treatment in sodium hydroxide; this can also be said, although to a less degree, of the area under the curve. At the same time the reduction is not very marked, many of the values being reduced only by an amount easily within the experimental error.

Some of the results of the impact test of this series are without value and are omitted here as they were obtained before the procedure had been adopted of turning the specimen down both at d and at D *after* the treatment. The results given here show that the material did not deteriorate at 100 degrees and only slightly at higher temperatures.

When the results of the repeated bending test are considered, however, the effect of sodium hydroxide in embrittling is at once apparent; the number of alternations of stress withstood after treatment is, on an average, about 80 per cent of the values for the untreated material at the two higher temperatures. There are only two cases in which there is no decrease.

In order to confirm these results and at the same time to test the effect of variations in time and temperature on the values obtained, two more series of tests were run, the results being presented in Tables 9 and 10.

It is to be noted in all the tests that at both temperatures, 280 and 180 degrees C, the brittleness increased for about a week and

TABLE 9

SERIES 2 OF TESTS SHOWING THE EFFECT OF ALKALI TREATMENT ON PHYSICAL PROPERTIES OF STEEL

SOLUTION	Time of Treatment in Days	Temperature of Treatment Degrees C	Tensile Test				Alternate Bending Test. No. of Alternations to Rupture*	Impact Test. Specific Impact Work*	Hydrogen Evolution
			Yield Point Lbs. per Sq. In.*	Ultimate tensile Strength Lbs. per Sq. In.*	Elongation in 1¼ Inches Per Cent*	Area under Stress-Strain Curve Per Cent*			
13.6N NaOH..	8	100	96	101	96	104	95	113	.....
	30	100	...	...	...	...	90	87	.....
	8	180	115	100	102	110	93	76	Strong
	3	280	...	...	...	...	83	97	Strong
	8	280	98	97	104	109	88	97	Strong
	8	180	100	102	90	97	103	100	None
13.N $Na_2Cr_2O_7$	8	280	94	102	88	96	96	122	Slight

*The results are expressed in terms of percentages of the values on original untreated material.

TABLE 10

SERIES 3 OF TESTS SHOWING EFFECT OF ALKALI TREATMENT ON PHYSICAL PROPERTIES OF STEEL

SOLUTION	Time of Treatment in Days	Temperature of Treatment Degrees C.	Alternate Bending Test. No. of Alternations to Rupture*	Impact Test. Specific Impact Work*	Hydrogen Evolution
13.6N NaOH	9	200	90	88	Strong
	14	200	106	89	Strong
	15	200	106	100	Strong
	14	200	106	100	......
25N NaOH..................	15	200	82	86	Strong
N/10 NaOH	15	200	108	100	None
13.6N NaOH................	9	200	106	104	None
13N $Na_2Cr_2O_7$	14	200	100	89	None
	15	200	...	108	None
25N NaOH................ 25N $Na_2Cr_2O_7$...........	15	200	...	93	None

*The results are expressed in terms of percentages of the values on original untreated material.

then decreased, the material recovering either partially (first series) or even wholly (second series) its original mechanical properties. This is indicated in the curves showing the results of the first and second series of repeated bending tests given in Fig. 11. Even more striking is the complete recovery noted in the third series. This was also noted by Andrews in his work. A tentative explanation of this rather curious phenomenon is presented in the following paragraph.

During the first period of the action of the alkali, before the oxide product of the corrosion has been formed, the hydrogen liberated by this action is actually given up in the nascent state on the iron

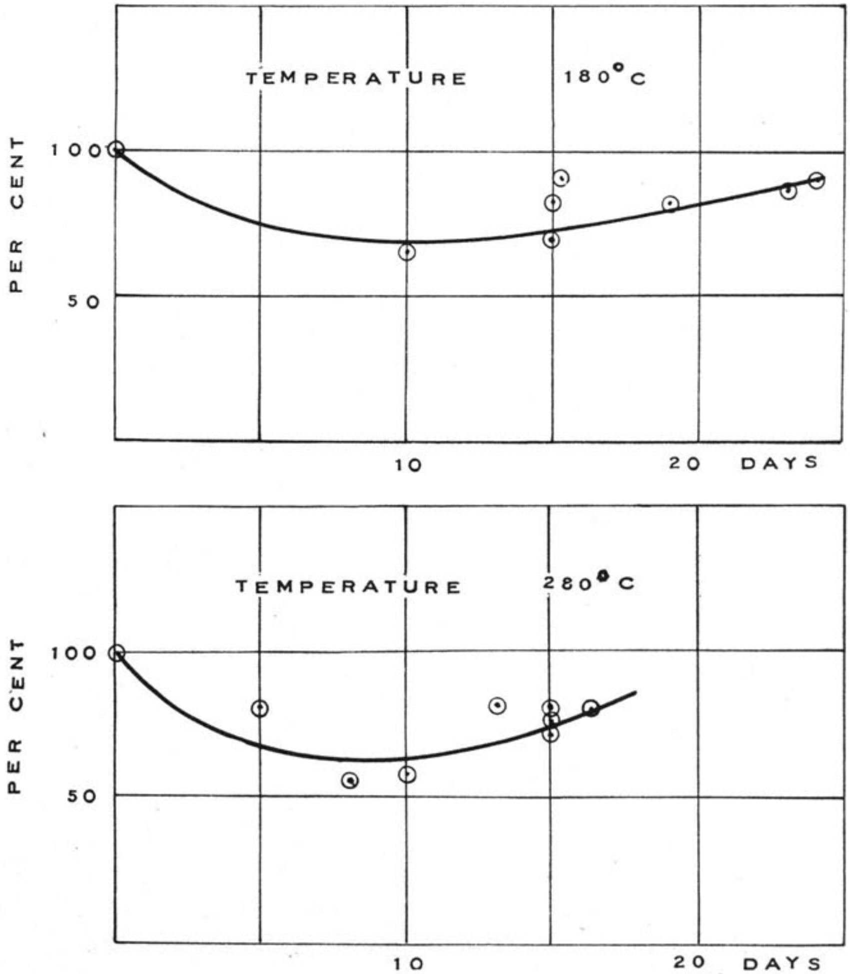

FIG. 11. EFFECT OF SODIUM HYDROXIDE TREATMENT UPON THE TOUGHNESS OF STEEL AS INDICATED BY THE ALTERNATE BENDING TEST. TEST SERIES 1

Abscissas....Length of time of treatment in days
Ordinates....Number of alternations to rupture expressed as percentages of this value on original untreated material

and absorbed by it. Later the H_2 formed by the anode solution of the iron is given up at the cathode, which is now the very electronegative oxide, and can come in contact with the iron itself only by secondary diffusion or after it has formed in the molecular state.

Such hydrogen has been shown to have little or no effect on the mechanical properties of steel. Therefore, as soon as the oxide has formed in a thick, dense layer over and near the iron, the embrittling action of the chemical agent ceases. It has also been shown by Heyn * and others that chemical (pickling) brittleness is relieved by heating for a short time at even such temperatures as 100 degrees C, the hydrogen evidently diffusing out of the material and leaving it in its original state. Therefore, after the embrittling action of the alkali has ceased, that brittleness which has already been induced is removed by the heating to which the material is further subjected.

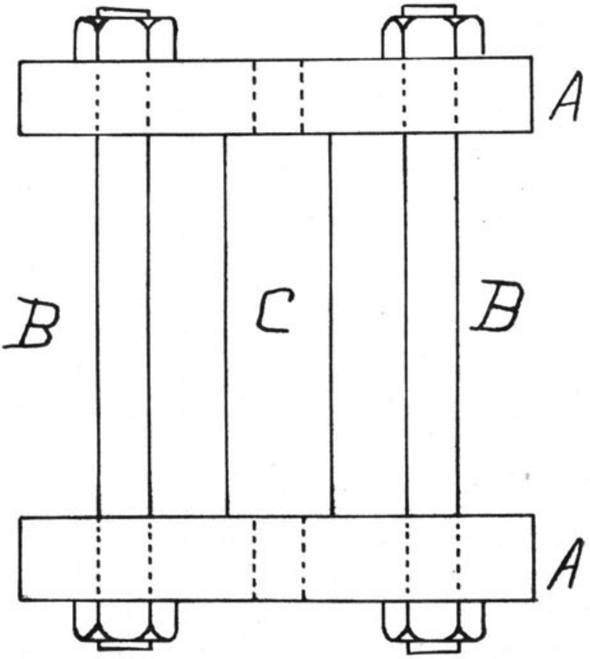

Fig. 12. Frame for Subjecting Steel to Corrosion Under Stress

The effect of the temperature of treatment on the results can be best seen in Table 12, from which it is evident that at the higher temperature the brittleness is developed in a shorter time than at the lower, and also the effect produced by the alkali is greater.

A survey of the results presented in the four tables shows, as would be expected, that the action of the alkali was more marked at

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*Stahl und Eisen, vol. 20, p. 837, 1900.

the higher concentration of 25N than at 13N, and that in two weeks no effect at all was produced by the 1/10 normal alkali at 200 degrees C, although there was quite noticeable corrosion.

As it has been suggested by Stromeyer that steel in tension was more affected by treatment with sodium hydroxide when under stress than when without stress, and as such a fact would, under the circumstances, be of great significance, some tests were carried out to determine whether such an acceleration of the embrittling action could be noticed. Two specimens were put in a frame, a sketch of which is presented as Fig. 12. The specimens BB were then put in tension by screwing up the bolts, the amount of the stress being measured approximately with a strain gage. Since the specimens were notched it was impossible to calculate the fiber stresses at the notch; the average stress applied to the bottom of the notch was about 15,000 pounds. Three of these frames were then welded up with the solution in a 14-inch length of 4-inch pipe and heated for the desired period. It was found very difficult to make the weld in 4-inch pipe absolutely tight and free from pinhole leaks.

The results of these tests are presented in Table 11.

TABLE 11

EFFECT OF SODIUM HYDROXIDE TREATMENT ON SOFT STEEL UNDER STRESS

SOLUTION	Time of Treatment in Days	Temperature of Treatment Degrees C.	Alternate Bending Test. No. of Alternations to Rupture*	Impact Test. Specific Impact Work*	Hydrogen Evolution
25N NaOH.................	8	180	76	86	....
25N NaOH.................	8(t)	180	95	65	....
13N NaOH.................	14	190	97	..	Slight
13N NaOH.................	14(t)	190	110	..	....

*The results are expressed in terms of percentages of the values on original untreated material.
(t) Specimens were in tension during treatment.

So far as can be seen from the results of the two runs made, material in tension shows, if anything, less tendency to undergo the embrittling attack of the alkali than material which is not. In view of the conflicting testimony on this point, it is probable that further investigations are needed.

Owing to the fact that the concentration of hydrogen is greatest at the surface and becomes less toward the center, the results of these tests probably do not give the proper evaluation of the amount of brittleness caused at the surface. Further, in turning down the specimen after the treatment, about 15 to 20 per cent of the material which is most affected by the treatment is removed, so that the actual values over the whole alkali-treated section must have been still smaller by some fraction of the measured reduction in the values.

15. *Cause of the Embrittling Effect.*—The evidence seems to show that the embrittling effect of sodium hydroxide on steel is due to the evolution of hydrogen and the absorption by the steel of the hydrogen in the nascent state. However, there are two other possibilities which may be considered:

First, there is the possibility that the alkali actually works into the metal eating out the "amorphous inter-crystalline cement" which, being thermodynamically less stable than the crystals, would be first attacked. This would cause a brittleness akin to that caused by burning or overheating and fracture would be intercrystalline.

Second, Andrews claims that sodium hydroxide causes a "crystallization," by which he means a coalescence of the smaller crystals into larger ones. This effect would also be the same as that caused by over-heating.

It is not believed by the author that sodium hydroxide acts in this latter way, or, at least, that the embrittling effect is due to any such action. It is, in the first place, difficult to see in just what manner the presence of sodium hydroxide could cause a coalescence to take place in the period of one week which it takes to develop this brittleness, at the comparatively low temperatures of 100 to 200 degrees, in material in which the coalescence is known to proceed at a scarcely appreciable rate at these temperatures.

It has been further shown that the material in contact with sodium hydroxide at higher temperatures undergoes a gradual recovery of the original mechanical properties, a phenomenon which has already been given an explanation, and which cannot possibly be reconciled with any theory making "recrystallization" responsible for this effect. There are presented herewith some photomicrographs to show that no such coalescence does actually take place. Besides the material used for the tests, some specimens of electrolytic iron were used in studying this question. Pieces of the material about one inch long were turned down to a uniform diameter and cut in two. One-half was now treated at any desired temperature with sodium hydroxide and the other held for comparison.

In order to create a favorable condition for crystallization all

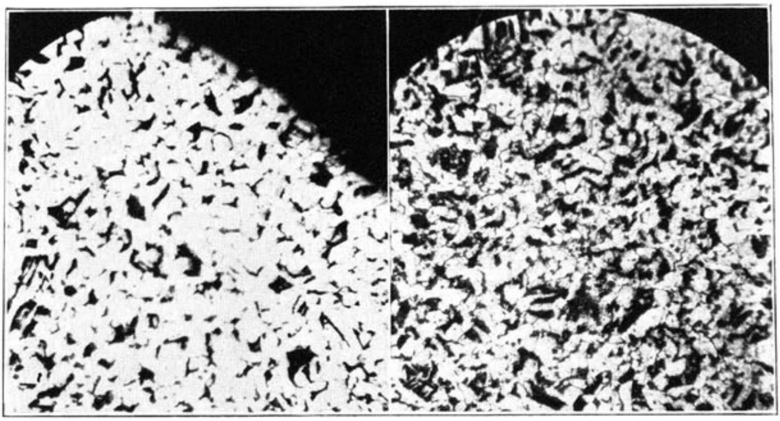

Fig. 13. Photomicrographs of Soft Steel, Before and After Treatment with Sodium Hydroxide

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of the electrolytic iron and some of the steel specimens were first heated above 900 degrees and cooled quickly in air, thus producing a fine, hence less stable, grain. After treatment a low melting alloy was cast around each specimen; in order that the structure at the edge where the alkali had acted might be observed, about 1 mm. was then ground off, and the specimen polished and etched with picric acid.

The specimens were examined and in no case was any increase in grain size noticed as a result of the action of the alkali (Table 12). Photomicrographs, Fig. 13, show the appearance of the steel used before and after treatment with sodium hydroxide at 200 degrees C for fifteen days.

TABLE 12

EFFECT OF ALKALI TREATMENT AT HIGH TEMPERATURE ON GRAIN SIZE OR CRYSTALLIZATION OF IRON AND STEEL

MATERIAL	Period of Treatment with Alkali	Temperature of Treatment	Solution
Steel annealed at 900 degrees and			
(1) cooled in furnace	21	280° C.	13.6 N NaOH
(2) cooled in air	15	200° C.	13.6 N NaOH
Electrolytic Iron Remelted annealed in vacuum and cooled in air	15	200° C.	13.6 N NaOH

Although it is possible that an effect similar to the first mentioned may be present as an auxiliary cause, all the facts seem to show that absorbed nascent hydrogen is the principal cause of brittleness. It is impossible at present to say in just what state the hydrogen is present in the iron, whether as a solid solution, as a compound, or as a solid solution of that compound. It is, indeed, probable that even to detect analytically the small amounts of H_2 present would have been extremely difficult, and for that reason it was not attempted. That hydrogen is evolved during the action of alkali on the iron could be observed at all temperatures above 100 degrees. Upon opening the pipes containing the alkali, a gas was found under considerable pressure, which analyzed about 94 per cent H_2.

A rather striking proof of the fact that some molecular change takes place in iron during the action of alkali is found in a study of its Emf toward any strength of solution, more conveniently N/10 sodium hydroxide, before and after treatment in concentrated alkali at temperatures of 100 degrees and more. This matter was studied first by Dr. Hirschkind and later by the author, and it was found by both of us that after treatment the potential is considerably higher than before, and that it extends into the specimen from the surface

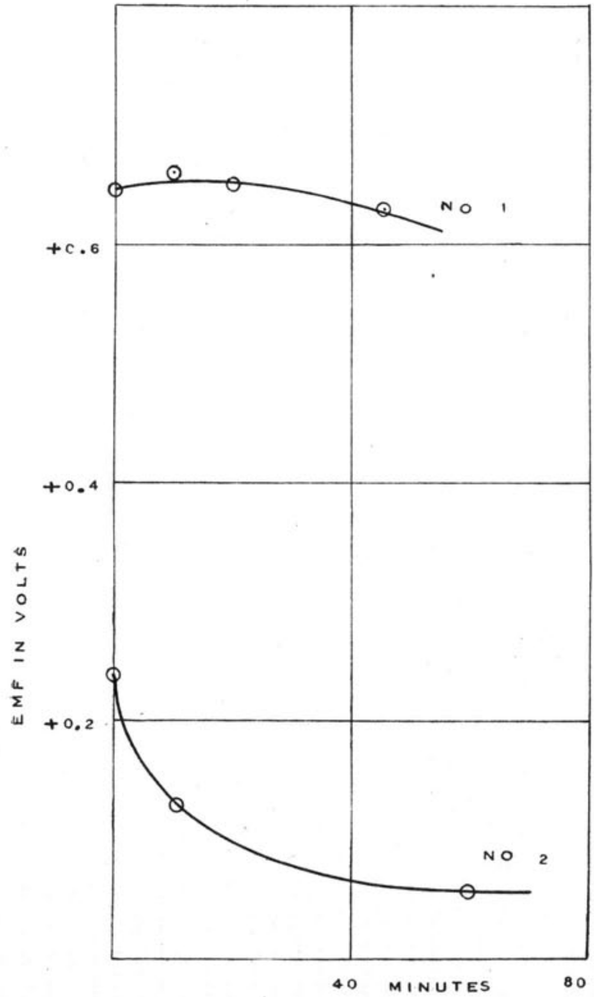

FIG. 14. EMF OF IRON TO N/10 NaOH BEFORE AND AFTER TREATMENT WITH CONCENTRATED NaOH

(Emf measured against the Hg/HgO/$\frac{N}{10}$NaOH electrode) for a considerable distance; this last fact was proved by turning off from 0.015 to 0.30 inch before measuring. This increase in potential is also caused by immersion for a few minutes in dilute acids or by cathodic polarization. The measurements, the results of which are shown in the curves in Figs. 14 and 15, were made by the ordinary compensation method. The specimens were in all cases sandpapered or turned down after alkali treatment and paraffined for about one inch below and above the surface of the solution while their potential was being measured. The curves, Fig. 15, are taken from Dr. Hirschkind's data; they show the potential in 1/10 normal sodium hydroxide of steel against Hg/HgCl. 1/10 normal KCl as a function of the time. Curve No. 3 gives the potential for the untreated steel; No. 2, for the same after a treatment of one week in 50 per cent sodium hydroxide at 100 degrees C; and No. 1, the potential after about ten minutes immersion in dilute sulphuric acid. It is to be noted that cathodic polarization gives the same effect as the sulphuric acid. The curves

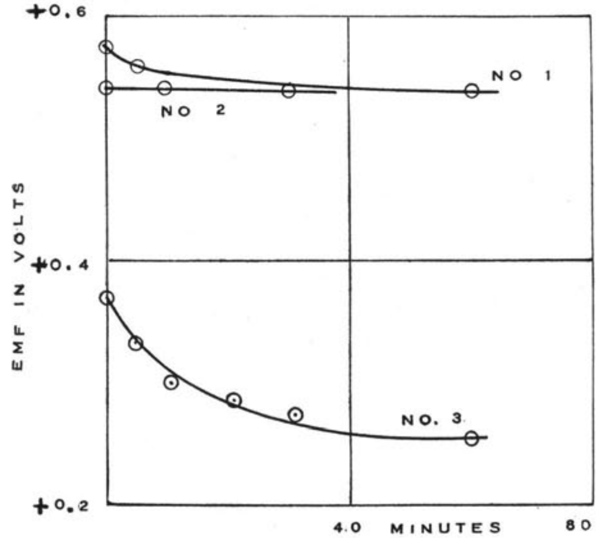

FIG. 15. EMF OF IRON TO NaOH BEFORE AND AFTER TREATMENT WITH 50 PER CENT NaOH AND WITH DILUTE H_2SO_4 (DR. HIRSCHKIND)

Curve 1....Emf after 10 minutes immersion in dilute H_2SO_4

Curve 2....Emf after one week treatment with 50 per cent NaOH at 110°C

Curve 3....Emf of original untreated material in Fig. 14 also show this effect, the measurements being in 1/10 normal sodium hydroxide against Hg/Hg0. 1/10 normal sodium hydroxide. No. 2 shows the potential of untreated material; and No. 1, the same after treatment in 13.6 N sodium hydroxide at 180 degrees for ten days. The potential is seen to be higher for all cases after treatment of any sort that evolves nascent hydrogen on the steel than for the original material. This fact would seem to point unmistakably to a molecular change in the iron.

This high potential seems to disappear in many cases after a lapse of time and after heating to from 100 to 200 degrees in air, but no relation was established between the presence of this potential and the existence of brittleness; the potential seemed to be increased during the treatment long before the brittleness manifested itself. It is, however, likely that there could be found such a parallelism, if the methods for testing the mechanical properties were as delicate as the potential measuring methods.

16. *Prevention of the Embrittling Effect.*—Another indication consistent with the hydrogen theory was found in studying means to prevent the deteriorative effect of sodium hydroxide. Of such means the first and most natural which suggests itself is the removal of the active agent.

If hydrogen is the cause of this brittleness, it should be possible to remove it by adding an oxidizing agent to the solution which would depolarize the iron electrode, as, for example, sodium dichromate. Preliminary measurements of the potential of iron to concentrated solutions of sodium hydroxide showed that at all temperatures readily accessible to such measurements (20 to 110 degrees), this potential was very considerably lowered by addition of the dichromate in equivalent proportions; that is, for one mol. of sodium hydroxide there was used 1/6 mol. of the dichromate. Curves showing this are given in Fig. 17; the measurements were made at 80 degrees C. Not only is Curve No. 1, which gives the potential of iron in 13.6N sodium hydroxide, higher (more electropositive) than No. 2 with the dichromate, but it also slopes upward, while No. 2 slopes the other way. Since the hydrogen potential in an alkaline solution of this concentration is calculated to be about $+ 0.930$, it would be impossible for it to be generated in the solution in which the $Na_2Cr_20_7$ is present. Similarily, judging from these data, the corrosion in the dichromate solutions should be less noticeable than that in the sodium hydroxide

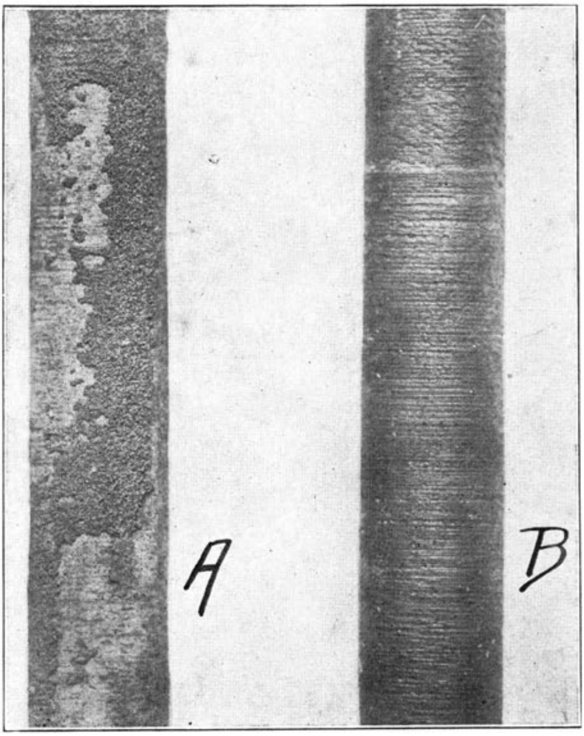

FIG. 16. THE CORROSION OF ¼-INCH STEEL WIRE

A—After 1 week in 13.6 N NaOH at 280° C

B—After 1 week in $\left\{\begin{array}{l}13.6\text{ N NaOH}\\13.6\text{ N Na}_2\text{Cr}_2\text{O}_7\end{array}\right\}$

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solutions alone. In order to settle these points parallel physical tests were run in which a solution with equivalent amounts (13N) of both the alkali and the dichromate was used. The results of these tests are also presented in Tables 8, 9, and 10.

It was first noticed in opening the pipes after the treatment that although, as has already been mentioned, H_2 was present in those pipes which contained sodium hydroxide alone, only a few of those containing the dichromate had generated hydrogen during the treatment. This fact is shown in the tables. The corrosion in all cases was much less, being almost negligible in the case of less than a week's treatment at 180 degrees, and was, moreover, of an entirely different character. This is shown in the photograph Fig. 16. With pure sodium hydroxide the surface was rough and covered with a porous, loose deposit of black Fe_3O_4, or a hydrated form of it, whereas the material deposited at the higher temperatures 180 to 280 degrees

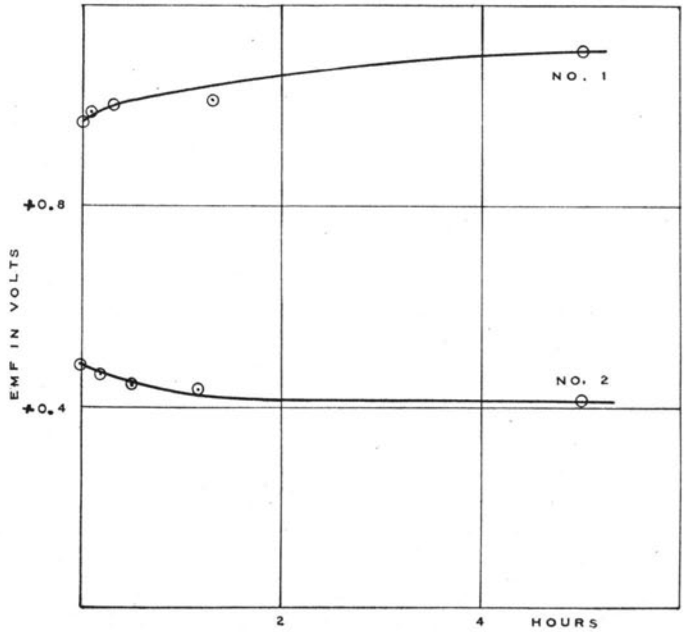

FIG. 17. EFFECT OF ADDITION OF SODIUM DICHROMATE UPON THE EMF OF IRON IN NaOH SOLUTION. TEMPERATURE 80 DEGREES C

Curve 1....Emf of iron to 13.6 N NaOH solution

Curve 2....Emf of iron to solution which is 13.6 N to both NaOH and $Na_2Cr_2O_7$

was of a beautiful black crystalline sheen. With the addition of $Na_2Cr_2O_7$ the surface was smooth and covered with a thin, dense, tightly adherent coating of brown Fe_2O_2. In the latter case the marks of the lathe tool were generally still visible, as can be seen in the photograph.

The toughness, as indicated by the repeated bending test, apparently suffers no deterioration under the action of sodium hydroxide and sodium dichromate in the periods of treatment employed.

APPENDIX A

BOILER WATER TREATMENT

Magnesium Sulphate.—The simplest method for counteracting the excessive alkalinity of the water used at the University of Illinois power plant would seem to be by the addition of a salt having properties which would cause it to react with the alkali and yield a harmless product. Magnesium sulphate ($MgSO_4 + 7H_2O$) is such a salt, the reaction being:

$$2\ NaOH + MgSO_4 = Na_2SO_4 + Mg\ (OH)_2$$

The resulting sodium sulphate remains in solution. The magnesium hydroxide, if the water is free from ammonia compounds, is insoluble and forms a precipitate or sludge. One pound of magnesium sulphate per 1,000 gallons of water will react with an equivalent of 3 grains per gallon of sodium carbonate. The water as used averages about 4.5 to 5 grains per gallon of sodium carbonate, requiring a theoretical treatment of about 1.5 pounds of $MgSO_4$ per 1,000 gallons.

Early in 1914 the use of magnesium sulphate was begun with amounts varying from ½ to 2 pounds per thousand gallons. It was found practicable to reduce the sodium hydroxide alkalinity to zero. Facilities were lacking, however, to accomplish an exact treatment of the raw make-up water owing to the large quantity and varying amount of condensate returned from the heating system. Treatment was, therefore, very irregular; and at times when the treatment was discontinued, the sodium hydroxide concentration would occasionally reach 75 grains per gallon in the boilers. About January, 1916, separate tanks for the make-up water were made available and in these the treatment could be carried out in a way which would be independent of the return water. Much more concordant results were obtained and until March 1 the treatment was confined to the use of one pound of the sulphate to 1,000 gallons of water. The average alkalinity of the water in the boilers was less than 10 grains per gallon. Earlier experience with two pounds per thousand gallons had demonstrated that it was feasible to maintain the hydroxide alkalinity at practically zero when using that amount of sulphate.

Sodium Dichromate.—Another chemical which has been suggested in this connection is sodium dichromate. The reaction involved would be:

$$Na_2Cr_2O_7 + 2\ NaOH = 2\ Na_2CrO_4 + H_2O$$

It is possible that this salt may serve a dual purpose, as indicated in Dr. Merica's discussion, by taking up the nascent hydrogen which might otherwise go into the iron, thus:

$$2\ Na_2CrO_4 + 9H = 4\ NaOH + Cr_2(OH)_3 + H_2O$$

One feature was in evidence as a result of the use of this chemical. Considerable hydrolization took place within the boiler, probably promoted by the presence of the organic matter, so that some chromium was precipitated in the form of hydroxide $Cr_2(OH)_6$, and this material mixed with other solids had a tendency to fuse or bake as an incrustation along the highly heated surfaces of the flues. While the use of this material was of advantage in indicating the location of leakage conditions in the boiler, its use was not continued long enough to prove its worth as a neutralizer of the hydrogen that might be formed.

Sulphuric Acid.—About March 1, 1916, sulphuric acid was used in an amount slightly more than the equivalent of 1 pound of magnesium sulphate per 1,000 gallons of water. At first the amount of acid was 0.39 pounds per 1,000 gallons. This was shortly increased to 0.54 pounds per thousand.

By reference to the composition of the water it will be seen that this amount of acid is sufficient to neutralize about 75 per cent of the sodium carbonate alkalinity, and that for the total alkalinity, including the magnesium and the calcium carbonates, the entire amount of acid required for neutralization would be about 2.5 pounds per 1,000 gallons, which leaves an ample margin of safety between the free acid employed and the total alkalinity of the water. This treatment was maintained steadily for 8 months. A quite uniform degree of sodium hydroxide alkalinity has resulted of approximately 9 per cent of the total solids present within the boilers. This has been accompanied by a sodium carbonate alkalinity of about 11 per cent of the total solids. This ratio of NaOH to Na_2CO_3 alkalinity is constant and evidently represents an equilibrium between the vapor and liquid phases of the constituents. A small amount of exudation with accompanying incrustation has been collected from one of the new drums. An analysis of this material shows:

Sodium Carbonate, Na_2CO_3 = 15.3 per cent
Sodium Hydroxide, NaOH = 1.3 " "
Sodium Sulphate = 72.7 " "
Water = 5.5 " "

Assuming that the sodium carbonate before exposure to the air came from the boiler in the fairly constant ratio of forty-five parts of NaOH to fifty-five parts of Na_2CO_3, we see that the active constituent, NaOH, is probably present at the point of exudation or contact with the boiler plate to the extent of about 8 per cent of the total solids. Whether this amount is low enough to preclude the possibility of hydrogen generation and consequent embrittling of the plate must remain for further inspection and experiments to determine. It may be said, however, that the new drums at the present time, after ten months of service with water that has been corrected for alkalinity, show no signs of trouble. The sudden rise in the price of magnesium sulphate and sodium chromate was the chief argument in deciding upon the use of the free acid. It offers an advantage also in that it adds no further solids to the water, and, from the viewpoint of the chemist, it is more logical to add a free acid which will form magnesium sulphate within the boiler than to add the more expensive magnesium sulphate already prepared. It may not be wise, however, to recommend the use of the free acid except under conditions where absolute control and reliable supervision are assured.

APPENDIX B

Bibliography

Graham,* 1866, discovered that hydrogen penetrates red hot iron and when the iron cools down it retains a part of this hydrogen.

Cailletet † and Johnson ‡ showed that iron at ordinary temperature absorbs electrolytically generated hydrogen, while gaseous hydrogen has no effect at all. Johnson's investigation is very interesting. He used soft iron wire which became brittle as soon as

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*Proc. Roy. Soc., vol. 17. p. 219. 1869.
†Compt. rend., vol. 80. p. 319. 1875.
‡Proc. Roy. Soc., vol. 23, p. 186. 1875.

electrolytic hydrogen was generated on it. If the wire was dipped in acid, it became brittle immediately.

Bellati and Lussana * used a barometer, closed with an iron plate, which was at the same time a cathode in an electrolytic cell. The generated hydrogen was diffused through the iron plate, as indicated by the falling of the barometer. The results of Bellati and Lussana were also verified by Shields.†

Heyn ‡ carried out a series of investigations on the effect of hydrogen on mild open hearth steel and found: first, that if a piece of steel was heated in contact with hydrogen to a temperature of from 730 to 1,000 degrees and was suddenly quenched in water, the metal became decidedly more brittle than if heated in the open air before quenching, and that slow cooling in hydrogen or heating to less than 330 degrees before quenching, had no effect which could be detected by a bending test; secondly, the hydrogen penetrated gradually from the surface inwards, but the effect could be neutralized by heating the specimens afterwards in air or in contact with nitrogen; thirdly, if the pieces rendered brittle by heating in hydrogen and subsequent quenching were exposed to the atmosphere for a long time, the toughness was restored wholly or in a great part. It was not possible to detect the least difference between the micro-structure of specimens heated in air and quenched.

E. Heyn gives further details of his experiments on the influence of hydrogen on iron. The brittleness of the iron, due to the hydrogen, can be very readily overcome. If the iron is heated very slightly or boiled in water or in oil, this brittleness is either wholly or in part eliminated. After the metal had been exposed to the air for fourteen days without any extra heating the brittleness of the open hearth iron completely disappeared, but in the case of the wire, also extremely low in carbon, the metal was as brittle at the end of fourteen days as initially. In 251 days the hardness and brittleness were nearly eliminated.

A very important contribution to the subject has been given by T. W. Richards and G. E. Behr § concerning the electromotive force of iron under different conditions and the influence of occluded hydrogen. As the first of many investigators, they determined the potential of an iron electrode in a normal solution of ferrous irons in the cell:

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*Z. physik. Chem., vol. 7, p. 229, 1891.

†Chemical News, vol. 65, p. 195, 1892.

‡Stahl und Eisen, vol. 20, p. 837, 1900.

§Z. physik. Chem., vol. 58, p. 301, 1907.

$$\mathrm{Fe\cdot FeSO_4\left(\frac{n}{10}\right)KCl\cdot HgCl\cdot Hg}$$

They found as the electromotive force 0.77 volt against the decinormal electrode for compact iron; for porous iron and iron sponge they found it to be 0.03 volt higher, namely, 0.8 volt. This is probably due to the larger surface in the latter case. It was also found that the enormous pressure of 350,000 kg. to the square centimeter caused no variation of the potential; that sudden cooling from a very high temperature had no influence; and that iron powder reduced at low temperature can take up considerable quantities of hydrogen without any change of the potential. Contrary to E. Heyn's statement, previously described, they found that iron heated in hydrogen above 730 degrees and rapidly cooled does not take up any hydrogen, but if the heated iron is rapidly cooled in water, active hydrogen is taken up which considerably increases the potential. They stated further that in this case it would not make any difference if the iron was heated in a hydrogen or nitrogen atmosphere. The hydrogen, which is taken up by the metal in sudden cooling in water, is driven out in the ferrous sulphate solution and the potential goes down to the normal value. The hydrogen in this case seems to be in any active form and equal to the nascent hydrogen which is taken up by the iron (Johnson and Cailletet) whether the hydrogen is generated chemically or electrolytically. E. Heyn in his reply objects to Richards' and Behr's statement that no active hydrogen is taken up by heating in a hydrogen atmosphere. This divergence is explained by the fact that Richards and Behr experimented with spongy iron and Heyn with compact iron.

Concerning the diffusion, occlusion, and solubility of hydrogen in iron we owe two careful studies to A. Sieverts.* He found that at constant temperature the solubility of hydrogen in solid and liquid metal is proportional to the square root of the gas pressure. At constant gas pressure the solubility of hydrogen is increased with the temperature. At the melting point the increase of the solubility is discontinuous. The transition of X into B iron and of B into Z iron cannot be recognized on the absorption curve.

If solid iron is slowly cooled down in hydrogen the dissolved hydrogen is nearly completely liberated. But if it is cooled down

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*Z. physik. Chem., vol. 60, p. 153, 1907.

rapidly, the hydrogen stays in the iron. Sieverts found that in iron heated to 800 degrees and slowly cooled down 0.16 per cent H_2 is liberated. Heyn found 0.16 per cent H_2 in a piece of iron which was treated in a hydrogen atmosphere at from 750 to 800 degrees and rapidly cooled down, which agrees with Sieverts results.

Charpy and Bonnerot,* two French investigators, studied the reactions accompanied by the osmosis of hydrogen through iron. They found no specifically new facts, but stated that molecular hydrogen penetrating through iron has no effect on its structure and strength.

Concerning the phenomenon which is called passivity of iron there is much literature, but only the most recent investigations are here noted.

The metals can be divided into two groups: The first that in which the potential difference between metal and electrolyte is purely a function of the concentration and temperature of the electrolyte; and the second (Fe, Ni, Cr) that in which the potential depends also on the state of the metal itself. We will not discuss all the numerous and different theories of passivity, but only the most recent one, which, it is true, is not as yet generally accepted, but which seems to give promise of proving correct.

A passive metal can be defined without respect to any theory as a metal in that state in which it does not send ions into the solution. That is to say, the reaction

$$Me \leftrightharpoons M^{++} + 2(-)$$

takes place with an extremely slow velocity. Foerster † first brought up the question as to whether the active state is due to a catalyzer. All the metals which exist in an active and passive state like iron, nickel, cobalt, or chrome take up hydrogen very easily. Electrolytic iron contains much hydrogen taken up by the metals which effects the active state as a catalyzer in the reaction described.

E. Grave ‡ claims as the result of his experiments that it is only the hydrogen ion which effects the active state in metals.

J. H. Andrew § describes a series of experiments wherein he was able to demonstrate the brittleness of strips of steel after submerging

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*Compt. r., vol. 156, p. 394, 1913.

†Abh. der deutschen Bunsenges, vol. 2, p. 25, 1909.

‡Z. physik. Chem., vol. 77, p. 513, 1911.

§Transactions Faraday Society, p. 316, March, 1914.

them in concentrated sodium hydroxide at 100 degrees for from one to seven weeks. The action of the caustic soda was accompanied by the evolution of hydrogen. The embrittling effect was more noticeable in the initial stages of the experiment and increased during the first few weeks of the treatment. This brittleness ultimately disappeared and malleability was again restored. These characteristics are especially interesting in the light of Dr. Merica's experiments with sealed solutions of caustic.

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