UNIVERSITY OF ILLINOIS BULLETIN
ISSUED WEEKLY
Vol. XXVIII October 21, 1930 No. 8
[Entered as second-class matter December 11, 1912, at the post office at Urbana, Illinois, under the Act of August 24, 1912. Acceptance for mailing at the special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 31, 1918.]

EMBRITTLEMENT IN BOILERS

A REPORT OF AN INVESTIGATION

CONDUCTED BY

THE ENGINEERING EXPERIMENT STATION

UNIVERSITY OF ILLINOIS

IN COÖPERATION WITH

THE UTILITIES RESEARCH COMMISSION

BY

FREDERICK G. STRAUB

BULLETIN No. 216

ENGINEERING EXPERIMENT STATION

PUBLISHED BY THE UNIVERSITY OF ILLINOIS, URBANA

PRICE: SIXTY-FIVE CENTS

THE Engineering Experiment Station was established by act of the Board of Trustees of the University of Illinois on December 8, 1903. It is the purpose of the Station to conduct investigations and make studies of importance to the engineering, manufacturing, railway, mining, and other industrial interests of the State.

The management of the Engineering Experiment Station is vested in an Executive Staff composed of the Director and his Assistant, the Heads of the several Departments in the College of Engineering, and the Professor of Industrial Chemistry. This Staff is responsible for the establishment of general policies governing the work of the Station, including the approval of material for publication. All members of the teaching staff of the College are encouraged to engage in scientific research, either directly or in coöperation with the Research Corps composed of full-time research assistants, research graduate assistants, and special investigators.

To render the results of its scientific investigations available to the public, the Engineering Experiment Station publishes and distributes a series of bulletins. Occasionally it publishes circulars of timely interest, presenting information of importance, compiled from various sources which may not readily be accessible to the clientele of the Station.

The volume and number at the top of the front cover page are merely arbitrary numbers and refer to the general publications of the University. *Either above the title or below the seal* is given the number of the Engineering Experiment Station bulletin or circular which should be used in referring to these publications.

For copies of bulletins or circulars or for other information address

THE ENGINEERING EXPERIMENT STATION,
UNIVERSITY OF ILLINOIS,
URBANA, ILLINOIS

UNIVERSITY OF ILLINOIS
ENGINEERING EXPERIMENT STATION

BULLETIN No. 216 OCTOBER, 1930

EMBRITTLEMENT IN BOILERS

A REPORT OF AN INVESTIGATION

CONDUCTED BY

THE ENGINEERING EXPERIMENT STATION
UNIVERSITY OF ILLINOIS

IN COÖPERATION WITH

THE UTILITIES RESEARCH COMMISSION

BY

FREDERICK G. STRAUB
SPECIAL RESEARCH ASSISTANT PROFESSOR IN CHEMICAL ENGINEERING

This Bulletin is a Partial Reprint

of

Bulletin No. 155, "The Cause and Prevention of Embrittlement of Boiler Plate"
by SAMUEL W. PARR and FREDERICK G. STRAUB (1926)

and

Bulletin No. 177, "Embrittlement of Boiler Plate"
by SAMUEL W. PARR and FREDERICK G. STRAUB (1928)
with the results of subsequent investigations to date

ENGINEERING EXPERIMENT STATION
PUBLISHED BY THE UNIVERSITY OF ILLINOIS, URBANA

6000 7 30 8630

UNIVERSITY
OF ILLINOIS
:: PRESS ::

CONTENTS

LIST OF FIGURES

LIST OF TABLES

EMBRITTLEMENT IN BOILERS

I. INTRODUCTION

1. *Purpose of Investigation.*—Since the early days of steam boiler operation the industry has been encountering various types of boiler failures. The quality of steel, the conditions of operation, and the design of the boilers, have been changed from time to time in order to prevent the occurrence of such failures. Much effort has been expended toward developing boilers which will be free from failure during the normal operating period. In the last twenty years the demands for higher steam pressures, minimum time of boiler outages, higher ratings, and safety of operation have caused the power plant operators to consider seriously the problem of design and operation in order to obtain boilers which will prove satisfactory over a period of years.

Various types of boiler difficulties have been already eliminated. Now it is the exception more than the rule to find cracks developing in steam boilers. In spite of the efforts of boiler manufacturers for many years to eliminate the condition, there is one type of crack which still occurs. This is the cracking which takes place in the riveted areas of the boiler going from rivet hole to rivet hole, often unseen and undetected until a dangerous conditions exists. Figure 1 shows the results of a boiler explosion caused by this type of cracking. The crack occurs in such a manner that the fracture (Fig. 2) resembles that of a brittle metal, such as cast iron. Therefore it has been said that the plate has become "brittle," and the cracking is termed "embrittlement."

In the early stages of experience with this particular type of boiler cracking, connection seems to have been made between this type of failure and failures of fabricated metal used in processes where caustic solutions were involved, as in the manufacture of sodium hydroxide, and under these conditions the term "caustic embrittlement" was employed. It was soon evident that a certain relationship existed between embrittlement resulting from the use of caustic solutions and embrittlement apparently occurring in boilers with certain waters, by reason of the fact that in the case of such occurrences the water in the boilers was also shown to be caustic. Hence the term "caustic embrittlement" which is often applied to this phenomenon might appear to be justified, but in the present discussion only the general term "embrittlement" is employed.

FIG. 1. POWER PLANT AFTER EXPLOSION DUE TO EMBRITTLEMENT

Attempts were also made in the early days of the study of this type of boiler cracking to connect the cracking with the brittleness produced in steel by atomic hydrogen. Consequently the term "hydrogen embrittlement" has also been applied to this phenomenon. As a matter of fact the two phenomena are widely different.

It is rather unfortunate that the term "embrittlement" has been used to describe this type of cracking. The plates are not brittle. The cracking resembles that of a brittle metal; but the metal immediately adjacent to the crack is ductile, and retains the physical properties of the original metal. However, since the term "embrittlement" had become fairly well fixed in the literature, it was deemed advisable to continue the use of the term in the present discussion.

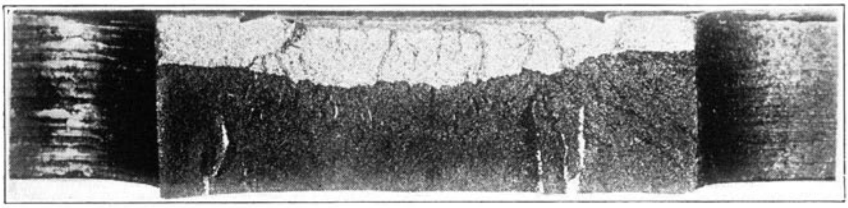


FIG. 2. CRACKED PLATE SHOWING NATURE OF FRACTURE

The purpose of this investigation has been to gather data relative to the occurrence of this particular type of boiler plate cracking in order to determine the cause of the difficulty and to devise methods of preventing it.

The investigation was undertaken by the Engineering Experiment Station of the University of Illinois for the purpose of obtaining information of general interest to all, whether concerned with the production of power or the fabrication of boilers. An attempt has been made to follow methods both in the assembling of information and in the acquiring of experimental data which would avoid any question as to the authenticity of the conclusions reached.

2. *Method of Investigation.*—The general method followed in conducting the investigation has involved the obtaining of data from industrial experience as well as from laboratory experiments. This has involved the collecting of a very large amount of information from power plants which have experienced cracking in steam boilers, as well as the conducting of a large number of laboratory tests. In reporting the results of the investigation the data obtained from the two sources will be kept separate as much as possible. Consequently the results will be discussed in two parts, one dealing with the results of industrial experiences, and the other with those of laboratory experiments.

3. *Sponsors of Investigation.*—The material embodied in this bulletin results from a research sponsored at the University during the last five years by the Utilities Research Commission representing the following companies:

Chicago North Shore and Milwaukee Railroad Company
Chicago Rapid Transit Company
Commonwealth Edison Company
Middle West Utilities Company
Midland United Company

Public Service Company of Northern Illinois
Sargent and Lundy
The Peoples Gas Light and Coke Company

The officers of the Commission are as follows:

Chairman—Mr. W. L. Abbott, Chief Operating Engineer, Commonwealth Edison Company.

Vice Chairman—Mr. J. L. Hecht, Vice President in charge of Operation, Public Service Company of Northern Illinois.

Vice Chairman—Mr. T. V. Purcell, Vice President in charge of Sales, The Peoples Gas Light and Coke Company.

Treasurer—Mr. G. W. Williamson, Treasurer, Commonwealth Edison Company.

Secretary—Mr. H. B. Gear, Assistant to Vice President, Commonwealth Edison Company.

Director—Mr. Wm. A. Durgin, Director of Public Relations, Commonwealth Edison Company.

The work has been carried on as Case No. 1 of the Utilities Research Commission, and has been under the direct charge of a subcommittee of that organization:

Mr. A. D. Bailey, Superintendent of Generating Stations, Commonwealth Edison Company, Chairman.

Mr. A. J. Authenrieth, Vice President, Ice Department, Middle West Utilities Company.

Mr. A. E. Grunert, Efficiency Engineer, Generating Stations, Commonwealth Edison Company.

Mr. R. B. Harper, Vice President, The Peoples Gas Light and Coke Company.

Mr. J. M. Lee, Assistant to Vice President, Public Service Company of Northern Illinois.

Mr. E. Mandel, Chemical Engineer, Testing Department, Commonwealth Edison Company

4. *Acknowledgments.*—Acknowledgment is made of the generous assistance and coöperation received from boiler makers, insurance inspectors, and boiler users. By maintaining a strictly neutral and unbiased relation to all interests concerned, and by omitting specific reference to the sources of information except where permission is given to do otherwise, the author has been accorded every facility

and help in pursuing these studies. Full recognition is here given and it is his desire to gratefully acknowledge this help.

This investigation has been a part of the work of the Engineering Experiment Station, of which DEAN M. S. KETCHUM is the Director; and is one of the researches in Applied Chemistry conducted under the direction of PROF. D. B. KEYES, Professor of Industrial Chemistry.

The investigation was under the direction of PROF. S. W. PARR until his retirement in 1927. Since this time he has kept a decided interest and has aided materially in the work. The author wishes to express his sincere appreciation to Professor Parr for his most excellent direction during the first few years and the kindly interest manifested since his retirement.

The preliminary results of this investigation, down to 1928, have already been published in Bulletin No. 155, "The Cause and Prevention of Embrittlement of Boiler Plate," by Samuel W. Parr and Frederick G. Straub, issued in 1926, and Bulletin No. 177, "Embrittlement of Boiler Plate," by Samuel W. Parr and Frederick G. Straub, issued in 1928. The interest shown by users of steam boilers in the results of the investigation has been so great that the original editions of these two bulletins have long been exhausted.

It seemed desirable, therefore, in preparing this new bulletin, to include a large part of the material already published in Bulletins Nos. 155 and 177, along with new matter representing the work done and the results obtained since the publication of Bulletin No. 177. The present bulletin, therefore, contains in one volume the complete results of the full five years' investigation of boiler plate embrittlement.

In addition to recording some more recent instances of embrittlement in steam boilers and caustic digestors, the new material deals chiefly with a study of the solubility of embrittlement-inhibiting agents in boiler water and of the concentration of solutions in capillary spaces, as well as tests of inhibiting agents other than sulphate or carbonate. This matter will be found in Sections 26 to 28, Chapter III.

In Appendix A the bibliography of the subject is brought up to date, while Appendix D describes the method of the determination of phosphate in boiler water.

II. INDUSTRIAL EXPERIENCE

5. *History of Embrittlement in Steam Boilers.*—An examination of the records of power plant operation reveals many cases of disastrous

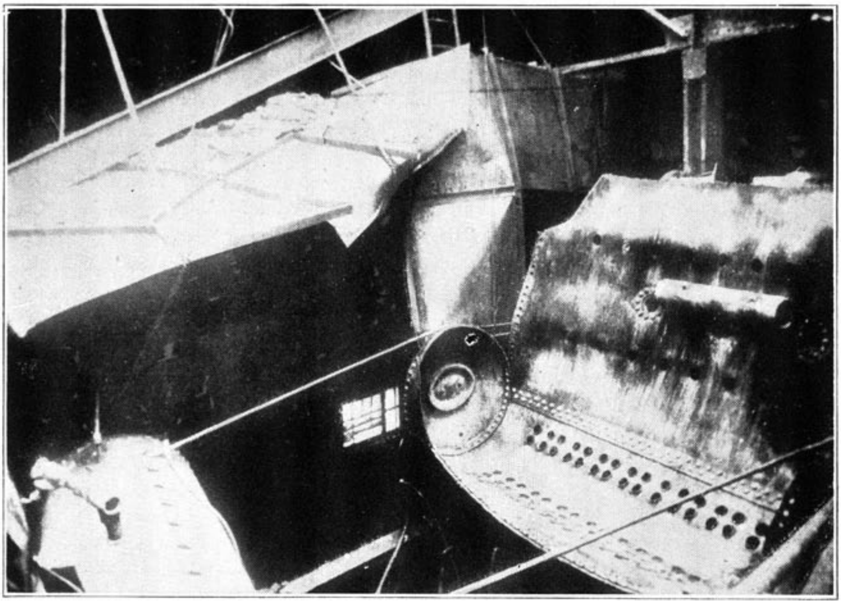


FIG. 3. BOILER WHICH EXPLODED DUE TO EMBRITTLEMENT

boiler explosions. Figure 3 shows a boiler which exploded during 1912 at Bloomington, Illinois. The explosion occurred through failure of the longitudinal seam, from rivet hole to rivet hole. Other boilers in the same plant were found to be badly cracked in the same manner. This particular explosion impressed the industry with the dangers associated with these so-called rivet hole or embrittlement cracks.

In 1895 cracks were detected in the drums of steam boilers which had been installed in 1893 in a plant at De Kalb, Illinois. The seams leaked and did not remain tight after caulking. Rivet heads cracked off, and cracks were found progressing through the steel from rivet hole to rivet hole. The metal away from the riveted areas was in good condition. New boilers were installed, and cracking again took place in the new drums. Similar drums installed in other locations did not encounter this type of trouble.

In 1899 a tubular boiler in an ice plant at Champaign, Illinois, exploded. The failure occurred in the riveted area, the plate cracking from rivet hole to rivet hole. About this time boilers exploded at Watseka and at Paxton, Illinois. In these cases also failure took place in the riveted area from rivet hole to rivet hole.

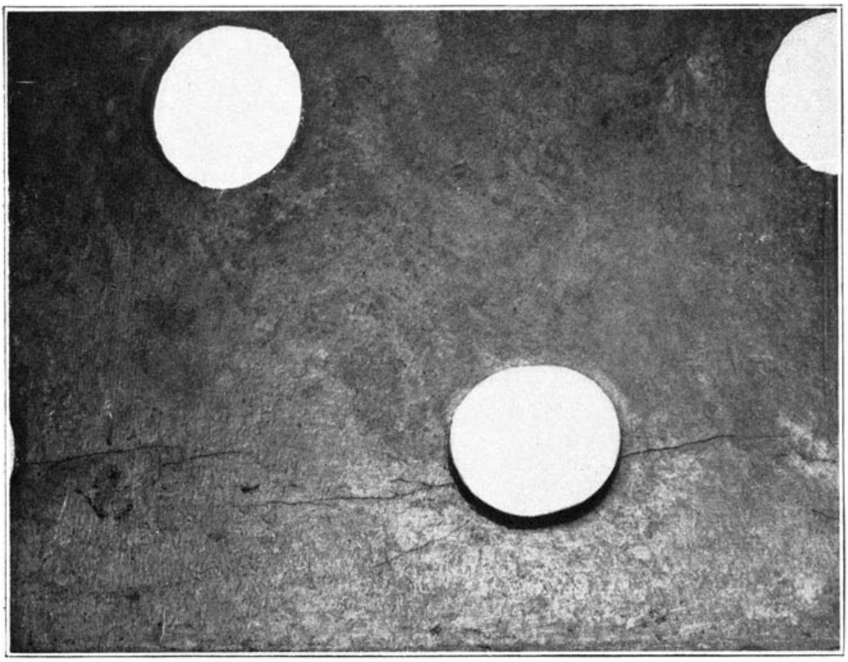


FIG. 4. EMBRITTLED PLATE FROM BLOOMINGTON, ILLINOIS

Numerous cases of boilers cracking in this same manner occurred in central Illinois during the next ten years. These cracked boilers were found at De Kalb in 1901, 1904, and 1911, and at Sycamore in 1901. Replacement boilers installed in the plant at De Kalb also cracked.

In 1912, as already noted, a boiler exploded at Bloomington, Illinois. Examination of the remaining boilers revealed numerous cracks in the riveted areas, as shown in Fig. 4. An investigation of this failure brought to light no evidence of excessive steam pressure. The steel outside the riveted areas was found in perfect condition. Chemical analyses and physical tests made on the boiler plate indicated that the steel was not defective.

In 1910 the boilers in the University of Illinois power plant were found to be leaking, and cracks were found in the riveted areas. Figure 5 shows a cracked blow-off flange removed about this time. The typical rivet-hole-to-rivet-hole cracking can be readily seen in this picture.

In 1911 a new boiler plant was put in operation at the University

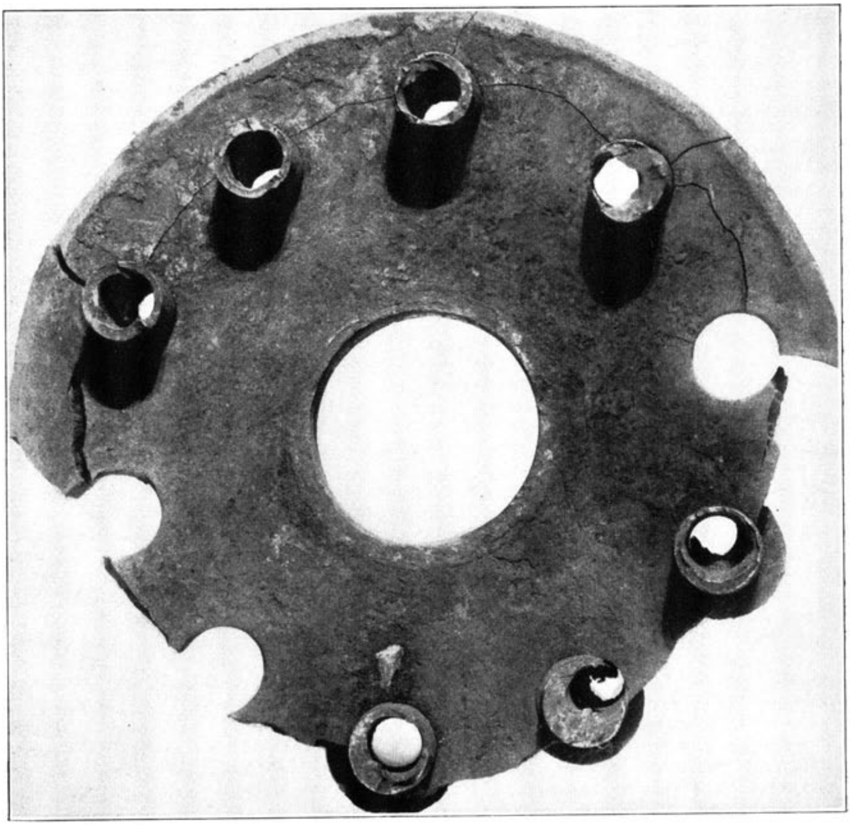


FIG. 5. EMBRITTLED BLOW-OFF FLANGE

of Illinois, and in 1915 the boilers in this plant were found so badly cracked that replacement was necessary.

A review at this time of the records of the steam-boiler insurance and inspection companies, as well as those of the boiler manufacturers, revealed the fact that these instances of cracked boilers were apparently isolated in a definite district of Illinois. Replacement boilers were cracking as rapidly as the original boilers. Boilers built at the same time and sent into other districts encountered no trouble. This apparently precluded the theory of faulty material or poor workmanship, and indicated that some local condition was contributing to this type of boiler failure.

In 1913 an investigation was begun by the Engineering Experiment Station of the University of Illinois in order to determine the probable cause of this particular type of failure in steam boilers, and to devise

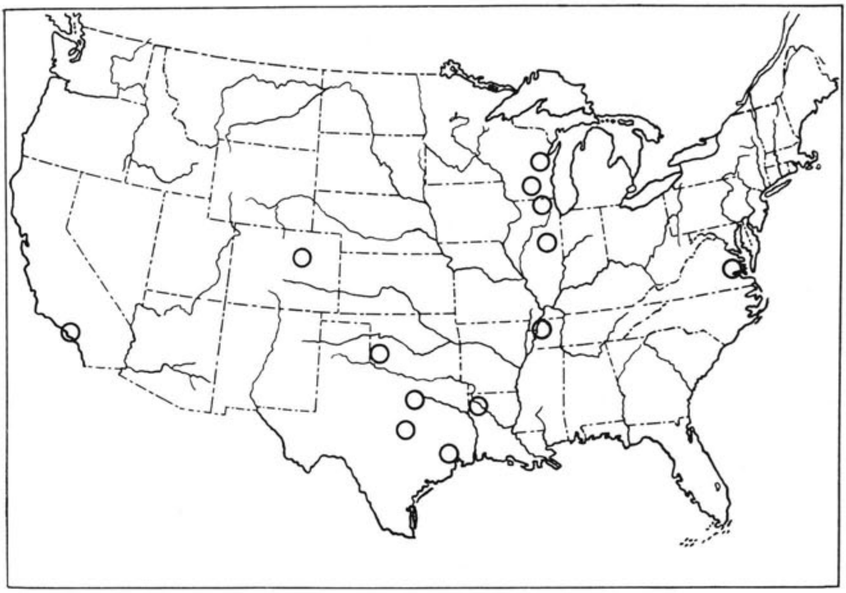


FIG. 6. AREAS IN WHICH BOILERS USING WELL WATERS HAVE BEEN EMBRITTLED

methods of preventing its occurrence. The results of this investigation were published during 1917 in Bulletin 94 of the Engineering Experiment Station entitled, "The Embrittling Action of Sodium Hydroxide on Soft Steel," by S. W. Parr. The data collected at that time showed that the boilers encountering this difficulty had been fed well water, and that these well waters contained sodium bicarbonate and only a small amount of sulphates. This type of well water is rather uncommon. The sodium bicarbonate rapidly broke down to form sodium hydroxide in the boiler. Assuming that there might be a connection between this particular type of cracking and the caustic soda in the water it was decided to treat the University of Illinois well water with sulphuric acid so as to "form a new compound which will not hydrolize in the boiler." This treatment has been in use since 1915, and no more cracking has developed at this power plant.

As a result of the publication of Bulletin 94 the attention of the industry was called to this particular type of boiler distress, and much effort has since been expended toward determining the true cause of this cracking. Consequently available data with regard to the more recent instances of embrittlement have been more nearly complete.

During the period between 1915 and 1925 data collected with regard to this particular type of boiler distress showed that it was oc-

TABLE 1

CHEMICAL ANALYSES OF STEEL FROM EMBRITTLED BOILERS

Location of Power Plant	Carbon per cent	Manganese per cent	Phosphorus per cent	Sulphur per cent
Buffalo, New York	0.18	0.33	0.020	0.040
Lawton, Oklahoma	0.23	0.38	0.010	0.040
Erie, Pennsylvania	0.26	0.34	0.014	0.021
Waukegan, Illinois	0.31	0.41	0.014	0.022
Steamship	0.31	0.38	0.031	0.023
Bloomington, Illinois	0.17	0.26	0.015	0.046
Hartland, Illinois	0.22	0.39	0.017	0.024
Champaign, Illinois	0.20	0.50	0.005	0.024
Los Angeles, California	0.22	0.54	0.013	0.036
Houston, Texas	0.26	0.34	0.014	0.025
Railway	0.14	0.37	0.018	0.018
San Diego, California	0.25	0.47	0.029	0.030
Colorado	0.33	0.45	0.025	0.019

curring in other districts of the United States. The majority of the cases were still found in boilers using well waters containing sodium carbonate. Figure 6 gives the location of power plants using well waters which have encountered cracking of this nature. A few instances of this type of cracking have been found where surface waters were used. It was also found that soda ash treatment or its equivalent had been given these waters. The boiler waters always had a high caustic alkalinity combined with a low sulphate content.

In 1925, a coöperative investigation sponsored by the Utilities Research Commission was begun at the University of Illinois Engineering Experiment Station to determine whether this particular type of cracking could be attributed to a definite type of feed waters. The complete plant data which have been collected are given in Appendix C, and reference to specific instances only will be made here.

6. *Possible Causes of Failure in Boiler Steel.*—In attempting to explain failure of boiler steel the following factors must all be given due consideration.

(a) Material
(b) Workmanship
(c) Conditions of Operation
(d) Nature of Feed Water Used

(a) Material

A steel having the wrong chemical composition or one receiving improper heat treatment will, in many instances, fail in service, but it is very easy to check cases of this kind. Table 1 shows the results of

TABLE 2

PHYSICAL TEST RESULTS OF STEEL FROM EMBRITTLED BOILERS

Location of Power Plant	Yield Point	Ultimate Strength	Reduction of Area per cent
	lb. per sq. in.		
Houston, Texas	39 160	63 800	49.4
Erie, Pennsylvania	47 100	59 800	57.1
Waukegan, Illinois	33 400	65 400	59.0
Excursion Steamship		63 500	59.0
Railroad	37 000	54 700	59.8
Los Angeles, California	40 100	58 800	61.4
Colorado	40 400	61 100	58.5

chemical analyses made on steel taken from boilers which have been embrittled. These analyses have been made on steels manufactured during the interval between **1905** and **1926**, and show that they meet the chemical specification for standard boiler steel.

Table 2 gives the results of physical tests made on plates from embrittled boilers. The test specimens were taken from between the rivet holes, and in some cases within an eighth of an inch of a crack. These results show no marked deviation from the specification requirements for boiler plate steel.

Microscopic examination revealed that, with very few exceptions, the steel had good crystal structure, with the carbon well distributed in even-grained pearlitic form. No microscopic indications of excessive cold work were present in the majority of cases.

(b) Workmanship

The question of workmanship is always open to debate. No riveted boiler is made with absolutely leak-proof, perfectly-fitting seams free from localized high stresses. It has not been the purpose of this investigation to suggest how boilers should be made, or to find fault with those already in service. The only question with regard to boiler design or workmanship to be answered in this investigation was—were the embrittled boilers of the standard of design and workmanship expected at the time they were manufactured? In almost every case investigated the representative of a steam boiler insurance company passed on the boiler as representing the average workmanship at the time the boiler was built. Furthermore, these boilers all bore the

A.S.M.E. and the insurance companies' stamps as being satisfactory when they left the manufacturer's plant. Naturally the boilers built in **1905** had punched holes, drifting was common, and caulking excessive. Newer boilers had holes drilled from the solid with the plates in position; butt seams replaced lap seams; caulking became less in evidence and was practiced both inside and outside. Seams laid up as perfectly as it was possible to do in a practical manner by the art of **1924** have been embrittled as well as old poorly fitting seams manufactured in **1905**. If embrittlement were the result of poor workmanship it would appear evident that if the good boilers of **1924** had trouble, then certainly all the boilers of **1905** should have cracked. Furthermore, boilers with evidence of extremely poor workmanship have served for thirty years without suffering from embrittlement, and when taken apart have been found free from trouble of this nature. All the evidence gained from a complete and unbiased examination of embrittled boilers points to the conclusion that poor workmanship alone never caused any boiler to become embrittled.

(c) Conditions of Operation

The condition of operation of a boiler may be a large contributing factor in causing trouble. The effects of operating at high rating, of hot gases in contact with the metal parts of the boiler, of frequent hydrostatic tests, of excessive caulking of leaky seams, and of the presence of high operating stresses at high temperatures over prolonged periods of time are all to be considered in trying to ascertain the causes of embrittlement. Due consideration has been given to every conceivable factor which might contribute to this difficulty, but throughout the numerous cases encountered no one factor of operation was common to all. A crack might be found in a seam where the colder feed water was on one side and the hot gases on the other; this would point toward high temperature differentials being a contributing factor; but the next case of cracking might occur in the setting, with small temperature difference in the seams. Likewise, a boiler working at high rating might crack, while the next instance of cracking might be found in a boiler operating at low rating. Boilers designed for a pressure of **200** lb. per sq. in., with a factor or safety of **6**, have cracked when operated at **150** lb.; and so forth. The files of the investigation contain numerous reports of instances of embrittlement which indicate that no one factor of operation or boiler design is common to the many cases of failure.

TABLE 3

ANALYSES OF WATERS WITH HIGH SULPHATE CONTENT TAKEN FROM BOILERS WHICH WERE NOT EMBRITTLED

No.	Steam Pressure Carried	Sodium Hydroxide	Sodium Carbonate	Total Alkalinity as Sodium Carbonate	Sodium Sulphate	Ratio $\frac{\text{Sodium Sulphate}}{\text{Alkalinity as Sodium Carbonate}}$
		Grains per U. S. Gallon				
1	150 lb. per sq. in. gage	2	10	13	200	15.4
2	175 lb. per sq. in. gage	5.8	6.1	14.2	42.2	2.9
3	175 lb. per sq. in. gage	7.6	19.9	30.5	71.5	2.4
4	125 lb. per sq. in. gage	36.3	8.7	59.5	102.4	1.7

(d) Nature of Feed Water Used

On examining the mass of data collected from cases of embrittled boilers it could be clearly seen that the type of feed water used in embrittled boilers was apparently a common factor. When the feed water used in such cases was analyzed the fact was disclosed that sodium carbonate was always present in considerable quantity, while the sulphate content was much lower. The boiler waters showed the presence of a high caustic alkalinity with a correspondingly small sulphate content.

Hardness in boiler feed water can be considered roughly under two heads, carbonate hardness and sulphate hardness. In carbonate hardness the carbonates of magnesium or calcium are present in excess, and only a small amount of the corresponding sulphates is found. This type of hardness has commonly been termed "temporary hardness," since it decreases on heating. The sulphates of calcium and magnesium are changed but little on heating, and hardness due to the presence of these sulphates has been termed "permanent hardness." In some natural waters in the United States sodium bicarbonate is present in appreciable amounts, and almost invariably the sulphate content is relatively low. When the water is heated in the boiler the sodium bicarbonate breaks down to give the carbonate, which in turn decomposes to give sodium hydroxide and carbon dioxide.

$$H_2O + Na_2CO_3 \rightleftarrows 2NaOH + CO_2$$

Water + sodium carbonate → sodium hydroxide + carbon dioxide.

The extent of the decomposition of the carbonate depends upon the temperature, or steam pressure, and the partial pressure of the carbon dioxide. In a boiler the steam carries away the carbon dioxide, favoring the formation of the hydrate. Boilers have been found where over **90** per cent of the sodium carbonate has been changed to sodium hydroxide.

Sodium hydroxide is found in nearly all boiler water, since soda ash is a common boiler compound; but the percentage occurring is not nearly so high as that found in embrittled boilers, and, furthermore, sulphates are generally present also in large amounts. Table **3** gives the analyses of boiler waters commonly encountered and shows the high sodium sulphate content generally occurring.

If calcium or magnesium sulphates are present, soda ash is added to form the less soluble carbonates and soluble sodium sulphate.

$$Na_2CO_3 + CaSO_4 \rightleftarrows Na_2SO_4 + CaCO_3$$

Sodium carbonate + calcium sulphate → sodium sulphate + calcium carbonate.

The sodium sulphate is increased, so that the addition of an excessive amount of soda ash would be necessary to bring about an excess over the sulphate in normal permanent hardness. A water containing small amounts of sulphates, however, could readily be changed to one in which the sodium hydroxide is in excess by soda ash treatment, and such types of water have been found in embrittled boilers.

Thus sodium carbonate may be present in the feed water in excess of the sulphate as a result of either one of two causes. First, naturally in a well water having the sodium carbonate present, and second, as the result of water treatment. The addition of an excess of soda ash will produce such a water, or it may result from the use of the zeolite process of softening. In this process the softening is accomplished by means of either a mineral or an artificial zeolite. The bicarbonates of calcium and magnesium are converted to bicarbonate of soda, and the sulphates of calcium and magnesium to sodium sulphate, thus furnishing a water with so-called zero hardness. The zeolite is rejuvenated by treating with sodium chloride solution. This system, when used on a water having a lower sulphate than carbonate hardness, will produce a water in which the carbonate of soda content will predominate over the sulphate content, resembling the feed waters used in boilers that have encountered embrittlement.

The districts in the United States where embrittlement has occurred in boilers using well waters containing sodium bicarbonate can readily be isolated. The map in Fig. 6 shows the location of these districts. Much effort has recently been directed toward treating these natural waters so as to overcome the effect of the excess of sodium bicarbonate, and cases of embrittlement with these waters are apparently decreasing in number. The increase in the use of water treatment on surface waters low in sulphates has brought about an increase in the use of the soda ash and zeolite systems of softening. Naturally, waters having too high a sodium carbonate content as a result of either of these systems of water treatment cannot be isolated in any particular districts, since low sulphate surface waters occur in practically all sections of the country. As a result of this trend in water treatment the number of cases of embrittlement resulting from the use of these types of softened waters is increasing.

Table 4 gives the analyses of eight of the waters used in embrittled boilers, and shows the type of feed water common to every case of boiler embrittlement encountered. The first five are waters which have been zeolite treated, in the sixth case soda ash treatment has been used, and in the last two natural sodium carbonate water was used. The table also shows that none of these waters meets the A.S.M.E. recommendation as to sulphate—carbonate ratio. No embrittlement has ever been experienced with waters meeting this code recommendation.

Table 5 gives the analyses of eight waters taken from boilers in plants which have encountered embrittlement, and illustrates to what extent the hydroxide is formed.

Table 6 gives the analyses of waters taken from boilers which have been operated on zeolite-treated waters, and natural sodium carbonate waters subsequently treated to meet the recommended sulphate—carbonate ratio. No embrittlement has ever been encountered in plants having waters such as these in the boilers.

7. *A.S.M.E. Boiler Code Recommendations.*—The A.S.M.E. boiler code committee in 1925 made a recommendation with regard to maintaining a definite ratio between the alkalinity and the sulphate content in boiler waters. This recommendation resulted from the gathering of data from embrittled boilers. These data showed that boilers having high caustic alkalinity in the absence of sulphate cracked, while boilers having high sulphate and low caustic alkalinity did not

TABLE 4

ANALYSES OF FEED WATERS USED IN EMBRITTLED BOILERS

No.	Source of Feed Water	Steam Pressure, lb. per sq. in.	Treatment Used	Calcium Carbonate	Magnesium Carbonate	Sodium Carbonate	Sodium Sulphate	Sodium Chloride	Ratio $\frac{\text{Sodium Sulphate}}{\text{Alkalinity as Sodium Carbonate}}$	Ratio $\frac{\text{Sodium Sulphate}}{\text{Alkalinity as Sodium Carbonate}}$ Recommended by A. S. M. E.
				Grains per U. S. Gallon						
1	Lake	200	Zeolite	0.15	0.10	9.33	2.23	1.10	0.23	2.0
2	River	250	Zeolite	0.0	0.0	11.47	10.30	3.18	0.90	3.0
3	Lake	200	Zeolite	0.0	0.0	5.83	1.63	1.25	0.28	2.0
4	Well	30	Zeolite	0.0	0.0	18.9	2.0	1.6	0.10	1.0
5	Lake	225	Zeolite	0.20	0.29	8.90	1.50	1.50	0.17	2.0
6	Lake	265	Lime-Soda	0.41	0.41	4.00	2.10	1.34	0.52	3.0
7	Well	225	None	3.16	1.98	9.05	0.12	10.50	0.01	3.0
8	Well	425	None	0.50	0.45	12.5	0.70	0.50	0.05	3.0

TABLE 5

ANALYSES OF BOILER WATERS TAKEN FROM EMBRITTLED BOILERS

No.	Source of Feed Water	Steam Pressure, lb. per sq. in.	Treatment Used	Sodium Hydroxide	Sodium Carbonate	Sodium Sulphate	Sodium Chloride	Total Alkalinity as Sodium Carbonate	Ratio $\frac{\text{Sodium Sulphate}}{\text{Alkalinity as Sodium Carbonate}}$	Ratio $\frac{\text{Sodium Sulphate}}{\text{Alkalinity as Sodium Carbonate}}$ Recommended by A. S. M. E.
				Grains per U. S. Gallon						
1	Lake....................	200	Zeolite	85.4	69.2	44.7	27.3	188.0	0.24	2.0
2	River....................	250	Zeolite	24.3	10.5	36.2	24.4	44.5	0.81	3.0
3	Lake....................	200	Zeolite	216.0	74.9	56.6	87.5	361.0	0.15	2.0
4	Well....................	30	Zeolite	25.6	25.5	13.3	33.9	61.1	0.21	1.0
5	Lake....................	225	Zeolite	63.2	11.3	14.9	18.7	94.8	0.15	2.0
6	Lake....................	265	Lime-Soda	99.2	25.9	82.6	45.0	164.9	0.50	3.0
7	River....................	60	Zeolite	51.2	12.4	3.6	....	84.1	0.04	1.0
8	Well....................	425	None	320	9.0	2.5	....	50.6	0.05	3.0

TABLE 6

ANALYSES OF BOILER WATERS TREATED TO INCREASE THE SULPHATE-CARBONATE RATIO

No.	Source of Feed Water	Treatment Used	Sodium Hydroxide	Sodium Carbonate	Sodium Sulphate	Total Alkalinity as Sodium Carbonate	Ratio $\frac{\text{Sodium Sulphate}}{\text{Alkalinity as Sodium Carbonate}}$	Ratio $\frac{\text{Sodium Sulphate}}{\text{Alkalinity as Sodium Carbonate}}$ Recommended by A. S. M. E.
			Grains per U. S. Gallon					
1	Well	Lime and Acid	22.	9.	90.	38.	2.4	2.0
2	Lake	Zeolite and Acid	28.2	5.3	89.8	42.7	2.1	2.0
3	Lake	Zeolite and Acid	22.0	15.4	116.1	46.2	2.5	2.0
4	Lake	Zeolite and Acid	36.3	14.6	119.7	55.4	3.1	3.0
5	Well	Lime and Aluminum Sulphate	14.1	17.0	72.8	36.6	2.1	2.0

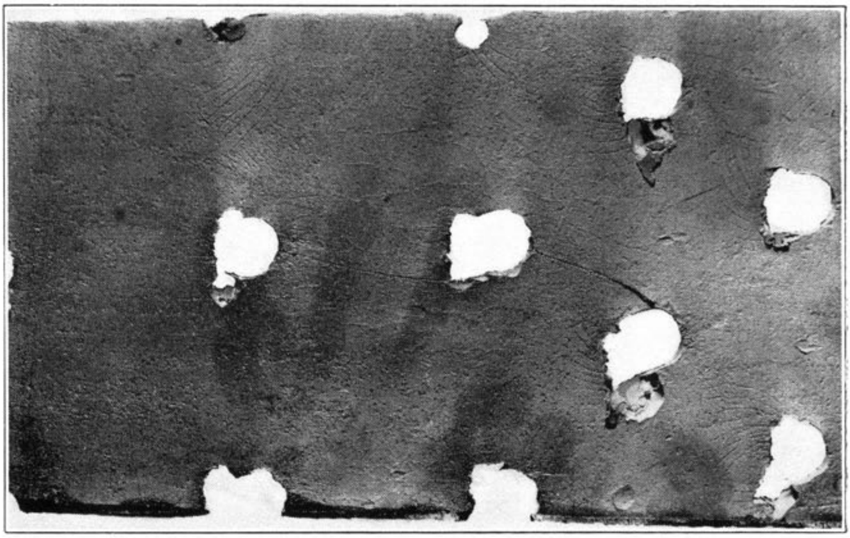


FIG. 7. FIRE SIDE OF CROWN SHEET FROM LOCOMOTIVE SHOWING STRAIN LINES AROUND STAY BOLT HOLES

crack, and that where boilers cracked and the water was changed so as to increase the sulphate the cracking did not occur again.

Realizing that some apparent relationship existed between the sulphate and the alkalinity and the prevention of embrittlement, the following recommendation was made.

"The attention of the committee has been called to the following exceptional cases in rivet-joint cracks described as intercrystalline in character and under the water level only:

(a) boilers in certain localities fed with well water containing sodium bicarbonate, but not an appreciable quantity of sodium sulphate (similar cracking has not been reported in the same localities in boilers fed with surface water free from sodium carbonate or containing sodium sulphate equal to or exceeding the sodium bicarbonate); (b) boilers fed with water in part composed of condensate from leaky caustic evaporators; (c) boilers fed with sea water distillate to which compounds were added resulting in high concentrations of sodium alkalinity.

In view of the particular cases of embrittlement cited above and pending further research, the maintenance of not less than the following ratios of sodium sulphate to the soda (methyl orange) alkalinity is recommended as a precautionary measure:

Working Pressure of Boiler lb. gage	Relation of Sodium Carbonate Alkalinity	to	Sodium Sulphate
0 to 150	1	to	1
150 to 250	1	to	2
250 and over	1	to	3

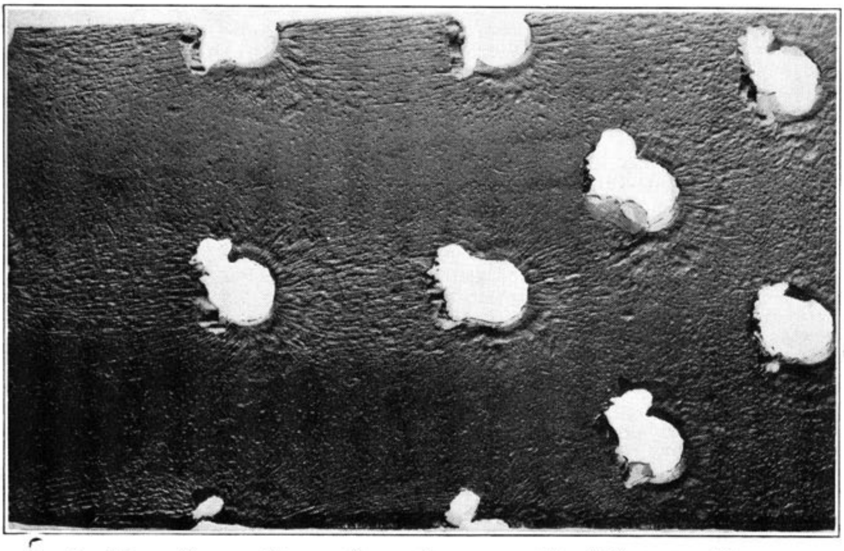


FIG. 8. WATER SIDE OF CROWN SHEET SHOWN IN FIG. 7 SHOWING CORROSION FOLLOWING LINES OF STRESS

Cracks of this particular character have not been reported in cases where water softening equipment has been intelligently used, maintaining close control over boiler concentrations and the boilers have been properly operated.

Pending further operating data from boilers in service, it is recommended that the requirements of Par. 1-44 of Section VI of the Code be extended to all riveted seams and that careful examination of all seams be made if leaks occur and do not remain tight after proper calking."

The increase in sulphate for higher pressures was recommended since it was felt that more hydroxide would form at higher pressures and necessitate the presence of more sulphate. This was merely a "rule of thumb" ratio which had been derived from plant operation.

8. *Types of Cracks Occurring in Steam Boilers.*—In order to study the matter of embrittlement it was deemed essential in the first place to develop some means of recognizing cases of embrittlement which would be reliable without question, and distinctly to differentiate such phenomena from other similar or related conditions. This led directly to a study of the cracking of rolled or fabricated plate. The studies along this line have revealed the fact that three types of cracks may occur, as follows:

(a) Corrosion cracks
(b) Fatigue cracks
(c) Embrittlement cracks

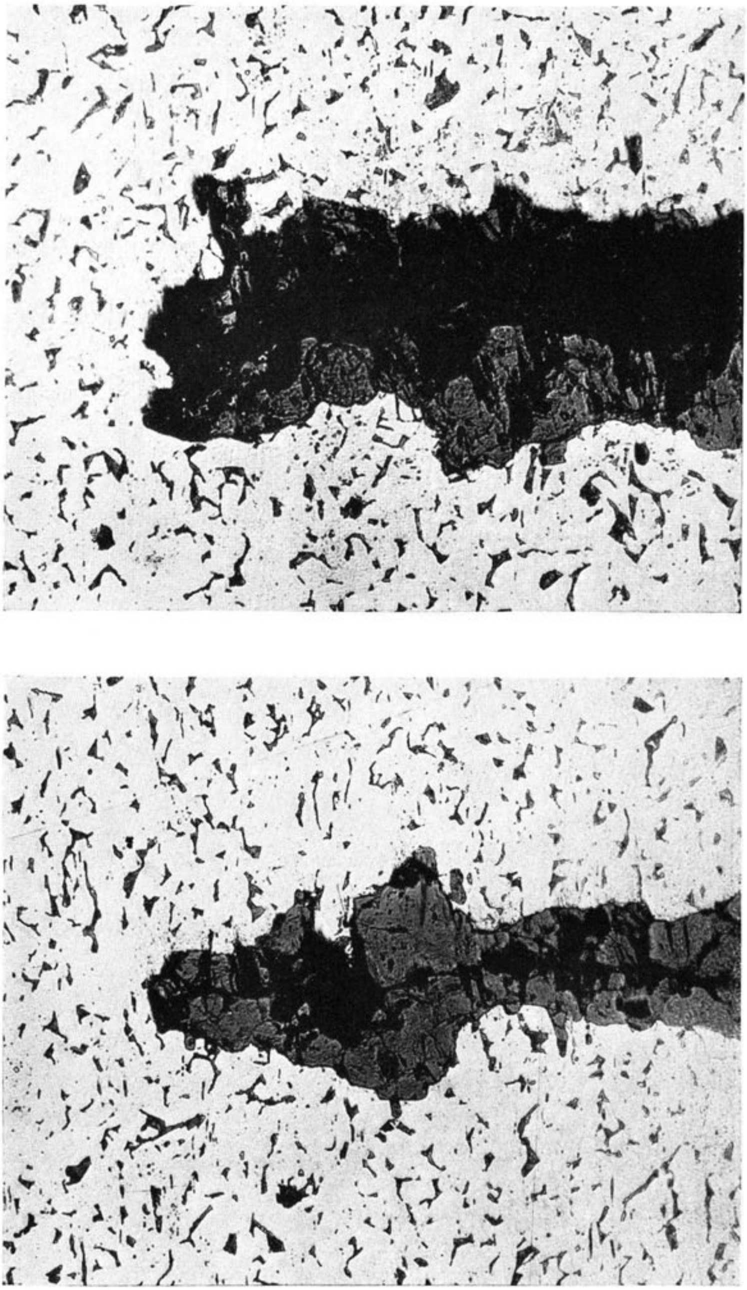


FIG. 9. MICROGRAPHS OF CORROSION CRACKS IN PLATE SHOWN IN FIGS. 7 AND 8
Etched, 2 Per Cent Nital, x 100.

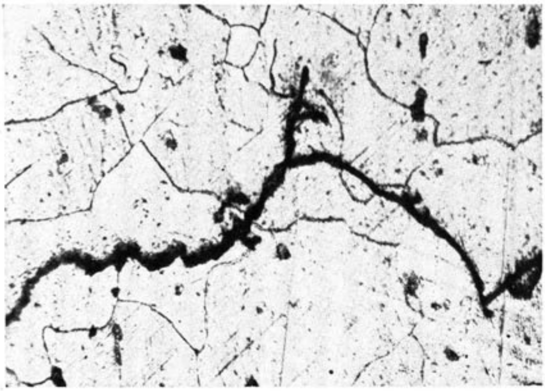
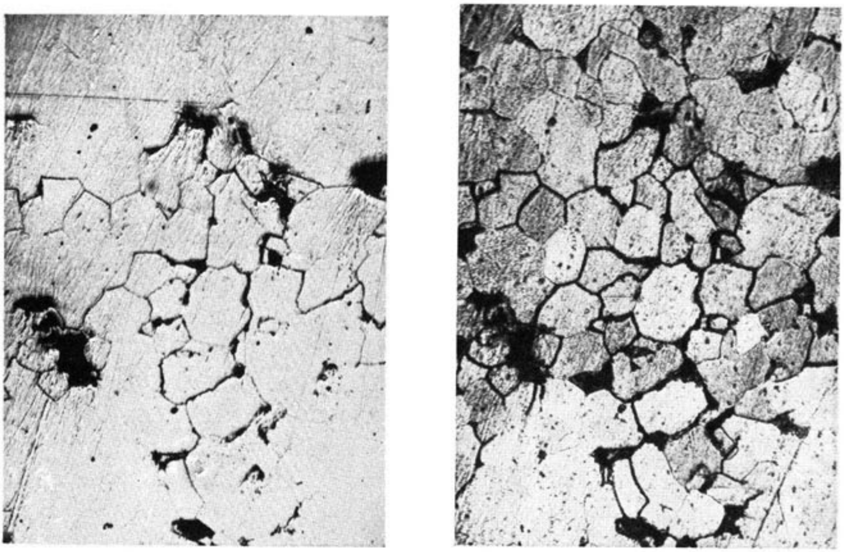


FIG. 10. MICROGRAPHS OF FATIGUE CRACKS IN ARMCO IRON

Micrographs by J. Muller, Laboratory of the Fatigue of Metals, University of Illinois, x 350

Each one of these three types is distinctive and can be definitely differentiated from the other by micrographic analysis. These characteristics may be briefly described as follows:

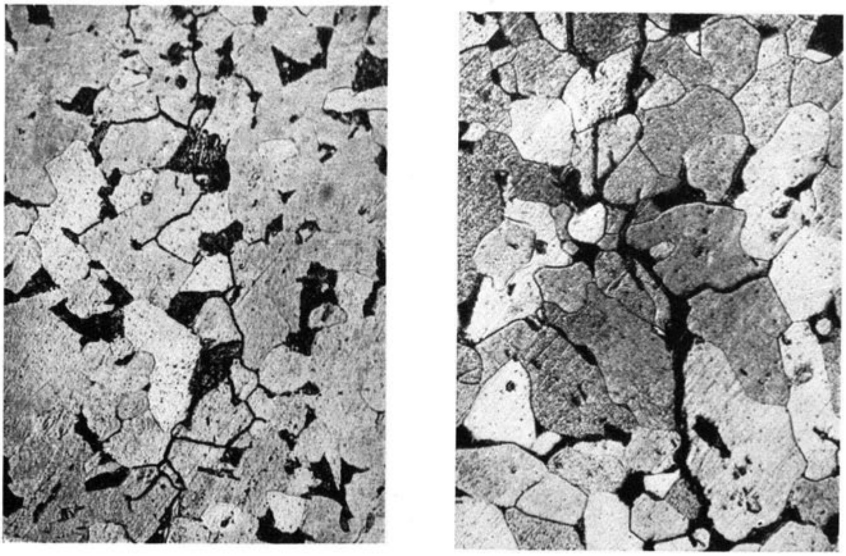
(a) Corrosion cracks, as the name implies, are due to direct corrosion of the metal. This follows in principle the well-known phenomenon where parts of a metal differ in composition or physical properties from other parts, due to strains, or density, or impurities. In the presence of an electrolyte, by reason of the fact that one portion of the



Unetched

Etched, 2 Per Cent Nital

Rivet Head—Same Specimen, x 250



Boiler Plate, Etched, 2 Per Cent Nital, x 250

FIG. 11. MICROGRAPHS OF EMBRITTLEMENT CRACKS FROM BOILERS

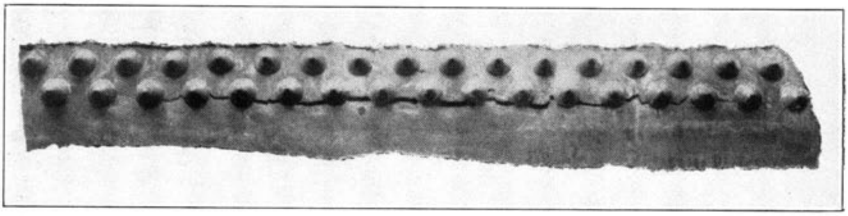


FIG. 12. EMBRITTLED DRUM WHICH RUPTURED UNDER 425-LB. STEAM PRESSURE

metal is electropositive to another, a galvanic circuit is set up, there is started a solution action on the positive side, and a corrosion area is thereby developed. These corrosion areas or cracks in the case of metal under stress will follow the lines of stress, as would naturally be expected. Also, since the solvent action is accentuated, or occurs in the presence of that type of ionization wherein the hydrogen ions predominate, one would expect to find such examples of corrosion in the presence of electrolytes, as nitrates, chlorides, or sulphates. Such corrosion phenomena would be checked or inhibited by the presence of hydroxyl ions or that condition where an alkaline state exists. This in itself will explain why one would not expect to find corrosion cracks in boilers using waters which are alkaline in character. A study of such corrosion does not necessarily require a micrographic analysis of the structure of the corroded surface. The accompanying illustrations, Figs. **7**, **8**, and **9**, show both the unmagnified and the magnified surfaces of cracks of this character. The specific feature should be noted in the micrographs, namely, that the direction of the cracks follows the lines of stress without regard to grain areas, that is, the cracks proceed across the grains and disregard the grain boundaries in their path of development.

(b) The development of cracks due to stress alone furnishes interesting illustrative material in the study of metal cracks. Because of the abundance of examples of this type available from the Laboratory of the Investigation of the Fatigue of Metals, a few illustrations are here introduced (Fig. **10**) because of their bearing on the general topic of cracking of plate. It seems that in metals placed under reverse stress, as failure is approached, cracks develop, which upon micrographic study reveal a positive characteristic serving as a ready means of identification. By examination of a few of this type of specimens it is obvious that the cracks which have been started as a result of fatigue do not respect the fact of grain structure in the metal, but follow a course quite independent of grain boundaries, and are hence

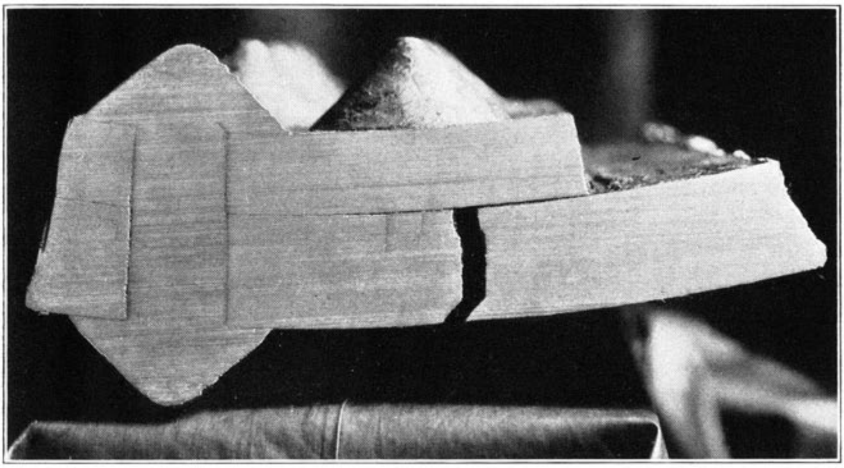


FIG. 13. SECTION OF CRACKED PLATE SHOWN IN FIG. 12

described as cross-granular as opposed to inter-granular in their directional development.

(c) It is now possible to differentiate those cracks which accompany embrittlement from either of the types already described for the reason that a micrographic study shows one distinctive characteristic of this type of crack. By reference to the micrographs of embrittlement cracks, especially when the surface is etched in such a manner as to bring out clearly the grain boundaries, it is very evident that these embrittlement cracks follow grain boundaries. A few typical micrographs illustrating the point are shown in Fig. 11.

With this very definite method of identifying any cracks which may occur in connection with boiler plate, it has been possible to make an extended survey of the situation geographically, as well as from the standpoint of boiler fabrication and of boiler water treatment.

9. *Characteristics of Embrittlement.*—The salient features which are characteristic of embrittlement may be more fully understood after a brief survey of a few typical examples taken from numerous cases which have come to the attention of the investigators.

Figure 12, for example, shows a section of a plate from a boiler which ruptured while operating at 425 lb. steam pressure. The cracking took place from rivet hole to rivet hole for a distance of over eight feet. A section of the cracked plate is shown in Fig. 13, and shows that the plates were well laid up during fabrication.

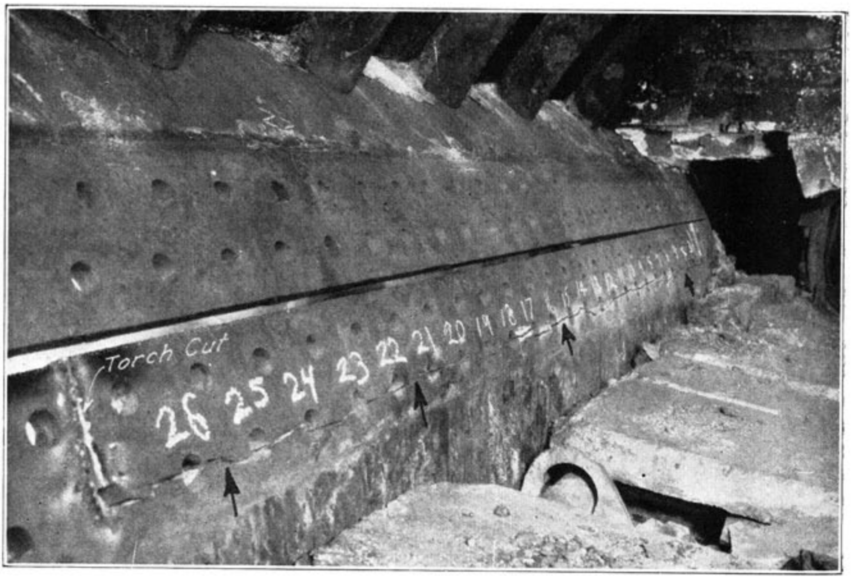


FIG. 14. OUTSIDE OF EMBRITTLED DRUM

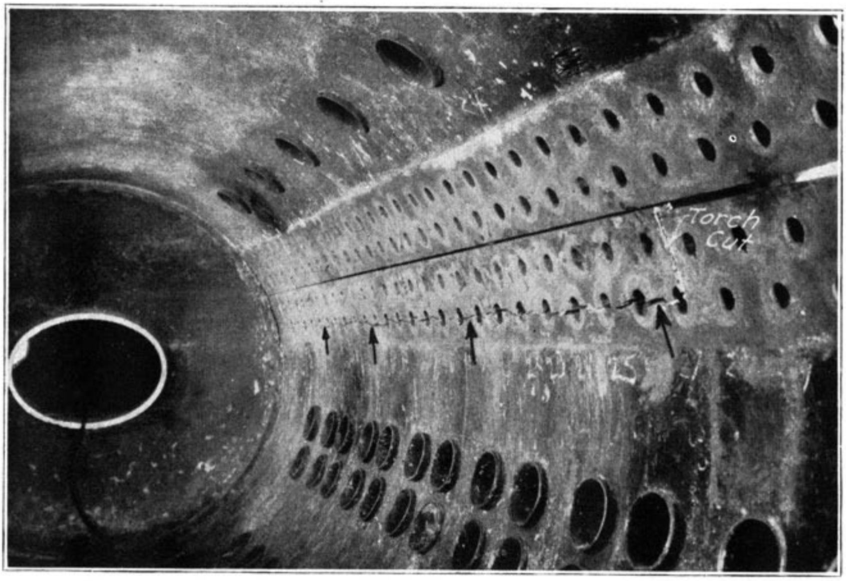


FIG. 15. INSIDE OF EMBRITTLED DRUM

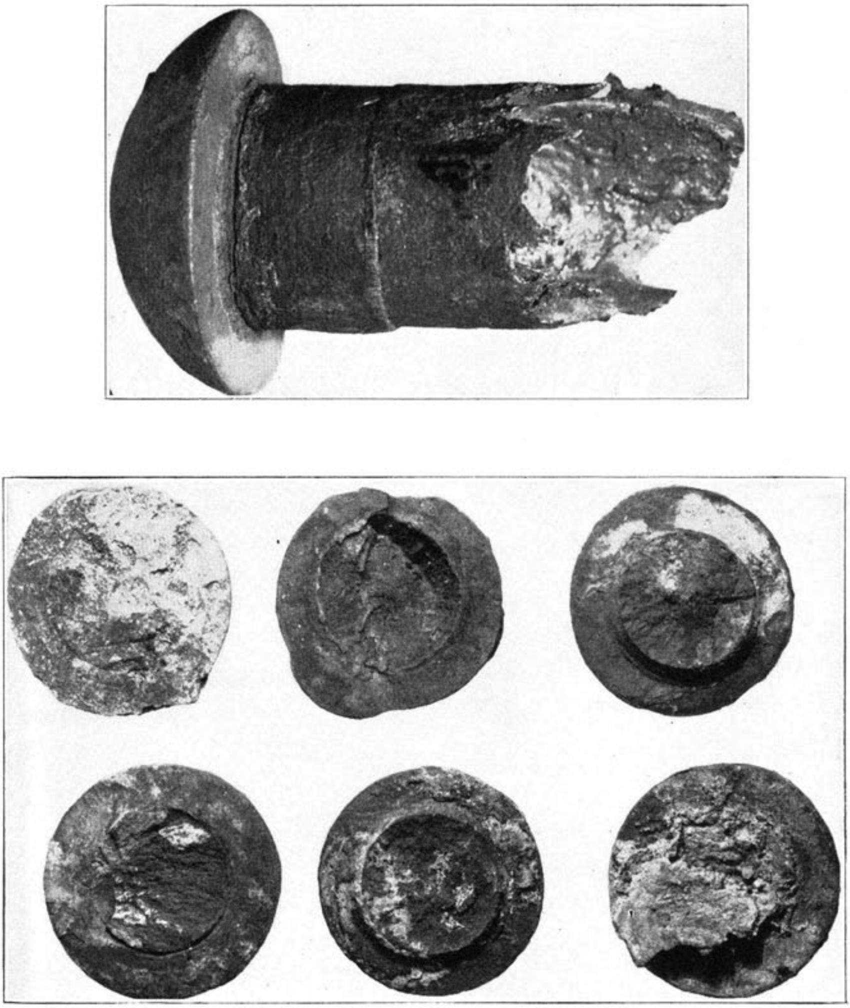


Fig. 16. Rivet and Rivet Heads from Embrittled Boiler

Figure 14 shows the outside, and Fig. 15 the inside, of a drum with a continuous crack for over twenty-six rivet holes. The cracked rivet and rivet heads shown in Fig. 16 were removed from embrittled drums, and show how the rivet heads crack.

Figure 17 shows a cracked drum head from another plant. Tubes often crack in a manner shown in Fig. 18. Figure 11 shows micrographic studies of embrittlement cracks in these same plates or tubes or corresponding ones which have failed in service.

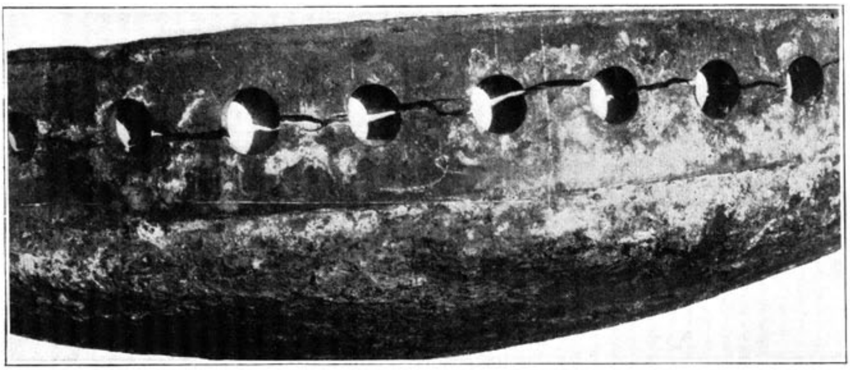


FIG. 17. EMBRITTLED DRUM HEAD FROM A 770 H.P. BOILER

The characteristics of these cracks may be summarized as follows:

(a) The cracks do not follow what is generally considered the line of maximum stress.

(b) They start on what is termed the dry side of the plate.

(c) They run, in general, from one rivet hole to another, though they often run past each other, leaving islands of plate.

(d) They are irregular in direction.

(e) They never extend into the body of the plate beyond the lap of the seam.

(f) There is no elongation of the plate.

(g) Where extreme action has occurred rivet heads crack off or are easily dislodged by a slight blow of the hammer.

A summary of conditions relating to the location of cracks in the boiler may be given as follows:

(a) They occur in seams under tension.

(b) They are found at places where the highest localized stresses might be assumed to occur.

(c) They occur in plates having practically perfect chemical composition and physical properties, as well as in plates of inferior make.

10. *Recent Instances of Embrittlement.*—During the interval between January 1925 and January 1930 twenty-five new instances of embrittlement involving some sixty boilers were brought to the attention of the investigators. At least one million dollars was involved in replacing or repairing these boilers. Property damage resulting from one explosion resulted in a loss of almost one quarter of a million dollars, as well as the loss of one life.

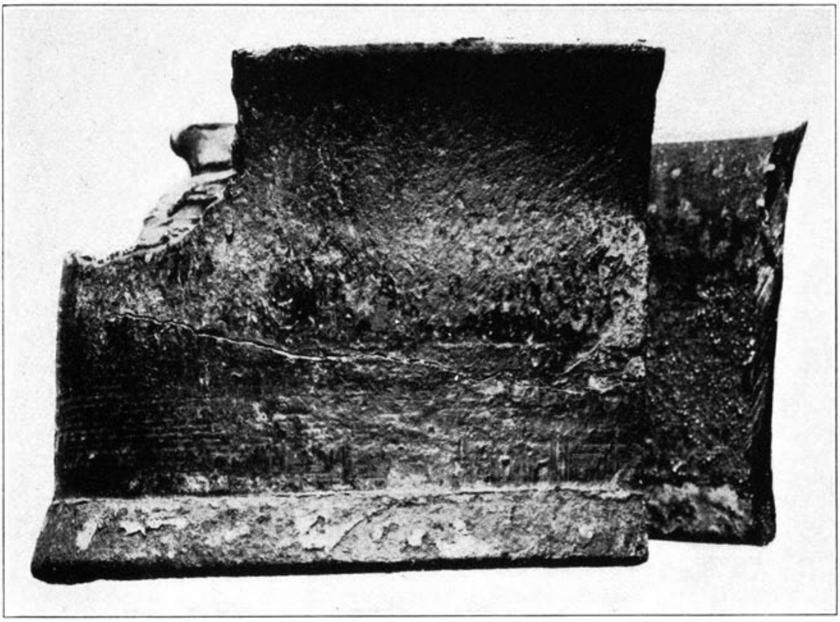


Fig. 18. Cracked Tube from Embrittled Boiler

These cases of embrittlement occurred on boilers operating with pressures as low as 30 lb. per sq. in. and as high as 425 lb. per sq. in., and on different types of boilers, thus illustrating further that the trouble is not confined to any one make or design of boiler. The cracks were found not only in riveted areas or tube ends but occurred at random in practically any seam in the boiler. Samples of steel from a large number of these cracked boilers were analyzed and tested, and no marked deviation from the original mill reports was evident. This tended to confirm the opinion previously stated that embrittlement is not confined to poor steel.

A full description of the amount of cracking which has taken place is given in Appendix B.

11. *Embrittlement in Caustic Digestors.*—Although the conditions of operation of digestors are somewhat different from those of steam boilers the attention of the investigators was called to the possibility of this type of cracking occurring in digestors using concentrated caustic under pressure. The particular digestors investigated were riveted spherical digestors operating at 150 lb. pressure. They were used to reclaim rubber from rubber tires, and old rubber products.

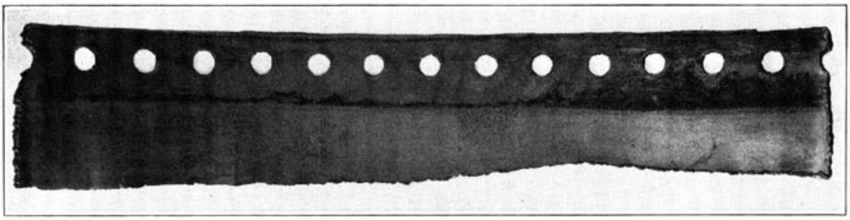


FIG. 19. EMBRITTLED PLATE FROM CAUSTIC DIGESTOR

The material to be reclaimed was put in the digestor along with a solution of about 20 per cent caustic, the digestor was then closed, steam admitted directly to the mixture, and the digestor rotated under pressure for about eighteen to twenty-four hours. One particular set of digestors operated on rubber products such as inner tubes while the rest were used to reclaim the tire casings.

Examination of the digestors used to regenerate the inner tube stock revealed very serious embrittlement in the riveted areas. Figure 19 shows the extent to which this cracking took place in one digestor. Three digestors were condemned and more repaired after they were found cracked. Typical embrittlement was found to have taken place in these digestors. It was found that when the caustic was added to the tire casing stock it was converted to sodium carbonate very rapidly. When the caustic was added to the inner tube material it was not converted to the carbonate, and a strong caustic solution remained in contact with the digestor during the period of operation. This explained the lack of cracking in the one set of digestors.

The influence of workmanship could be readily studied in these digestors. The workmanship was extremely bad in all the digestors. In many instances the holes were badly drifted and the rivets were poorly driven. The evidence of an extreme amount of caulking was present. Despite this evidence of extremely bad workmanship the majority of these digestors had operated for years, and when rivets were removed no evidence of cracking was detected. The cracking was entirely confined to those digestors using a specific type of rubber product which allowed the caustic content to remain high. Here, as in the steam boilers, the common factor of high caustic content in the absence of much sulphate or carbonate was also present. When the carbonate was high no cracking resulted.

12. *Apparent Cause of Embrittlement in Steam Boilers.*—The results that have been obtained from the assembling of information

obtained from almost 400 cracked boilers may be briefly summarized as follows:

(1) Neither the design nor the workmanship appear to be the fundamental cause of the cracking. This conclusion is drawn since boilers made in practically every large boiler shop in the United States have cracked, and at the same time standard boilers made over a period of thirty years have cracked, the newer ones as fast as the older ones.

(2) No fault can be found with the material of the boiler plate, since the quality was fully up to specification requirements in the greater number of cases. Boiler steel made in 1900 cracked as rapidly as boiler steel made in 1925. Plate made in practically every large steel mill has cracked.

(3) The operation of the boilers has in general been satisfactory since other boilers have operated under similar conditions for years without encountering this difficulty.

(4) A caustic condition of the boiler water, with a low sulphate content, was found in all cases of embrittled boilers.

(5) Increasing the sulphate content has been found to be effective in stopping or inhibiting embrittlement cracking in steam boilers.

When this information is given thorough consideration it is realized that there are two factors common to all embrittled boilers, namely, caustic boiler water and highly stressed areas adjacent to the rivets and tubes. The cracking only takes place in the areas which are highly stressed, and where concentration of boiler water might take place. It is only logical to conclude that the cracking results from the action of the caustic concentration in the crevices attacking the highly stressed metal. Any condition which will favor either the concentration of solution or the over-stressing of the metal will naturally tend to accelerate the cracking.

13. *Methods of Preventing Embrittlement in Steam Boilers.*—Since the cause of embrittlement cracking is undoubtedly the action of concentrated caustic on highly stressed metal one would expect to be able to stop the cracking by either one of the following methods:

(a) Prevent the caustic boiler water from concentrating.
(b) Eliminate the highly stressed areas.
(c) Neutralize or inhibit the action of the concentrated caustic.

All boilers which have cracked have had the seams caulked outside, or both outside and inside. This brings about a condition which is extremely favorable to concentration of the boiler water. The laboratory experiments reported in Chapter III show clearly how this concentration is brought about. If the boilers are so constructed that the seams and rivets are all properly caulked on the inside and left uncaulked on the outside the seepage of the boiler water into the riveted areas will be prevented. At the same time the tubes should be so rolled that they are tightest at point of contact with the inside of the drum or header. If any boiler water should pass the inside caulking the outside being uncaulked will leave an opening for this water to go through and a free leak will result. Concentration is not so likely to take place. When the leak is discovered the inside and not the outside should be caulked to stop the leak.

In some installations at higher pressure the use of seamless drums is to be recommended since drums made in this manner will not have any seams. The highly stressed areas where boiler water may concentrate are practically eliminated. The tube ends are the only sections left where the cracking might occur and if these are properly rolled the possibility of trouble here is reduced to a minimum.

These improved methods of boiler design and construction will undoubtedly go a long way toward decreasing the possibility of the occurrence of embrittlement, but at present they are only applicable to boilers for higher pressures and large installations. In smaller boilers built for lower pressures the grade of workmanship necessary for the making of these improved seams and seamless drums cannot be used without a reasonable cost being exceeded. Furthermore, this would mean that the plant using a water not potentially embrittling would have to pay for protection necessary only for plants in which there is a possibility of embrittlement. Another fact to be considered is that boilers now in use cannot be changed, but should operate their rated lifetime. The only means of protecting old boilers and making the new ones doubly safe against embrittlement is by the treatment of the feed water so as to counteract the embrittling effect of the caustic in the boiler water.

The proper method of water treatment to be used to prevent embrittlement depends entirely upon the type of feed water and the boiler water. The laboratory work reported in Section 26 shows that the amount of sodium sulphate necessary in the boiler water is dependent on the amount of sodium hydroxide formed, as well as the amount of sodium carbonate left undecomposed. Figure 41 shows a curve which may be used in determining the boiler water conditions necessary to prevent embrittlement. A systematic analysis should be made of the actual boiler waters over a period of time determining the sodium hydroxide, sodium carbonate, and sodium sulphate. Methods of analyses such as referred to in Chapter III should be used so as to be certain that the results are accurate. The ratios of $\frac{Na_2CO_3}{NaOH}$ and $\frac{Na_2SO_4}{NaOH}$ should be calculated and plotted. If the plotted values fall well above the curve shown in Fig. 41 it would indicate that the water is not embrittling in nature and the system of water treatment in use could be continued. Of course if scale, dirty steam, or other distressing conditions are evident, the water treatment should be changed so as to eliminate these conditions. If, however, the plotted values fall close to or below the curve some method of water treatment should be inaugurated which will do one of two things: (1) increase the ratio of $\frac{Na_2CO_3}{NaOH}$ or (2) increase the ratio of $\frac{Na_2SO_4}{NaOH}$. Which one of these ratios may be changed depends entirely upon the conditions of the plant under consideration. The direct addition of sulphates, or the use of sulphuric acid to increase the sulphate content, should be begun only under the advice of a chemical engineer familiar with this phase of water treatment, and frequent analyses should be made to see that the treatment is correct.

If the conditions of operation are such that it becomes practically impossible to increase the sulphate to hydrate ratio so as to be protective, then the use of another method of preventing embrittlement should be resorted to. The laboratory work has shown that phosphate may be effective in preventing embrittlement if properly used. It should be realized that phosphate, if not used under a definite control, might not only be useless but also dangerous.

During 1929 a large industrial plant experienced embrittlement in its steam boilers. The make-up was low and was partly evaporated the rest being water from one of the Great Lakes. In order to soften this lake water trisodium phosphate was added. This resulted in an appreciable caustic alkalinity in the boilers, with the sulphate too low. The following equations show how the addition of phosphate did nothing more than soften the water and cause high hydrate formation in the boiler water:

$$\begin{aligned}
2\,Na_3PO_4 + 3\,CaCO_3 &\rightarrow Ca_3(PO_4)_2 + 3\,Na_2CO_3 \\
2\,Na_3PO_4 + 3\,CaSO_4 &\rightarrow Ca_3(PO_4)_2 + 3\,Na_2SO_4 \\
Na_2CO_3 + H_2O &\rightarrow 2\,NaOH + CO_2
\end{aligned}$$

If sufficient phosphate had been added so that a minimum of about

40 parts per million PO_4 had been in the boiler water at all times this plant would undoubtedly have been protected from embrittlement.

This serves to illustrate that the phosphate which is effective to prevent embrittlement is not the total phosphate added but only that which is in solution in the boiler water above a certain value.

At present several large plants have been relying on phosphate to prevent embrittlement for over two years. Until more plant data are available as to the effectiveness of this salt in preventing embrittlement it would be well to restrict its use to those plants which may not be readily treated so as to increase the sulphate content.

In these plants, the amount of phosphate being used varies, due to operating conditions. In boilers operating at pressures of 250 lb. or lower, the phosphate is kept over 40 parts per million (about 2 grains per gallon) soluble PO_4 in the boiler water. Where boilers operate at a higher pressure, but keep the alkalinity below 1300 parts per million (about 75 grains per gallon), the soluble PO_4 is also kept over 40 parts per million. In case the alkalinity increases, the phosphate is increased about 20 parts per million for each 400 parts per million increase in alkalinity.

Maintenance of soluble phosphate is contingent on the fact that calcium, if it is allowed to enter the water, will remove the phosphate. Calcium salts will often reach the feed water through the treated water or condenser leakage. It is interesting to note that, in one plant where 15 lb. of phosphate is added per day, 13 lb. reacts with the calcium which passes a zeolite softener and the calcium which enters by condenser leakage, thus leaving only 2 lb. to be effective for prevention of embrittlement.

Plants have been investigated where water treating companies have recommended the use of phosphate to prevent embrittlement. These recommendations have been based solely on the published laboratory tests and have given no consideration to the effect of calcium salts on the maintenance of soluble phosphate. One such plant was advised to add 1 lb. of phosphate salt per day to prevent embrittlement with an alkaline concentration of 2400 parts per million (about 140 grains per gallon). The phosphate necessary to precipitate the calcium alone in the feedwater was 9 lb. per day. Consequently the boilers would have no protection whatsoever. This plant had never been told to maintain soluble phosphate in the boiler water at all times. Thus the most essential part of the phosphate treatment had been lost sight of.

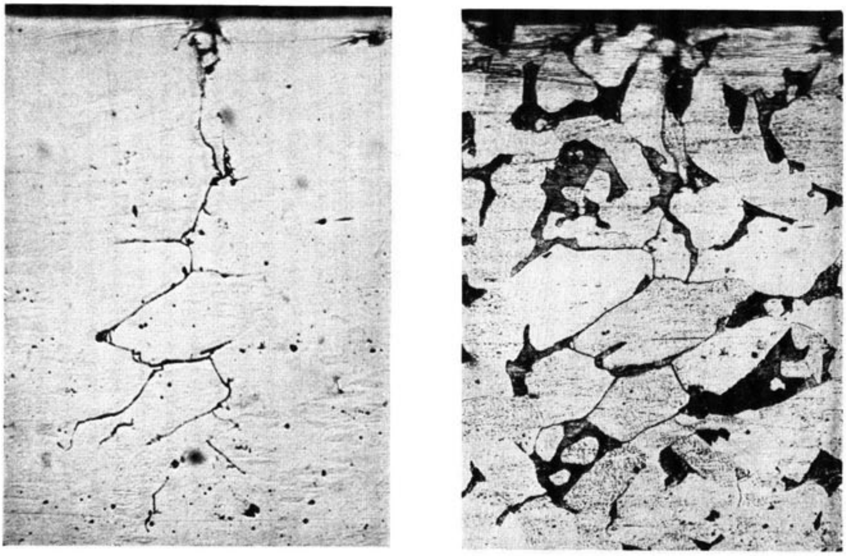
In power plants using evaporators entirely for make-up, and having no chemical treatment whatever, the question of proper ratio involves the accurate determination of the sodium hydroxide and sodium carbonate. Quite often the sodium hydroxide and sodium carbonate are so low that the solubility of calcium carbonate and magnesium hydroxide becomes appreciable in determining the total alkalinity. Methods of analyses which allow for the calcium carbonate and magnesium hydroxide should be used in determining the sodium hydroxide and sodium carbonate which may be used for determining the ratios. If this is done many plants of this nature which are now apparently not meeting the recommended ratio will be found to be in the protected area as far as embrittlement is concerned.

III. LABORATORY EXPERIMENTS

14. *Micro-Examination of Embrittled Metals.*—Samples of cracked steel were obtained from different instances of this type of boiler distress. When these were examined under the microscope, the cracks were shown to be intercrystalline. The manner in which mild steel fails under ordinary stress, either static or fatigue, is almost invariably transcrystalline. The fact that embrittlement cracks progress between the grains indicates that this is not a normal fracture. Furthermore, the crack progresses without any marked deformation of the grain, another deviation from the general behavior of mild steel static failures.

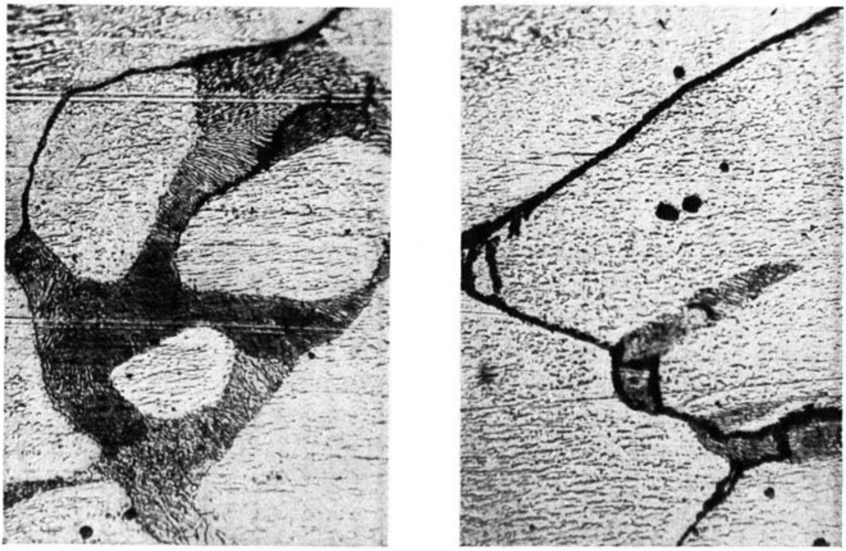
In examining cracked plates in order to determine the type of crack present it was necessary to seek out the small incipient cracks which had not been overstressed or pulled apart. One would expect to find evidence of strain cracking wherever the cracks had progressed far enough so that the plates had pulled apart. The majority of plates examined showed evidence of strain cracks around the larger cracks which had started to pull open. The small microscopic cracks in the embrittled plate almost invariably showed the typical branching intercrystalline cracking. Whenever a sufficient number of fine microscopic cracks showed the typical intercrystalline cracking and the plate was otherwise normal, it was felt that it could be classed as an embrittled plate.

If the cracking happened to be detected first in an area where extremely high stresses had prevailed due to heavy caulking, etc., it was almost invariably found that the type of cracking was obscured due to the high stresses. Consequently, only a few intercrystalline cracks could be found. However, if other portions subjected to lower stresses were examined, the clean-cut intercrystalline cracking could



Unetched, x 150

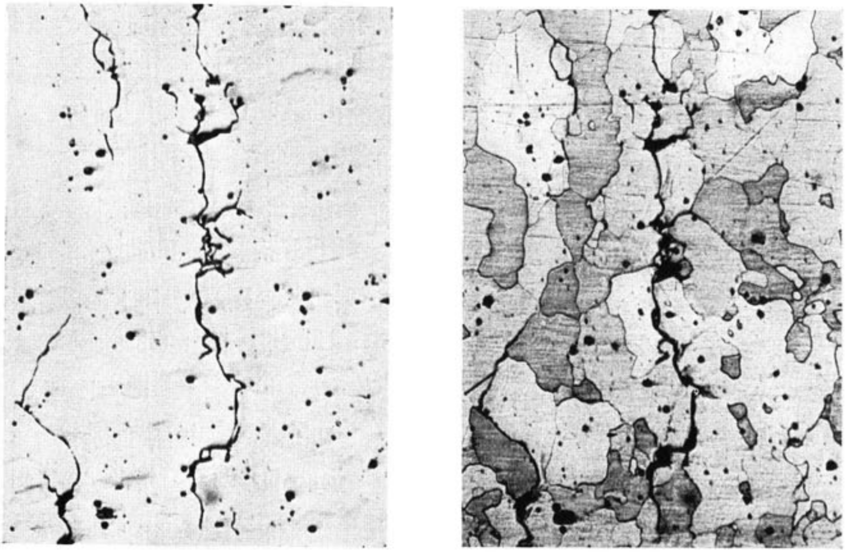
Etched, 2 Per Cent Nital, x 150



Etched, 2 Per Cent Nital, x 900

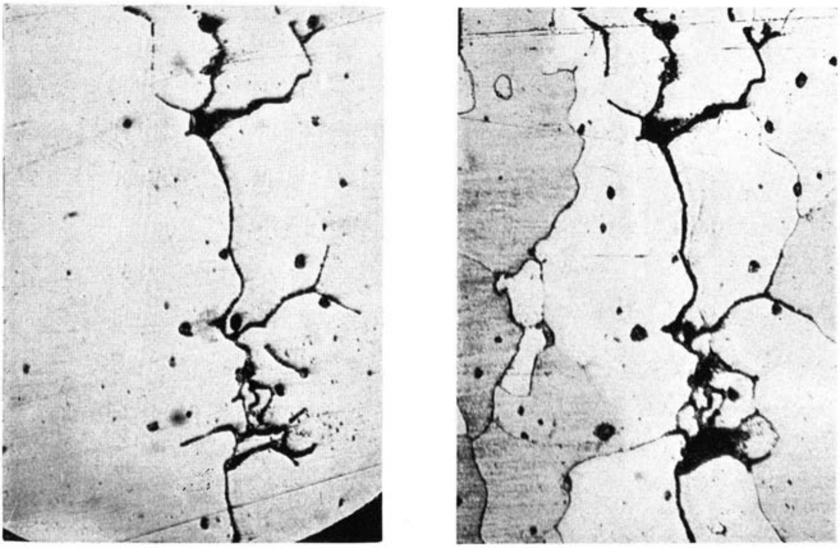
FIG. 20. MICROGRAPHS OF FLANGE STEEL EMBRITTLED IN TESTS

All from the same specimen.



Unetched, x 100

Etched, 2 Per Cent Nital, x 100

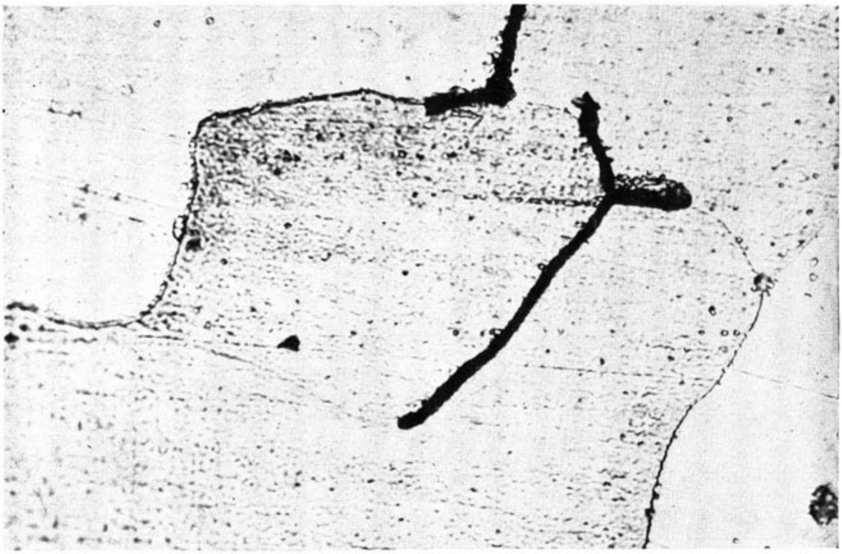


Unetched, x 250

Etched, 2 Per Cent Nital, x 250

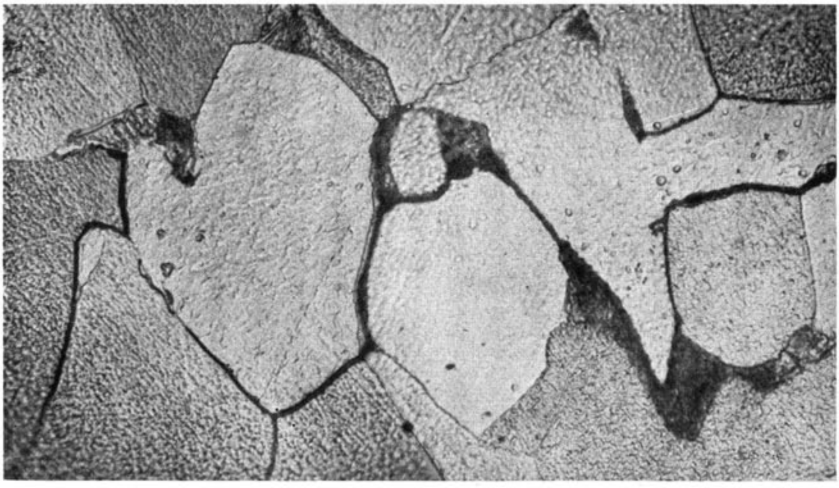
FIG. 21. MICROGRAPHS OF MAGNETIC IRON EMBRITTLED IN TESTS

All from the same specimen.



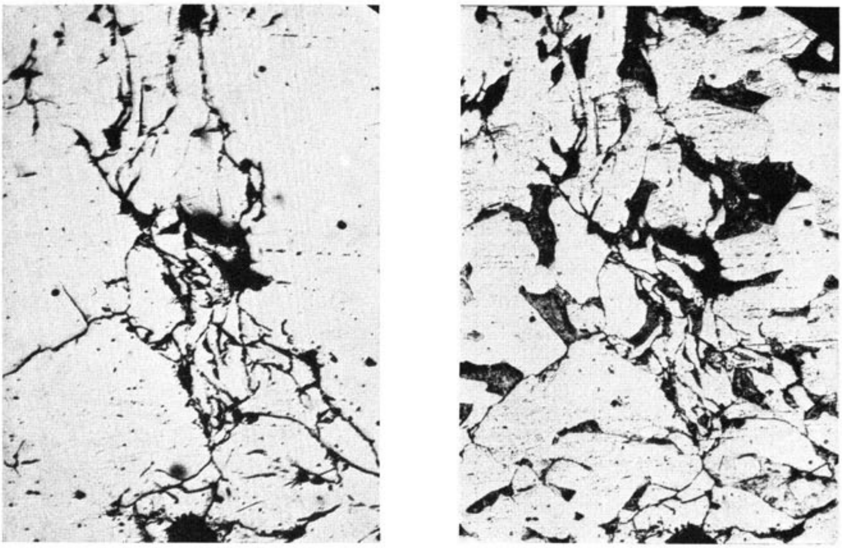
Magnetic Iron, Etched, 2 Per Cent Nital, x 3000

FIG. 22. MICROGRAPH OF EMBRITTLEMENT CRACKS



Etched, 2 Per Cent Nital, x 1000

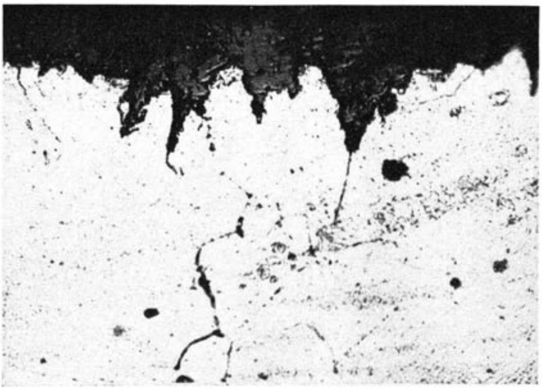
FIG. 23. MICROGRAPH OF EMBRITTLEMENT CRACKS FROM BOILER



Unetched, x 250

Etched, 2 Per Cent Nital, x 250

FIG. 24. MICROGRAPHS OF EMBRITTLEMENT CRACKS FROM LABORATORY TESTS



Etched, 2 Per Cent Nital, x 250

FIG. 25. MICROGRAPH OF ARMCO IRON EMBRITTLED IN TESTS

The dark portion has resulted from chemical action and is not due to impurities in the iron.

be found. In view of these facts, the finding of transcrystalline cracks along with the intercrystalline cracks has not been considered sufficient to class the cracking as strain cracking.

The specimens embrittled in the laboratory have been examined and found to have a large number of cracks progressing into the strained portion of the metal, and they are intercrystalline without any marked deformation of the grain, as shown by the micrographs in Figs. 20 and 21. When examined under higher magnification the crack is observed to pass between the smaller grains of pearlite which make up the carbon areas. Examples of this intercrystalline cracking are shown in Figs. 22, 23, and 24.

The presence of apparent impurities at the grain boundaries in some cases of embrittlement has been noticed. In the laboratory experiments an attempt was made to reproduce impurities of this nature in a piece of metal originally free from them. A specimen of Armco iron was machined so as to preclude any possibility of impurities on the surface. Figure 25 shows this specimen after being embrittled. The products of the chemical action can be seen to be forming as the chemical penetrates into the metal.

15. *Reproduction of Embrittlement Cracking in Steel.*—The fact that embrittlement cracks were apparently intercrystalline suggested a means of attacking the problem in the laboratory. Except in cases of embrittlement the occurrence of intercrystalline cracking in boiler plate had never been reported under conditions which simulated boiler operation. A few isolated instances where selective corrosion had attacked the grain boundaries of steel had been noted, but the conditions under which this occurred were such as could not be encountered in operation. Cracks in boiler plate subjected to high stresses, impact tests, fatigue tests, corrosion-fatigue, etc., are almost invariably transcrystalline and follow the line of maximum stress. They may pass along one or two grain boundaries, but in general are transcrystalline.

The cracks in embrittled boiler plates are in general found to be intercrystalline, and it is the exception when they cut across a grain. This observed peculiarity has been used as a means of detecting embrittlement cracks. Since this distinct difference could be found between cracks due to normal failure and those resulting from embrittlement, attempts were made early in the investigation to reproduce this type of cracking at will under known test conditions.

Steel was subjected to rapid and slow loading at room temperatures and at the blue heat. Specimens were subjected to fatigue tests. Holes drilled in steel were subjected to excessive drifting, etc. The

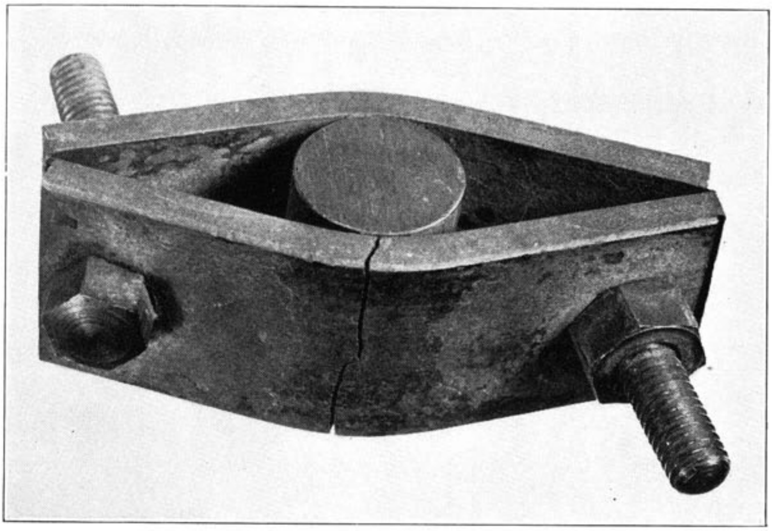
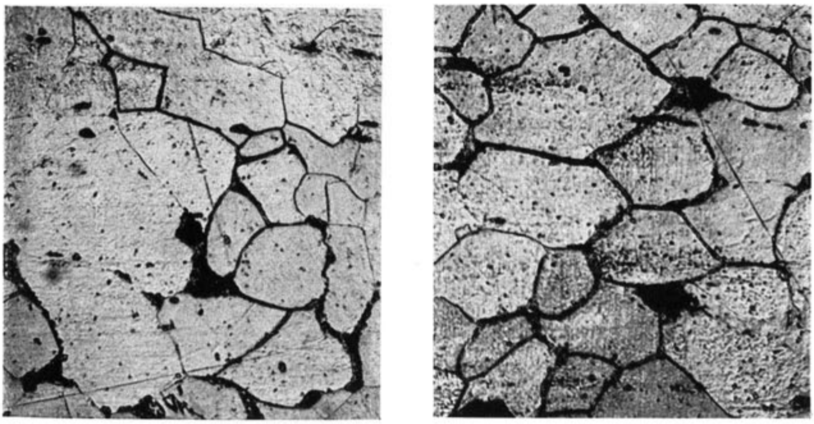


FIG. 26. SPECIMEN FIRST USED IN REPRODUCTION OF EMBRITTLEMENT



Etched, 2 Per Cent Nital, x 250

FIG. 27. MICROGRAPHS OF CRACKS SHOWN IN FIG. 26

cracks which developed were examined under the microscope, and they were found to be typical strain cracks crossing the grains and seldom following the grain boundaries.

Two hot rolled pieces of flat steel were bent over a rod and the ends bolted down, as shown in Fig. 26. No evidence of cracking could

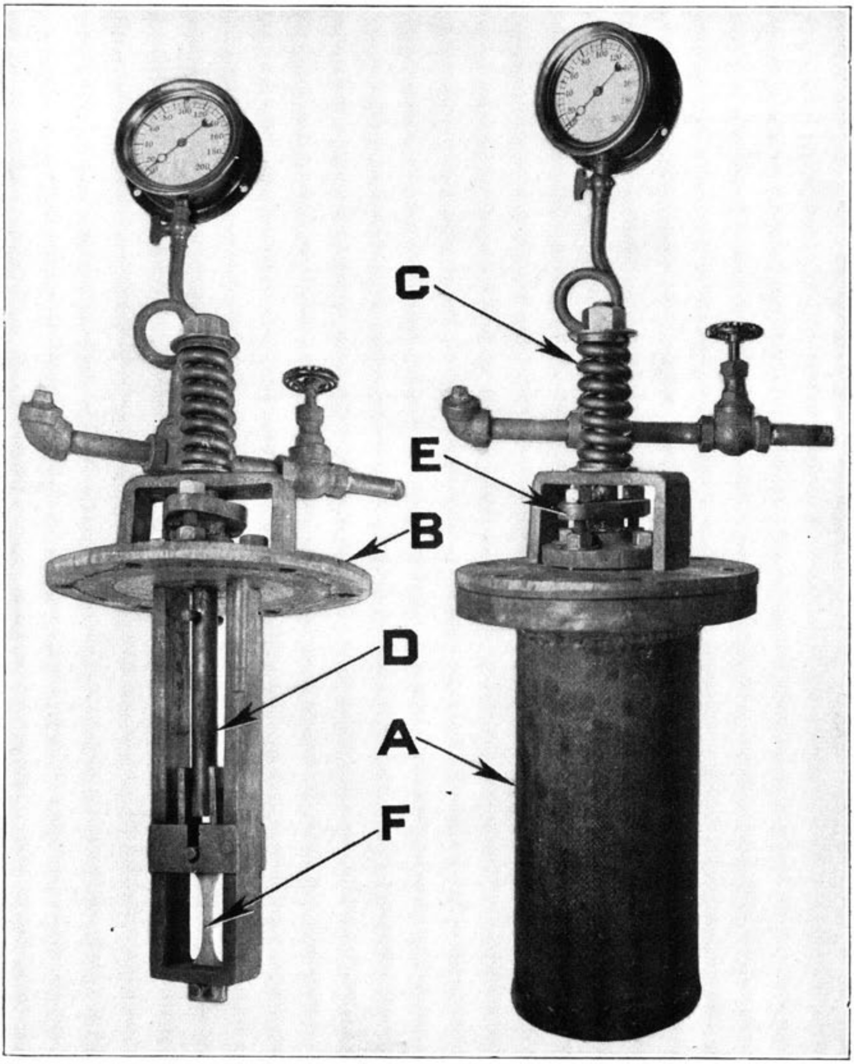
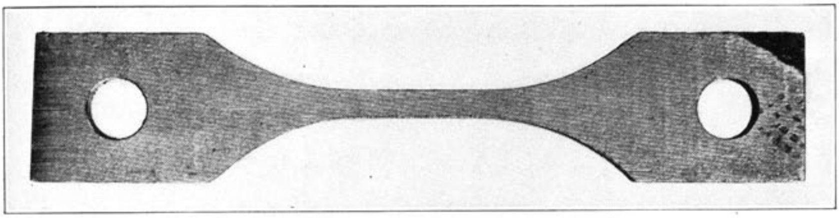
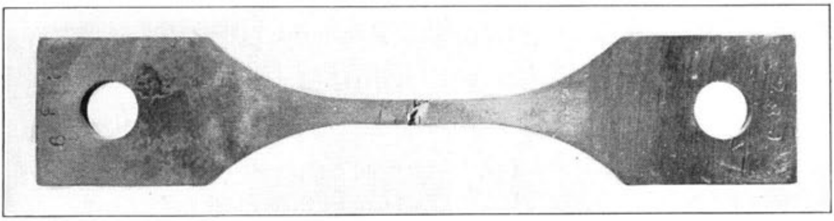


FIG. 28. FIRST APPARATUS USED FOR ACCELERATED TESTS

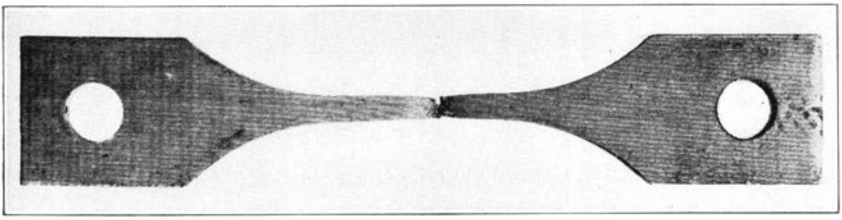
be detected even when the plates were bent at a blue heat. One's knowledge of the ductility of boiler plate would lead one to expect the plate to withstand this bending without fracture. The bent plates, still bolted together, were put in a solution of sodium hydroxide of 400 grams per liter in an autoclave and heated up to about 40 lb. steam pressure. After three days the specimen was removed and found



Test Specimen



Fracture of Embrittled Specimen



Fracture of Unembrittled Specimen

FIG. 29. TEST SPECIMENS

cracked as shown in Fig. 26. An examination of the fine cracks under the microscope revealed the fact that the cracks were intercrystalline, as shown in Fig. 27.

The results of this test were very interesting in that they showed that a perfectly normal piece of boiler plate subjected to a load which it should stand indefinitely without cracking would crack within a few days when in contact with hot caustic soda solutions. Furthermore, the type of cracking was identical with that encountered in the cracked boilers. It was immediately thought that the reproduction of embrittlement cracking had been accomplished, and a second test was made under similar conditions. Again the steel was found cracked. A third test was run using pieces of flange steel, and no cracking could be detected.

TABLE 7

CHEMICAL ANALYSES OF METALS TESTED IN FIRST TESTS

Reference	Description	Content Per Cent						
		C	Mn	P	S	Si	Ni	Mo
F. S.	Flange Steel	0.18	0.45	0.012	0.027	....	....	....
Armco	Armco Iron	0.023	0.017	0.003	0.010	0.01	....	....
M. I.	Magnetic Iron	0.04	0.020	0.004	0.007	0.01	....	....
C. R.	Cold Rolled	0.30	0.42	0.015	0.044	0.04	....	....
1112	S. A. E. 1112	0.15	0.76	0.215	0.126	0.01	....	....
2312	S. A. E. 2312	0.115	0.45	0.018	0.025	0.20	3.5	....
2212	Special	0.13	0.45	0.018	0.020	0.26	1.57	0.25
2330	S. A. E. 2330	0.30	0.478	0.023	0.015	0.05	3.42	....

TABLE 8

TENSION TESTS OF MATERIALS USED IN FIRST TESTS

Reference	Description	Heat Treatment	Proportional Elastic Limit	Yield Point	Ultimate Tensile Strength	Reduction of Area Per Cent
			lb. per sq. in.			
F. S.	Flange Steel	As received	32 600	35 200	60 400	61
Armco	Armco Iron	Annealed 950°C	32 000	40 600	52 600	70
M. I.	Magnetic Iron	Annealed 950°C	25 000	30 000	50 700	72
C. R.	Cold Rolled	As Received	70 000	84 000	85 500	55
C. R. A.	Cold Rolled	Annealed 850°C	......	36 400	64 700	55
1112	S. A. E. 1112	Annealed 900°C	47 500	49 000	74 000	56
2312	S. A. E. 2312	Annealed 900°C	37 000	40 000	74 800	75
2212	Special	Annealed 900°C	35 000	36 800	75 000	75
2330	S. A. E. 2330	Annealed 850°C	41 000	49 200	77 300	57

Annealed specimens heated to temperature indicated for 30 minutes and furnace cooled.

A series of similar tests were then run and it was found that there was very little consistency in the cracking. About one out of every three specimens tested would crack. In attempting to explain this inconsistency it was found that the residual stress in the steel varied over a wide range. In some tests when the bolts were loosened the plates would pull apart about an eighth of an inch, in others there would be practically no pulling apart.

It was thought that if stress were necessary to produce the cracking it would be advisable to have the steel under a definite load at all times; consequently, apparatus was designed which would subject a specimen of steel to a known load while in contact with solutions under steam pressure.

16. *First Apparatus for Accelerated Tests.*—The apparatus first used for the reproduction of embrittlement is shown in Fig. 28. It consists of a welded steel container *A*, which holds the solution, and *B*, the tension producing equipment. The tension is produced and maintained by means of the spring *C* and the plunger *D*. The gland *E* allows the plunger to enter the container steam tight. The specimen is shown at *F*. Part *B* fits into *A* and is secured by bolts (not shown). The proper temperature and pressure are maintained by means of an electric furnace.

17. *Materials Tested in First Tests.*—The materials used for the embrittling tests were all mild steels. Table 7 gives the chemical analyses and reference numbers of the different metals tested; Table 8 gives the physical properties.

18. *Test Specimens.*—The materials to be tested were cut to the shape shown in Fig. 29. Care was taken in machining the specimens to have the holes aligned so as to distribute the stress properly. The specimens were finished by polishing the small section with No. 1 polishing emery paper. The direction of the polish was made parallel to the length of the specimen.

19. *Procedure in Tests.*—The specimen to be tested was measured with a micrometer and the area calculated. The load necessary to give the required stress was calculated and the compression of the standardized spring to give this load determined. The specimen was set in the yoke and pinned to the plunger, which was tightened by screwing down the nut on the upper end. When the spring had been compressed to the right length the gland was tightened and the upper part placed on the container, which had previously been filled with the

TABLE 9

EFFECT OF STRESS AND CONCENTRATION OF SOLUTION ON FLANGE STEEL

Solution Grams per liter NaOH	Stress lb. per sq. in.	Container No.	Time		Gauge Pressure lb. per sq. in.
			Break	No Break Days	
415	30 000	1		22	65
400	31 600	4		18	65
400	33 000	4		16	70
415	34 400	1		27	90
400	35 400	1	1½ days		60
400	39 200	4	2 days		55
400	44 300	4	30 hrs.		50
400	46 000	2	1½ days		45
400	50 500	4	27 hrs.		50
40	50 000	1		17	55
200	47 000	3		16	40
210	47 600	3		21	65
345	46 000	4	14½ days		65
405	50 000	4	4½ days		50
400	39 200	4	2 days		55
455	52 000	3	2¾ days		95
575	46 700	3	8½ days		50

TABLE 10

EFFECT OF SOLUTIONS OF SALTS OTHER THAN SODIUM HYDROXIDE ON FLANGE STEEL

Salt Used	Concentration Grams per Liter	Stress lb. per. sq. in.	Container No.	Time No Break Days	Gauge Pressure lb. per sq. in.
None	Distilled Water	48 600	1	28	50
Na_2CO_3	500	50 000	3	34	70
Na_2SO_4	500	45 000	4	30	70

desired solution. After the parts had been tightly bolted together they were placed in an electric furnace and heated until the desired pressure was obtained. A record of the pressure, temperature, and spring length was taken at regular intervals. When embrittlement had progressed sufficiently to break the specimen the spring forced the plunger up, thus indicating that the specimen had broken. The release of the spring was in all cases found to be very rapid and free from any indications of slow yielding.

The average area of the test specimens was 0.05 sq. in. The accuracy of the estimated load on the specimen was within 1000 lb. per sq. in. when the stress was in the range of 40 000 lb. per sq. in. In calculating the stress allowance was made for the stress added by the steam pressure acting on the plunger.

Table 11

Effect of Cold Work

Specimen Tested	Stress Before Testing	Stress During Test	Container Number	Time		Gauge Pressure lb. per sq. in.
				Break	No Break Days	
F. S.		39 200	4	2 days		50
F. S.	55 000	25 000	2		22*	50
F. S.	Cold worked 20% elongation	25 000	1		27	55
F. S.	Previous specimen continued	45 000	1	12 hrs.		60
C. R.		25 000	2		24	85
C. R.		38 000	2		24	85
C. R.		45 000	2	17½ days		80
C. R.		55 000	2	28 hrs.		85
C. R. A.		38 000	2	36 hrs.		85

*Tested for tensile strength after 22 days in solution. Ultimate tensile strength 69 200. Reduction in area 52 per cent.

Table 12

Effect of Chemical Composition

Specimen Tested	Solution Grams per Liter NaOH	Stress lb. per sq. in.	Container Number	Time		Gauge Pressure lb. per sq. in.	Yield Point lb. per sq. in.
				Break	No Break Days		
Armco	409	40 200	2		14	75	40 600
Armco	400	45 000	2	21 hrs.		70	40 600
M. I.	405	35 000	2	23 hrs.		50	30 000
F. S.	418	50 000	2	20 hrs.		60	35 200
1112	409	55 000	2	3½ hrs.		50	49 000
1112	400	40 000	2	15 hrs.		80	49 000
1112	427	35 000	4		20	80	49 000
1112	427	25 000	4		25	85	49 000
2312	375	48 000	2	29 hrs.		80	40 000
2312	450	43 000	4	8½ days		85	40 000
2212	385	45 000	2	20 hrs.		65	36 800
2330	375	55 000	4	3½ days		65	49 200

20. *Test Data from First Tests.*—The results of the tests on the various metals tested are given in Tables 9 to 13 inclusive.

These results indicate that two conditions must be present simultaneously to cause embrittlement of mild steel: first, the actual stress must be above the region of the yield point of the metal; and second, concentrated sodium hydroxide must be in contact with the specimen.

The variation of pressure up to 200 lb. per sq. in. seemed to have no marked effect on the rate of embrittlement.

Distilled water, sodium carbonate solution, or sodium sulphate solution used in place of sodium hydroxide did not affect the metal

TABLE 13

EFFECT OF PREVIOUS HEAT TREATMENT, CHEMICAL ACTION, AND PRESSURE ON FLANGE STEEL

Solution Grams per Liter NaOH	Stress lb. per sq. in.	Container Number	Time		Gauge Pressure lb. per sq. in.	Treatment
			Break	No Break Days		
400	39 200	4	2 days		55	No treatment
400	50 000	2	2 days		55	Annealed 1050°C.
418	50 000	2	20 hrs.		55	No treatment
407	50 000	2	20 hrs.		45	Dil. HCl 20 minutes
407	50 000	2	17 hrs.		55	Lower half $PtCl_3$ Solution
400	50 000	2	36 hrs.		55	All $PtCl_3$ Solution
404	50 000	4		16	0*	
400	46 000	2	1½ days		45	
390	50 000	2	2 days		200	

*Open to air.

even when the stress was up to the point of failure when sodium hydroxide was used.

The temperature of the previous complete annealing had no marked effect on the rate of embrittlement, neither had the stress, once the yield point was passed.

If the metal has been cold worked to an excessive degree previous to testing for the rate of embrittlement the stress necessary to start this effect will not be lowered, but from the evidence at hand it appears that a higher stress will be required than for the original unworked metal.

The embrittled specimens are not corroded but are covered with a thin shiny blue-black coherent coat of magnetic oxide of iron. They show no marked elongation or reduction of area at the break. Figure 29 shows the fracture of an embrittled specimen as compared with that of a regular unembrittled specimen, and Fig. 30 shows the typical cracking in more detail.

21. *Accelerated Testing Apparatus Finally Adopted.*—The apparatus used for the reproduction of embrittlement at higher pressure is shown in Figs. 31, 32, and 33. The idea of a constant spring load is used. The containers were furnished through the courtesy of the Babcock & Wilcox Co., and are capable of holding steam pressures up to 2000 lb.

22. *Materials Tested in Final Tests.*—Table 14 gives the chemical analyses and Table 15 the physical properties of the metals tested.

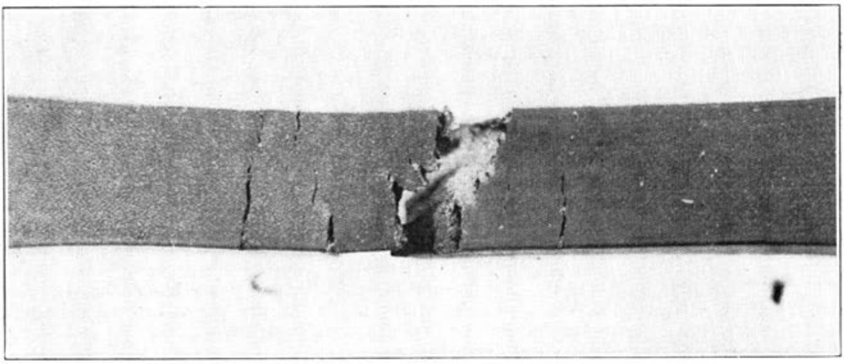


FIG. 30. EMBRITTLED SPECIMEN

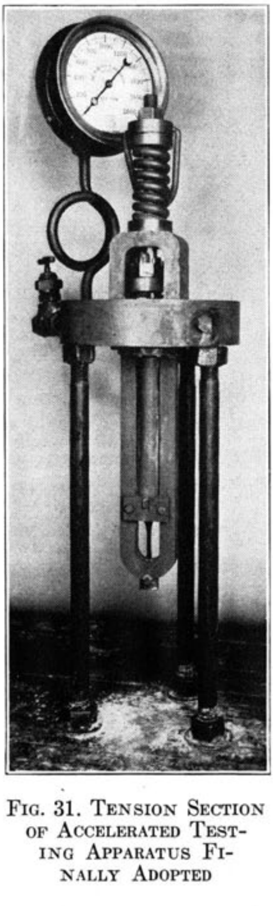


FIG. 31. TENSION SECTION OF ACCELERATED TESTING APPARATUS FINALLY ADOPTED

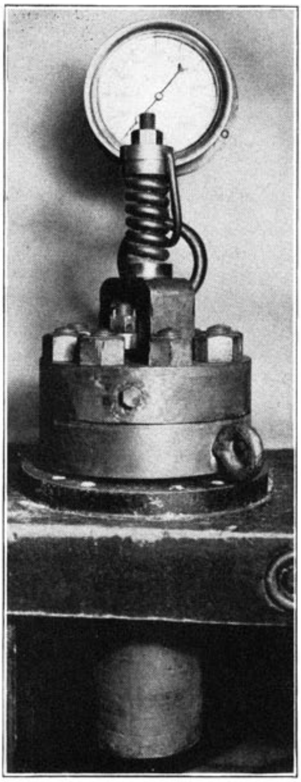


FIG. 32. TEST CONTAINER USED IN LATER EMBRITTLEMENT TESTS

23. *Procedure in Final Tests.*—Several series of tests were conducted in the attempt to answer the following questions in regard to the embrittling action:

(1) Can a time factor be established which will serve to indicate the lowest possible concentration of sodium hydroxide which will produce cracking even over a prolonged period of time?

(2) Is the rate of cracking dependent on the stress? Is it possible to predict whether cracking will take place over a long period of time at a stress below the yield point?

(3) What is the effect of changing the chemical composition of the steel?

(4) Can a retarding influence be produced by heat treatment of the boiler steel?

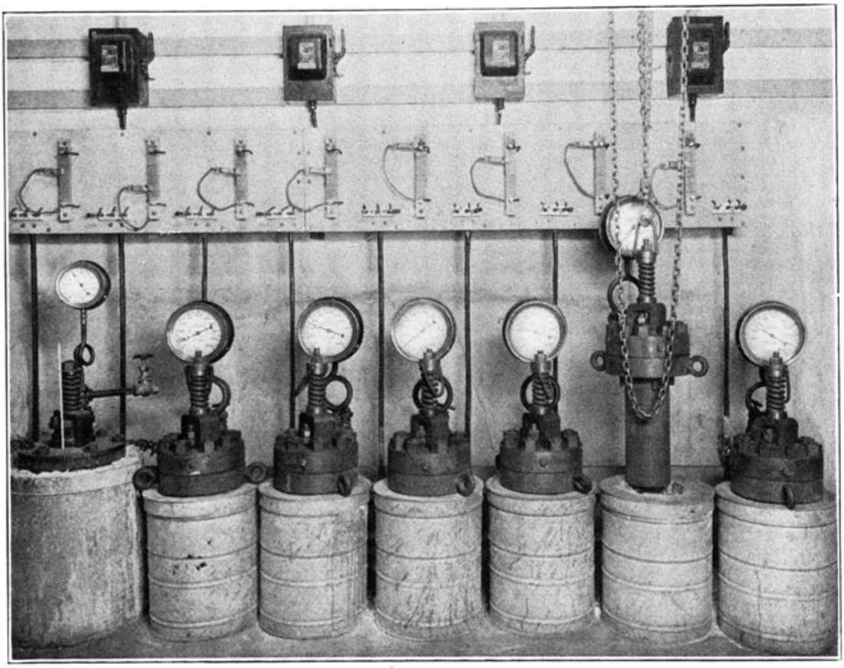


FIG. 33. TEST UNITS USED FOR HIGH PRESSURE TESTS

(5) What influence does increased steam pressure have upon the rate of cracking?

(6) What is the effect of increasing the sodium chloride content?

(7) Is it possible to develop a steel which will resist the caustic attack?

The tests that were conducted with the object of obtaining information to answer these questions were run with special precautions to guard against results which might not be representative. The total number of specimens tested was about 500. Duplicate tests were made whenever definite conclusions were to be drawn from the results. Specimens which did not fail with the solutions and stresses employed in the original test were later tested with standard solutions and stresses in order to show whether they were resistant to the general attack.

24. *Data from Final Tests.*—The results of the tests on the various metals tested are given in Tables 16 to 22, inclusive. These indicate the following:

TABLE 14

CHEMICAL ANALYSES OF STEELS TESTED

Reference	Description of Material	Carbon per cent	Manganese per cent	Phosphorus per cent	Sulphur per cent	Silicon per cent	Nickel per cent	Chromium per cent	Zirconium per cent	Vanadium per cent	Molybdenum per cent	Aluminum per cent
F. S.	Flange Steel	0.18	0.45	0.012	0.027	.....	.....	.....	.....	....	....	....
M. I.	Magnetic Iron	0.023	0.017	0.003	0.010	0.01	.....	.....	.....	....	....	....
Ni	Nickel Steel	0.18	0.54	0.035	0.028	0.23	2.62	.....	.....	....	....	....
Si	Silicon Steel	0.34	0.75	0.027	0.034	0.29	.....	.....	.....	....	....	....
Mn	Low Manganese Steel	0.35	2.13	0.020	0.026	0.023	.....	.....	.....	....	....	....
Acid	Acid Open Hearth Steel	0.42	0.46	0.036	0.044	0.051	.....	.....	.....	....	....	....
W.	Steel from Embrittled Boiler	0.22	0.55	0.015	0.035	.....	.....	.....	.....	....	....	....
G.	Old German Steel Plate	0.06	0.33	0.012	0.035	.....	.....	.....	.....	....	....	....
Izett	Special German Steel Plate	0.17	0.41	0.020	0.031	0.053	0.030	.....	.....	....	....	....
E.	English Steel	0.16	0.35	0.018	0.018	0.040	.....	.....	.....	....	....	....
1020	S. A. E. No. 1020 Steel	0.18	0.56	0.012	0.040	0.005	.....	.....	.....	....	....	....
1112	S. A. E. No. 1112 Steel	0.15	0.65	0.086	0.156	0.028	.....	.....	.....	....	....	....
1	High Chromium Steel	0.07	0.34	0.004	0.012	0.51	.....	16.83	.....	....	....	....
2	Low Chromium Steel	0.25	0.49	0.034	0.045	0.24	.....	3.04	.....	....	....	....
3	High Chromium Steel	0.10	0.40	0.003	0.002	0.92	.....	19.43	.....	....	....	....
4	High Chromium Steel	0.11	0.40	.....	.....	1.00	0.15	16.73	.....	....	....	....
1A	Zirconium Steel	0.30	0.006	.....	.....	.....	.....	.....	0.13	....	....	....
2A	Zirconium Steel	0.21	0.69	.....	.....	0.01	.....	.....	0.003	....	....	....
S. A.	Chromium Nickel Steel	0.18	0.33	.....	.....	0.33	8.76	18.65	.....	....	....	....
275	Vanadium Steel	0.03	0.09	0.006	0.036	0.06	.....	.....	.....	0.24	....	....
276	Low Chromium Steel	0.03	0.006	0.002	0.032	0.06	.....	2.86	.....	....	....	....
479B	Zirconium Steel	0.38	0.18	0.031	0.052	0.66	.....	.....	0.33	....	....	....
W1	Special Boiler Steel	0.39	0.48	0.013	0.021	0.031	.....	.....	.....	....	....	....
W2	Special Boiler Steel	0.31	0.63	0.020	0.027	0.28	.....	.....	.....	....	....	....
W3	Special Boiler Steel	0.51	0.55	0.014	0.021	trace	.....	.....	.....	....	....	....
R. I.	Rustless Iron	0.08	0.33	.....	.....	0.27	0.15	12.51	.....	....	....	....
9266	Low Chromium Steel	0.28	0.55	0.019	0.02	0.15	.....	1.40	.....	....	0.18	0.70

TABLE 15
TENSION TESTS OF STEELS TESTED

Reference	Description of Material	Heat Treatment	Yield Point	Ultimate Tensile Strength	Reduction of Area
			lb. per sq. in.		per cent
F. S.	Flange Steel	As received	35 200	60 400	61.
Sorbitic	Flange Steel	Oil quenched 850° C. Reheated to 600 °C.	53 000	68 600	64.7
Spheroidized	Flange Steel	Oil quenched 850° C. Reheated to 675° C. 8 hours.	50 600	61 100	67.0
M. I.	Magnetic Iron	Annealed at 950° C.	30 000	50 700	72.0
Ni	Nickel Steel	As received	45 000	75 300	59.3
Si	Silicon Steel	As received	43 000	87 000	48.0
Mn	Low Manganese Steel	As received	47 000	103 000	55.0
Acid	Acid Open Hearth Steel	As received	33 000	74 000	46.0
W.	Steel from Embrittled Boiler	As received	33 400	65 400	50.0
G.	Old German Steel Plate	As received	32 000	56 500	65.3
Izett	Special German Steel Plate	As received	32 000	56 500	67.5
E.	English Steel	Annealed at 950° C.	27 000	50 000	....
1020	S. A. E. No. 1020 Steel	Annealed at 950° C.	31 000	56 000	67.5
1112	S. A. E. No. 1112 Steel	Annealed at 950° C.	41 000	63 500	58.0
1	High Chromium Steel	As received	none	100 000	32.0
2	Low Chromium Steel	As received	none	190 000	44.5
3	High Chromium Steel	As received	none	82 000	37.0
4	High Chromium Steel	As received	46 600	74 300	....
1A	Zirconium Steel	As received	39 500	75 800	....
2A	Zirconium Steel	As received	60 800	77 500	....
S. A.	Chromium Nickel Steel	As received	75 000	136 500	....
275	Vanadium Steel	As received	47 000	59 000	....
276	Low Chromium Steel	As received	23 000	61 000	....
479B	Zirconium Steel	As received	50 000	88 000	....
W1	Special Boiler Steel	As received	43 500	77 500	....
W2	Special Boiler Steel	As received	40 000	74 000	....
W3	Special Boiler Steel	As received	35 300	63 000	....
R. I.	Rustless Iron	As received	none	193 000	....
9266	Low Chromium Steel	As received	86 000	128 500	....

TABLE 16

EFFECT OF CONCENTRATION OF SOLUTION ON TIME REQUIRED TO EMBRITTLE FLANGE STEEL

Steam Pressure, 100 and 500 lb. per sq. in.
Tension on Specimen, 54 000 lb. per sq. in.

Steam Pressure lb. per sq. in.	Concentration Sodium Hydroxide Solution grams per liter	Time of Cracking days
100	425	3
100	380	4
100	350	5½
100	310	9
100	200	30
500	330	1¼
500	280	½
500	240	¾
500	200	1½
500	150	4½
500	125	14½
500	115	38

TABLE 17

EFFECT OF STRESS ON TIME RATE OF EMBRITTLEMENT OF FLANGE STEEL

Steam Pressure, 500 lb. per sq. in.
Concentration of Solution, 300 grams Sodium Hydroxide per liter

Total Load lb. per sq. in.	Time of Cracking hr.	Time Rate of Penetration sq. in. per hr.
54 000	12	0.0004
54 000	12	0.0004
44 000	24	0.0005
35 500	36	0.0005
33 000	No crack in 35 days	0.0000

(1) With reference to the relation of time of cracking to concentration of solution, the data given in Table 16 and shown in graph form in Fig. 34 indicate that the time of cracking varies inversely with the concentration, and show that cracking can be predicted at a much lower concentration than heretofore found. It would not be unreasonable to predict cracking at a concentration as low as 100 grams per liter, or approximately 6000 grains per gallon under the test conditions. This concentration is only 15 times that reached in the main body of many boilers.

(2) As to the effect of total stress on the rate of cracking if it is assumed that the final rupture is purely a static failure produced when the intercrystalline cracking has weakened the metal until the

TABLE 18

EFFECT OF CHEMICAL COMPOSITION OF STEEL ON TIME RATE OF EMBRITTLEMENT

Steam Pressure, 500 lb. per sq. in.
Concentration of Solution, 300 grams Sodium Hydroxide per liter

Reference	Description of Material	Yield Point	Ultimate Tensile Strength	Total Load During Test	Time of Cracking hr.	Time Rate of Penetration sq. in. per hr.
		lb. per sq. in.				
F.S.	Flange Steel	35 200	60 400	54 000	12	0.0004
F.S.	Flange Steel	35 200	60 400	35 500	36	0.0005
M.I.	Magnetic Iron	30 000	50 700	45 000	7	0.0005
Ni	Nickel Steel	45 000	75 300	57 000	22	0.0005
Si	Silicon Steel	43 000	87 000	60 000	8	0.0018
Acid	Acid Open Hearth Steel	33 000	74 000	54 000	12	0.0010
Mn	Low Manganese Steel	47 000	103 000	64 000	22	0.0008
W.	Steel from Embrittled Boiler	33 400	65 400	54 000	24	0.0004
G.	Old German Steel Plate	32 000	56 500	40 000	13	0.0010
Izett	Special German Steel Plate	32 000	56 500	40 000	24	0.0004
Izett	Special German Steel Plate	32 000	56 500	40 000	20	0.0005
E.	English Steel	Specimen too small for regular tests—Cracked in caustic				
1020	S.A.E. No. 1020 Steel	31 000	56 000	49 000	10	0.0004
1112	S.A.E. No. 1112 Steel	41 000	63 500	54 000	54	0.0001
1112	S.A.E. No. 1112 Steel	41 000	63 500	54 000	60	0.0001

TABLE 19

EFFECT OF HEAT TREATMENT ON TIME RATE OF EMBRITTLEMENT OF FLANGE STEEL

Steam Pressure, 500 lb. per sq. in.
Concentration of Solution, 300 grams Sodium Hydroxide per liter

Steel Tested	Yield Point	Ultimate Tensile Strength	Total Load During Test	Time of Cracking	Time Rate of Penetration
	lb. per sq. in.			hr.	sq. in. per hr.
Untreated	35 200	60 400	54 000	12	0.0004
Spheroidized	50 600	61 100	54 000	12	0.0004
Sorbitic	53 000	68 600	59 000	14	0.0005
Sorbitic	53 000	68 600	49 000	28	0.0005
Sorbitic	53 000	68 600	38 000	No crack in 20 days	0.0000

TABLE 20

EFFECT OF STEAM PRESSURE ON TIME RATE OF EMBRITTLEMENT OF FLANGE STEEL

Concentration of Solution, 200 grams Sodium Hydroxide per liter

Steam Pressure lb. per sq. in., gage	Time of Cracking hr.	Time Rate of Penetration sq. in. per hr.
100	720	0.000013
500	30	0.00017
1000	10	0.0013

TABLE 21

EFFECT OF INCREASING SODIUM CHLORIDE CONTENT ON TIME RATE OF EMBRITTLEMENT OF FLANGE STEEL

Steam Pressure, 500 lb. per sq. in.
Concentration of Solution, 300 grams Sodium Hydroxide per liter

Sodium Chloride Content grams per liter	Time of Cracking hr.
0	24
15	18
30	7
50	10
100	15
150	Gas generated stopped test

TABLE 22

RATE OF CRACKING OF SPECIAL STEELS

Steel Tested	Yield Point	Ultimate Tensile Strength	Total Load During Test	Rate of Cracking, Flange Steel as Unity
	lb. per sq. in.			
1	None	100 000	75 000	No cracking
2	None	190 000	45 000	30
3	None	82 000	70 000	No cracking
4	46 600	74 300	70 000	No cracking
R. I.		193 000	90 000	No cracking
1A	39 500	75 800	43 000	1
2A	60 800	77 500	55 000	1
S. A.	75 000	136 500	50 000	30
275	47 000	59 000	40 000	1
276	23 000	61 000	35 000	1
479B	50 000	88 000	60 000	0.2
W1	43 500	77 500	55 000	1
W2	40 000	74 000	45 000	1
W3	40 000	63 000	55 000	No cracking
W3	40 000	63 000	60 000	1
9266	86 000	128 500	80 000	30

stress produced by the spring and the steam action is sufficient to cause failure, then the rate of penetration of the intercrystalline cracking can be calculated.

In order to determine this rate the following formula was used:

$$T = \frac{a - \frac{L}{U}}{t}$$

where T = time rate of penetration in sq. in. per hr.
a = area of specimen in sq. in.
L = total load on plunger in lb. (spring plus steam)
U = ultimate tensile strength of specimen in lb. per sq. in.
t = time of cracking in hr.

The results of tests run at a pressure of 500 lb. per sq. in. and at the optimum concentration, 300 grams per liter, with varying intensities of stress, are tabulated in Table 17. These results indicate that for the steel tested the time rate of penetration is independent of the total stress once the stress passes the region of the yield point. Below the yield point no cracking occurs. This shows that apparently for static loads no cracking can be predicted even over prolonged periods of time when the localized stress is below the region of the yield point of the boiler plate.

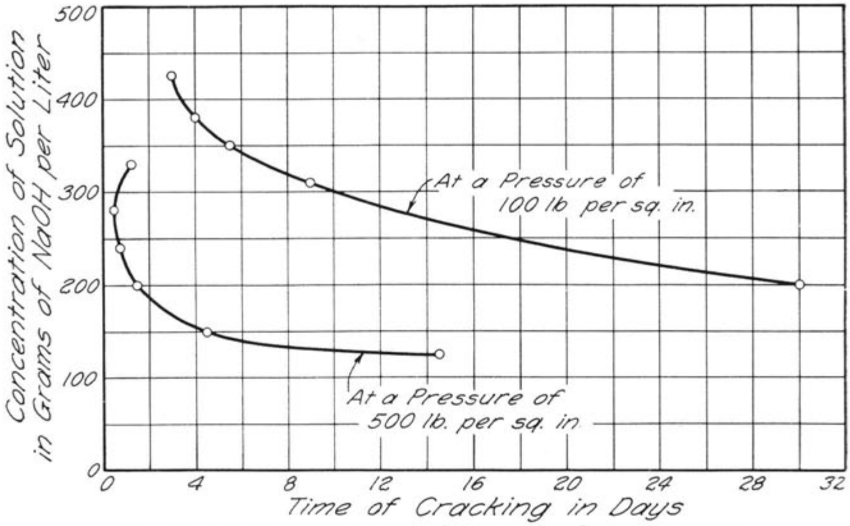


FIG. 34. RELATION OF TIME OF CRACKING TO CONCENTRATION

(3) In order to investigate the effect of the composition of the steel, specimens of the first twelve steels listed in Tables 14 and 15 were tested, and their corresponding time rate of cracking determined. The results as given in Table 18 show that all the steels cracked within a reasonable time. The acid, the old German, the silicon, and the mild manganese steels cracked at an appreciably faster rate than normal boiler plate. The other steels, including some from embrittled boilers, all cracked at about the same rate. Particular attention should be paid to steel No. 1112, a high phosphorus and sulphur steel, which had a time rate much lower than that of pure iron or boiler plate. This indicates that even high phosphorus and sulphur content does not make the steel more susceptible to cracking of this nature.

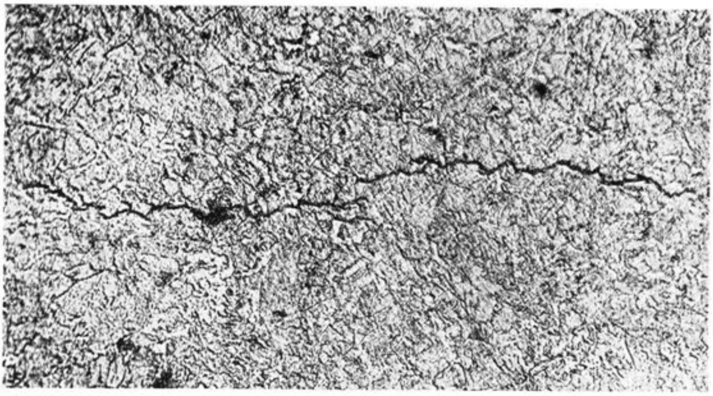
The English steel tested was furnished through the courtesy of Dr. Walter Rosenhain, who has done considerable work on the intercrystalline cracking of metals. He conducted a series of tests on this steel "with a view of producing fracture under prolonged loading in mild steel stressed to various intensities at a temperature of 300 deg. C. in air" and showed that this treatment failed to produce fracture even after five years of exposure. In commenting on this he said, "This certainly suggests that some subsidiary agency of a corrosive nature is necessary to produce failure in a reasonable time, although it is quite possible that the particular sample of steel which I employed was not one subject to intercrystalline fracture under prolonged loading." This steel when tested at a load above its yield point cracked in a period of less than three days. Due to the specimens being so small no quantitative data are available as to time rate of penetration. The test does serve to illustrate, however, that while this metal would normally stand a load of high magnitude for years without failure the presence of the caustic solution brought about fracture very rapidly.

Fry recently reported a new type of steel manufactured by Krupp in Germany which retained high impact values even after being cold worked. He also reported the results of bending specimens of this steel and subjecting them to strong caustic attack, stating that the caustic did not embrittle the steel. Three different samples of this steel called Izett were obtained, and under test showed no better resistance to embrittling attack than the regular American boiler plate.

(4) As to the effect of heat treatment, the suggestion has been made that a heat treatment which will make the grain boundaries very rough or indistinct, such as exists in the sorbitic and spheroidized condition, might have a retarding influence on the crackings.

Tests were accordingly run on samples of flange steel previously heat treated so as to produce these types of structure. The results as tabulated in Table 19 show that the existence of the sorbitic or spheroid condition does not stop the cracking of the boiler plate. Micrographs are shown in Fig. 35. A point of particular interest is that making the steel sorbitic raises the yield point; but the cracking takes place below this new yield point, yet above the yield point of the untreated metal. This shows that cracking is not a real function of the yield point but happens to require an initial stress which is in the region of the yield point. The results obtained from testing a cold-rolled specimen previously reported showed that raising the yield point by cold work also raised the stress necessary for embrittlement, but not in proportion to the rise in yield point produced by cold work.

(5) As to the effect of higher steam pressures on the rate of cracking, the results of tests conducted at various steam pressures are tabulated in Table 20, and show that the time of cracking decreases with an increase in temperature. These results also illustrate the fact that the concentration of solution required for the optimum cracking time would decrease with an increase in pressure. If the highly concentrated solutions necessary for the lower pressures are used at the higher pressures the solutions attack the steel with the free evolution of hydrogen, and corrode the specimen instead of cracking it.



Sorbitic Steel

Spheroidized Steel

FIG. 35. MICROGRAPHS OF EMBRITTLED SPECIMENS OF HEAT-TREATED STEEL

Etched, 2 Per Cent Nital, x 250

(6) In studying the effect of adding sodium chloride, tests were conducted with varying amounts of sodium chloride at a pressure of 500 lb. per sq. in., and 300 grams of sodium hydroxide per liter gave the results shown in Table 21. These show that for this concentration small amounts of sodium chloride accelerate the cracking, while larger amounts tend to reduce this effect. When 150 grains of sodium chloride were added per liter a rapid generation of pressure occurred as soon as a pressure of 500 lb. per. sq. in. was reached. The removal of the source of heat caused this pressure to decrease as rapidly, and when

heat was reapplied it returned. This phenomenon occurred also with a pure sodium chloride solution without the caustic. No residual gas remained on cooling. This fact eliminated the possibility of hydrogen being generated, and suggested that hydrochloric acid was being formed. The vapor pressure of hydrochloric acid from the sodium chloride ionized in the water at a temperature corresponding to a steam pressure of about 500 lb. per sq. in. must become of such a magnitude that it increases the pressure. On cooling, the hydrochloric acid recombines with the sodium hydroxide.

(7) Various steels were tested in order to see if any steel would prove to be resistant to the caustic attack even when subjected to heavy loads. The results of the tests made are given in Table 22.

These results show that the addition of small amounts of Nickel, Zirconium, Vanadium, and Chromium would not stop the caustic attack. When the Chromium was 1.4 and 3.04 per cent the specimen cracked 30 times faster than regular flange steel. However, when the chromium was increased to 12.5 and 19.4 per cent the steel was resistant to the caustic attack and did not crack. It is extremely interesting to note that with the Chromium 18.6 per cent and with 8.76 per cent Nickel present, as in steel S.A., the addition of Nickel made this steel very susceptible to the caustic action. The results obtained with steel W_3 are especially interesting. With an ultimate tensile strength of 63 000, the steel withstood a load of 55 000, and the caustic did not attack it; however, with a load of 60 000 lb. the caustic attacked the steel and cracking took place.

The only steel or iron which has proven to be resistant to the caustic attack is chromium iron with the chromium about 12 per cent or more and the nickel low or entirely absent.

25. *Laboratory Tests on Sodium Sulphate and Sodium Carbonate as an Inhibitant of Embrittlement.*—Since embrittlement is the result of the combined action of chemicals and stress on the metal it appears possible to stop it by at least one of two methods. One of these would be reducing the stress to a point where embrittlement will not occur. This might be possible if the actual concentrated stresses, such as at rivet heads, around rivet holes, etc., could be calculated, and the boiler constructed so as to keep these stresses low enough. Even this would not insure an absolute prevention, since some unknown localized stresses might still exist and give rise to the embrittlement condition.

The other method, namely, the removal of the cause of the chemical action, in the absence of which embrittlement would not occur, would

TABLE 23

EFFECT OF INCREASING SODIUM SULPHATE—SODIUM HYDROXIDE AND SODIUM CARBONATE—SODIUM HYDROXIDE RATIOS

Solution Grams per Liter NaOH	Ratio $\frac{Na_2SO_4}{NaOH}$	Stress lb. per sq. in.	Container Number	Time		Gauge Pressure lb. per sq. in.
				Break days	No Break days	
455	0	50 000	3	2½		90
447	0.7	50 000	3	4½		90
365	1.2	40 000	3	6½		90
500	1.8	40 000	3	10½		90
430	2.1	40 000	3		41	100
	Ratio $\frac{Na_2CO_3}{NaOH}$					
398	0.	40 000	1	2½		90
415	0.3	40 000	1	5		100
430	0.7	40 000	1	11		100
400	1.5	40 000	1		40	100

be the best procedure; but even this is prevented in some cases by the fact that a change of water is not always possible. A close approach could be made to this condition by neutralizing the alkalinity with some chemical, but complete neutralization would be impossible without endangering the boiler.

When it is noticed that embrittlement never has occurred even in carbonate waters when the sulphate content is high, the question is raised as to whether or not the existence of a definite ratio between the sodium sulphate and the sodium hydroxide is sufficient in itself to prevent this cracking.

On comparing sodium sulphate with sodium carbonate as to solubility in sodium hydroxide it is found that these two salts are very similar in this respect. This fact, coupled with the knowledge that sodium carbonate in solution will not produce embrittlement, appears to indicate that the undecomposed carbonate in a boiler might also act as an inhibitant.

Tests as to the effectiveness of the various ratios of sodium sulphate to sodium hydroxide and of sodium carbonate to sodium hydroxide have been made in the laboratory. The results of these tests are given in Table 23.

In testing for the inhibiting effect of sodium sulphate and sodium carbonate it was found that these salts are not very soluble in the hydroxide solution used. When the regular test apparatus was used

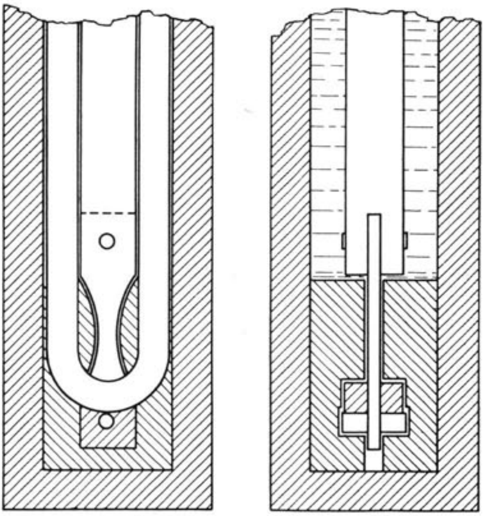


FIG. 36. APPARATUS USED IN DETERMINING THE INFLUENCE OF SULPHATE AND CARBONATE IN PREVENTING EMBRITTLEMENT

the introduction of sulphate up to a ratio of two parts of sulphate to one of hydroxide had no effect on the time of embrittlement. The sulphate was found to be precipitated on the bottom of the container and out of contact with the specimen.

The container was then modified so that the specimen was surrounded by a steel jacket which left a space of about one thirty-second part of an inch around the specimen for the solution to penetrate. A dilute solution was used at first, and this was concentrated by releasing steam from the container until the proper concentration of the hydroxide was obtained. In this manner conditions approaching those of concentration in the seam of a boiler were obtained. The results tabulated in Table 23 were obtained using this modification of the testing apparatus. When the containers were opened the inhibiting salts were found to have crystallized on the surface of the test specimen.

These tests were run in the first testing apparatus, and were necessarily run at low pressures. Further tests were run in the final testing apparatus at 500 lb. per sq. in. pressure. In the tests run in the older testing equipment it was shown that to produce the inhibiting effect of sodium sulphate the solution must be brought around the specimen in such a manner that the salt precipitating out will form on the

TABLE 24

EFFECT OF SODIUM SULPHATE IN INHIBITING EMBRITTLEMENT OF FLANGE STEEL

Steam Pressure, 500 lb. per sq. in.
Stress on Specimen, 50 000 lb. per sq. in.

Concentration of Sodium Hydroxide Solution grams per liter	Time of Cracking days	Ratio $\frac{\text{Sodium Sulphate}}{\text{Sodium Hydroxide}}$	Ratio $\frac{\text{Sodium Sulphate}}{\text{Alkalinity as Sodium Carbonate}}$
135	1½	0.0	0.0
120	1¾	1.6	1.1
127	3	2.1	1.5
120	3	2.6	1.8
140	2	3.1	2.2
120	4	4.0	2.8
135	No crack in 30 days	5.0	3.6

test specimen. To do this, the specimen was surrounded by steel, allowing but $\frac{1}{32}$ in. of space between the specimen and the surrounding steel, as shown in Fig. 36. A dilute solution of the salts was originally used, and this was slowly concentrated by the removal of steam. When the proper caustic concentration was obtained the test was started.

To adapt this to the higher pressures, tests were conducted using the lowest concentration of caustic that would produce cracking in a reasonable length of time. This was done because if the inhibiting action is due to a solubility effect, the lower the sodium hydroxide content the higher will be the solubility of the sulphate. In this manner the most protective ratio can be obtained. If sodium chloride is also introduced then the best conditions for cracking are obtained, and if the sulphate can stop embrittlement under this ideal condition, the conclusion can be drawn that the ratios obtained are protective. The results given in Table 24 show that a ratio of sodium sulphate to sodium hydroxide of 5.0 to 1 or of sodium sulphate to alkalinity as sodium carbonate of 3.5 to 1 stops embrittlement at a pressure of 500 lb. per sq. in. This apparently substantiates the correctness of the ratios suggested by the A.S.M.E. code.

26. *Solubility Studies Applied to the Prevention of Embrittlement.*—The A.S.M.E. Boiler Code recommends the maintenance of definite ratios between the sodium sulphate and total alkalinity in the boiler water for the prevention of embrittlement. These ratios are based upon

the results of power plant experience, and have been recommended until more accurate ratios may be determined.

The total alkalinity has been expressed as sodium carbonate, since it is assumed that the total alkalinity is potential hydroxide. If the ratio is based on the total alkalinity, it should be safe when the hydrate formation in the boiler is high. On the other hand, when the hydrolization is low, the protection should be greater. However, when the hydrolization is low, some credit should be given for this in the form of allowing less sulphate. Many power plant operators have asked whether the undecomposed carbonate could be considered as additive to the sulphate in preventing embrittlement.

Data are available from boilers which have operated for years on waters which do not meet these ratios without encountering embrittlement. On the other hand, a few boilers operating at lower pressures have met the lower ratios and are apparently experiencing embrittlement. In order to explain these cases and at the same time to establish the ratios on a scientific basis, an extensive study has been made of the solubility of sodium sulphate and sodium carbonate in sodium hydroxide solutions at various steam pressures.

In the laboratory work the reproduction of embrittlement was brought about by subjecting test specimens of boiler steel to known static loads while in contact with heated solutions of sodium hydroxide under known steam pressures. It was shown that the steel failed when under a load greater than the yield point, and when in contact with a concentrated solution of sodium hydroxide.

Figure 34 shows the effect of the concentration of hydroxide on the time rate of cracking, and also shows the effect of temperature on the time rate of cracking. It can be readily seen that, as the concentration of hydroxide diminishes, the time of cracking rapidly increases. It may be concluded that 100 grams per liter is the lowest concentration of caustic which would produce cracking.

In order to study methods of preventing the cracking, sodium sulphate was added to the hydroxide, but it was found that the sulphate was not readily soluble. The container was modified, as shown in Fig. 36. The specimen was now surrounded by steel, allowing $\frac{1}{32}$ in. of space between the specimen and the surrounding steel. A dilute solution of caustic soda, sodium chloride, and sodium sulphate was added to the container, and by taking steam off while under pressure the required hydrate concentration was obtained. The results of these tests are given in Tables 23 and 24. These results appear to substantiate the correctness of the higher ratio recommended by the A.S.M.E. code.

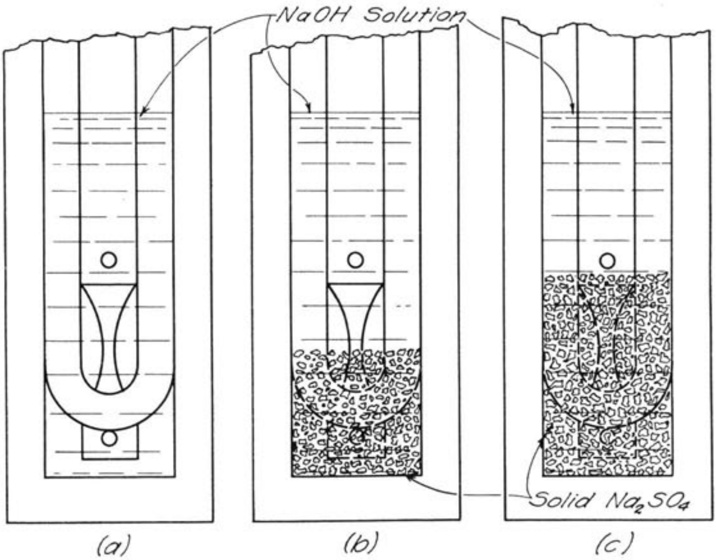


FIG. 37. LOCATION OF SOLID SODIUM SULPHATE IN RESPECT TO SPECIMEN FOR PREVENTION OF EMBRITTLEMENT

There was much reason to doubt the real scientific value of these results. If the precipitated salt stopped the cracking, the size of the crevice around the specimen would influence the ratio, and part of the salt might precipitate away from the crevice. The ratio determined is partially dependent upon the total volume of solution originally used. Thus, a larger volume of solution would contain more sodium sulphate for a given ratio of $\frac{Na_2SO_4}{NaOH}$ and more sodium sulphate would precipitate out in the crack. In view of these conditions it was thought advisable to conduct further experiments toward determining more satisfactory methods of establishing the real ratios necessary to prevent embrittlement.

In order to determine the action of sodium sulphate in stopping the cracking the following tests were run: A solution of sodium hydroxide saturated with sodium sulphate was used, and cracking took place in the same time as when no sulphate was present. Sufficient sodium sulphate was then added so that one half of the specimen was covered with sulphate, as shown in Fig. 37b. Cracking took place in the portion of the specimen above the sulphate salt. A third test was then made using enough sulphate to cover the entire specimen, as shown in Figure 37c. No cracking took place. These tests indicate that the inhibiting effect of sulphate is produced only when the solid sodium sulphate salt is in contact with the steel. If the solution penetrating the seam of the boiler contains sufficient sodium sulphate so that the solubility limit of the sulphate is reached before the hydroxide becomes sufficiently concentrated to produce embrittlement, then the sodium sulphate would crystallize out in the fine capillary spaces in the seam and prevent embrittlement. If the solubility of sodium sulphate were known at various concentrations of hydroxide at different steam pressures, one could readily calculate the amounts of sulphate necessary to prevent embrittlement.

Attention has already been called to the fact that undecomposed sodium carbonate also acts as an inhibitant. Little attention has been paid to this property of the sodium carbonate, since it was realized that under average boiler conditions it would be difficult to maintain the sodium carbonate content of the boiler water high in respect to the hydroxide. Tests have been conducted, however, to determine whether the sodium carbonate acted in a manner similar to sodium sulphate in preventing the cracking. Tests similar to those run on sulphate were made using sodium carbonate, and similar results were obtained. Consequently, it was concluded that sodium sulphate and sodium carbonate both prevented embrittlement when present in sufficient amounts. In order to determine the amount of sulphate necessary to prevent embrittlement it would be necessary to know the influence of sodium carbonate on the solubility of the sulphate. None of these data were available. Consequently, a laboratory study was made of the solubility of these salts separately and combined at various steam pressures.

(a) Solubility of sodium sulphate in sodium hydroxide solutions

The solubility of sodium sulphate in sodium hydroxide solutions of various concentrations at 215 and 250 deg. C. has been determined. Fig. 38 shows the results obtained.

(b) Solubility of sodium carbonate in sodium hydroxide solutions

The solubility of sodium carbonate in sodium hydroxide solutions of various concentrations at 215 and 250 deg. C. has been determined. The results are shown in Fig. 39.

(c) Solubility of sodium carbonate and sodium sulphate in sodium hydroxide solutions

The solubility of sodium carbonate and sodium sulphate at 175, 215, 250, and 300 deg. C. in a solution of sodium hydroxide of 100

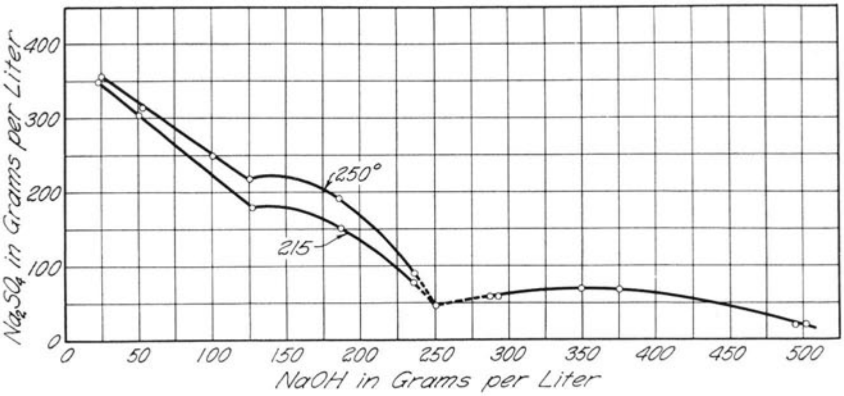


FIG. 38. SOLUBILITY AT 215 AND 250 DEG. C. OF SODIUM SULPHATE IN SODIUM HYDROXIDE SOLUTIONS

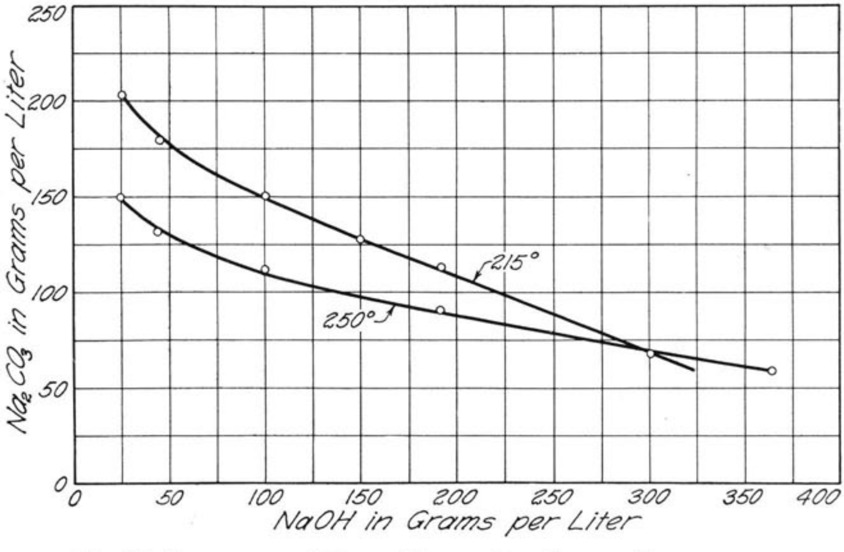


FIG. 39. SOLUBILITY AT 215 AND 250 DEG. C. OF SODIUM CARBONATE IN SODIUM HYDROXIDE SOLUTIONS

grams per liter has been determined. The results of these tests are given in Fig. 40. These results show that the presence of a relatively small amount of sodium carbonate reduces the solubility of the sodium sulphate to a marked extent. The sodium sulphate has a maximum solubility at a temperature of about 230 deg. C. The solubility of the

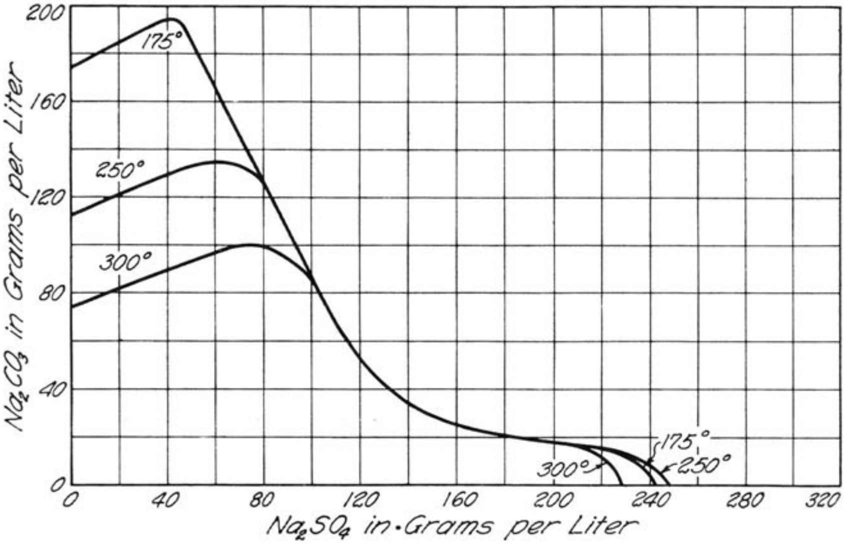


FIG. 40. SOLUBILITY AT 175, 250, AND 300 DEG. C. OF SODIUM CARBONATE AND SODIUM SULPHATE IN SODIUM HYDROXIDE SOLUTIONS OF 100 GRAMS PER LITER

mixed salt sodium carbonate and sodium sulphate is not changed to any marked extent by the increase in concentration of the sodium hydroxide solution.

With these solubility data available, it is not difficult to determine the amount of sulphate necessary to prevent embrittlement in the presence of a known amount of carbonate. If it is assumed that 100 grams per liter of sodium hydroxide is necessary to produce cracking, and the solubility of sodium carbonate and sodium sulphate in 100 grams per liter of sodium hydroxide is known, then by dividing these solubilities by 100 and plotting the results we will obtain the curves shown in Fig. 41 for temperatures between 175 and 300 deg. C. This represents the ratios of $\frac{Na_2CO_3}{NaOH}$ and $\frac{Na_2SO_4}{NaOH}$ which will be necessary to prevent embrittlement. If the plotted data from the actual boiler water fall above the curve, one would not expect embrittlement to take place. If they fall below the curve, embrittlement could be predicted. The curves may be used to determine the proper ratios if the following reasoning is correct. Assume that 100 grams per liter of sodium hydroxide is necessary for embrittlement to start. If the plotted values of $\frac{Na_2CO_3}{NaOH}$ and $\frac{Na_2SO_4}{NaOH}$ of the boiler water fall above the curve, it means

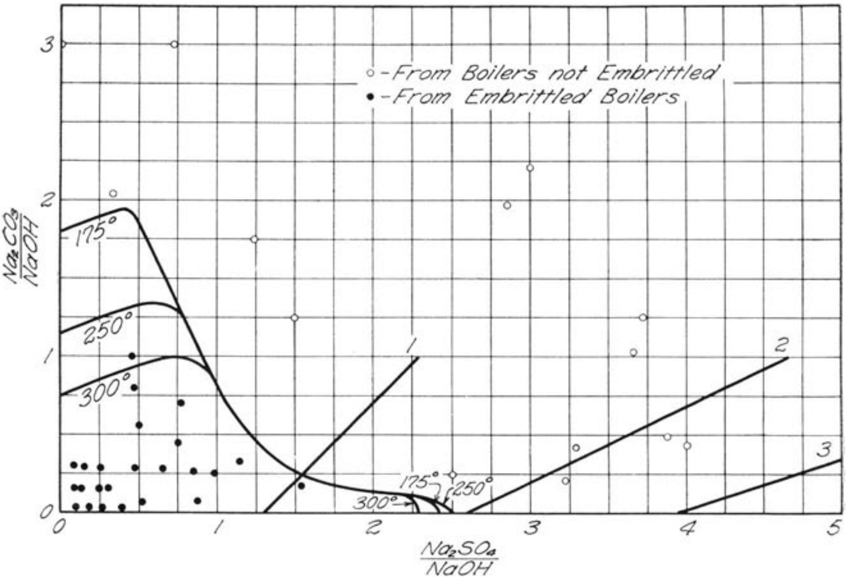


FIG. 41. RATIOS OF $\frac{Na_2CO_3}{NaOH}$ AND $\frac{Na_2SO_4}{NaOH}$ NECESSARY TO PREVENT EMBRITTLEMENT

that before the boiler water which is concentrating in the seams reaches 100 grams per liter of sodium hydroxide, the saturation point in respect to sodium carbonate and sodium sulphate would be passed, and solid salt would have crystallized out in the seam in contact with the highly stressed steel and embrittlement would not take place. If the plotted values fall below the curve, the sodium hydrate could concentrate to 100 grams per liter without any salt separating out. This would allow embrittlement to take place.

The whole theory is based upon the minimum value of sodium hydroxide which will produce embrittlement. If the value is less than the assumed value, the ratios should increase. In order to check these ratios with those used in plant operation, the recommended A.S.M.E. ratios are plotted in Fig. 41. The A.S.M.E. ratios are based upon total alkalinity as sodium carbonate. If it is assumed that 100 per cent conversion were to take place, the ratio of $\frac{Na_2SO_4}{NaOH}$ would be 1.3 when $\frac{Na_2SO_4}{NaOH \text{ as } Na_2CO_3}$ equals 1. Plotting the one, two, and three ratios for various values of hydrolization of the carbonate, it is readily seen that the ratios of two and three are apparently protective for all values of hydrolization of the carbonate. The ratio of 1 is low if the sodium hydroxide formed in the boiler is high, but is amply safe if the sodium hydroxide is not so high in respect to the sodium carbonate.

Only one plant which has met the A.S.M.E. recommended ratio has encountered any indications of embrittlement. This plant maintained a 1:1 ratio at 140 lb. pressure. The ratio of $\frac{Na_2CO_3}{NaOH} = 0.2$ and that of $\frac{Na_2SO_4}{NaOH} = 1.5$. These figures fall beneath the curve.

In order to establish this curve more definitely, the ratios of $\frac{Na_2CO_3}{NaOH}$ and $\frac{Na_2SO_4}{NaOH}$ obtained from a large number of embrittled plants have been plotted. At the same time these ratios from boilers not encountering embrittlement have also been plotted. These values are given in Fig. 41. All the cases of embrittled boilers fall beneath the curve and all those not embrittled are above the curve. This correlation of laboratory and plant data indicates that the given curves are sufficiently accurate to be used in determining the necessary ratios for boiler waters.

It may be readily seen from the curve in Fig. 41 that a ratio of $\frac{Na_2SO_4}{\text{Total alkalinity as } Na_2CO_3}$ of 3 should be protective for practically all pressures even when the maximum hydrolization takes place. A ratio of 2 should be protective, but when extremely high hydrolization takes place the ratio may be a trifle low. When a ratio of 1 is maintained and high hydrolization takes place the boilers are not protected, but if the hydrolization is lower the boilers are protected.

If it becomes difficult to maintain a ratio of 2 or 3, a study of the boiler water conditions in the plant under consideration will show the minimum values of $\frac{Na_2CO_3}{NaOH}$ and $\frac{Na_2SO_4}{NaOH}$ in the boiler water, and if the plotted values fall above the curve, the addition of more sulphate is not necessary. If they fall below the curve, more sulphate is necessary.

(d) Determination of sodium carbonate and sodium hydroxide

The ordinary method of determining sodium hydroxide and sodium carbonate by titrating with sulphuric acid using phenolphthalein and methyl orange as indicators is open to much error. The end point of the methyl orange becomes obscure and often is high. This in turn

TABLE 25

EFFECT OF PHOSPHATE IN INHIBITING EMBRITTLEMENT OF FLANGE STEEL

Steam Pressure, 500 lb. per sq. in.
Stress on Specimen, 45 000 lb. per sq. in.

Concentration of Sodium Hydroxide Solution grams per liter	Amount PO_4 Radical in Solution grams per liter	Time of Cracking hr.	Ratio $\frac{PO_4}{\text{Alkalinity as Sodium Hydroxide}}$	Ratio $\frac{PO_4}{\text{Alkalinity as Sodium Carbonate}}$
295	0	24	0.0	0.0
280	0.4	20	0.0014	0.0010
280	0.6	No crack in 13 days	0.0021	0.0015
280	0.6	No crack in 30 days	0.0021	0.0015
280	1.0	No crack in 13 days	0.0035	0.0025
280	1.0	No crack in 17 days	0.0035	0.0025
280	2.0	No crack in 13 days	0.0070	0.0050

indicates high sodium carbonate and low hydrate. These results cannot be used in determining the ratios.

The following method of analysis has been used in determining the actual sodium carbonate and sodium hydroxide in boiler water by several laboratories, and the results obtained appear to be more accurate and not affected by high organic matter in the water. One hundred cc. of water is titrated with standard $\frac{N}{50}$ sulphuric acid using phenolphthalein as an indicator, using A cc. of acid. A second sample of 100 cc. is then taken, 20 cc. of a 10 per cent solution of $BaCl_2$ added, and titrated with the standard acid again, using phenolphthalein as an indicator (using B cc. of acid).

$$B \times 8 = \text{sodium hydroxide in parts per million}$$
$$2(A\text{-}B) \times 10.6 = \text{sodium carbonate in parts per million}$$

27. *Tests on Inhibiting Agents Other than Sulphate or Carbonate.*—The solubility effect, however, may not be the dominating factor, and electrolytic potential may have equal or greater importance. In event of the electrolytic potential being a controlling factor in inhibiting embrittlement the use of salts of phosphates, chromates, nitrates, acetates, tannates, etc., ought to be effective.

TABLE 26

EFFECT OF SODIUM CHROMATE IN INHIBITING EMBRITTLEMENT OF FLANGE STEEL

Steam Pressure, 500 lb. per sq. in.
Stress on Specimen, 45 000 lb. per sq. in.

Concentration of Sodium Hydroxide Solution grams per liter	Amount CrO_4 Radical in Solution grams per liter	Time of Cracking Days	Ratio $\frac{CrO_4}{\text{Alkalinity as Sodium Hydroxide}}$	Ratio $\frac{CrO_4}{\text{Alkalinity as Sodium Carbonate}}$
285	0.5	1	0.002	0.001
285	1.0	1	0.003	0.002
285	2.0	No crack	0.007	0.005
285	4.0	No crack	0.014	0.010
285	8.0	No crack	0.028	0.020

TABLE 27

EFFECT OF SODIUM NITRATE IN INHIBITING EMBRITTLEMENT OF FLANGE STEEL

Steam Pressure, 500 lb. per sq. in.
Stress on Specimen, 45 000 lb. per sq. in.

Concentration of Sodium Hydroxide Solution grams per liter	Amount of NO_3 in Solution grams per liter	Time of Cracking Days	Ratio $\frac{NO_3}{\text{Alkalinity as Sodium Hydroxide}}$	Ratio $\frac{NO_3}{\text{Alkalinity as Sodium Carbonate}}$
285	1	1	0.003	0.002
285	2	1	0.007	0.005
285	4	No crack	0.014	0.010
285	8	No crack	0.028	0.020

TABLE 28

EFFECT OF SODIUM ACETATE IN INHIBITING EMBRITTLEMENT OF FLANGE STEEL

Steam Pressure, 500 lb. per sq. in.
Stress on Specimen, 45 000 lb. per sq. in.

Concentration of Sodium Hydroxide Solution grams per liter	Amount Sodium Acetate in Solution grams per liter	Time of Cracking hr.	Ratio $\frac{\text{Sodium Acetate}}{\text{Alkalinity as Sodium Hydroxide}}$	Ratio $\frac{\text{Sodium Acetate}}{\text{Alkalinity as Sodium Carbonate}}$
280	0	20	0.0	0.0
290	20	28	0.069	0.049
285	50	42	0.175	0.125
285	75	No crack in 25 days	0.263	0.187
290	100	No crack in 20 days	0.345	0.246

TABLE 29

EFFECT OF TANNIC ACID IN INHIBITING EMBRITTLEMENT OF FLANGE STEEL

Steam Pressure, 500 lb. per sq. in.
Stress on Specimen, 45 000 lb. per sq. in.

Concentration of Sodium Hydroxide Solution grams per liter	Amount Tannic Acid Added to Solution grams per liter	Time of Cracking hr.	Ratio $\frac{\text{Tannate}}{\text{Alkalinity as Sodium Hydroxide}}$	Ratio $\frac{\text{Tannate}}{\text{Alkalinity as Sodium Carbonate}}$
250	0	20	0.0	0.0
275	5	20	0.018	0.013
290	10	No crack in 30 days	0.034	0.024
290	10	No crack in 20 days	0.034	0.024
275	15	No crack in 30 days	0.120	0.090
270	50	No crack in 10 days	0.185	0.130

TABLE 30

EFFECT OF ARSENIC IN INHIBITING EMBRITTLEMENT OF FLANGE STEEL

Steam Pressure, 500 lb. per sq. in.
Stress on Specimen, 45 000 lb. per sq. in.

Concentration of Sodium Hydroxide Solution grams per liter	Amount of As_2O_3 in Solution grams per liter	Time of Cracking days	Ratio $\frac{As_2O_3}{\text{Alkalinity as Sodium Hydroxide}}$	Ratio $\frac{As_2O_3}{\text{Alkalinity as Sodium Carbonate}}$
285	1	1	0.003	0.002
285	2	1	0.007	0.005
285	6	1	0.021	0.015
285	10	1	0.035	0.026
285	30	No crack	0.105	0.078

Laboratory tests show that these salts are very effective in stopping embrittlement. The results of the tests are given in Tables 25 to 30 inclusive.

The results of the tests on phosphate are given in Table 25. They indicate that comparatively small amounts of this radical will retard the embrittling action of sodium hydroxide. Thus as low as 0.6 gram per liter of phosphate radical (PO_4) prevented embrittlement in the presence of 280 grams per liter of sodium hydroxide, at a steam pressure of 500 lb. per sq. in. The phosphate radical appears to be about 1500 times as effective as the sulphate radical.

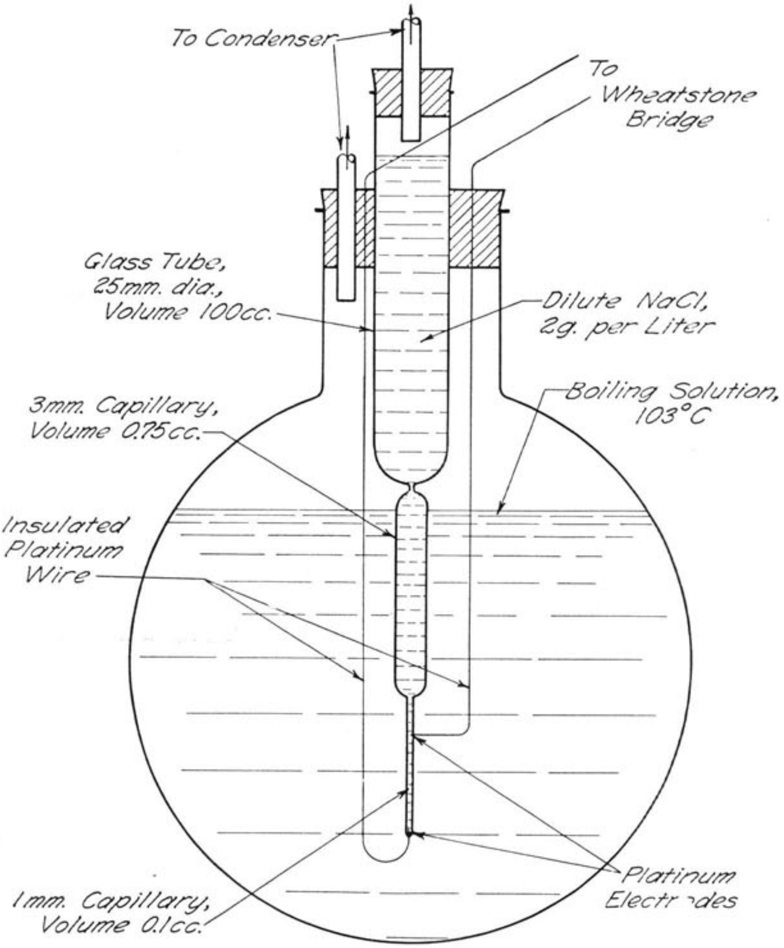


FIG. 42. APPARATUS USED TO DETERMINE CONCENTRATIONS IN CAPILLARY SPACES

The results of the tests on chromates are given in Table 26. These also show that small amounts of this radical will stop the embrittling action of the caustic soda. The results of the tests on nitrates, acetates, tannates, and arsenic are given in Tables 27 to 30 inclusive.

28. *Concentration of Solutions in Capillary Spaces.*—If any attempt is made to explain embrittlement cracking in steam boilers using the laboratory data obtained it immediately becomes evident that the solutions used in the laboratory are much more concentrated than the

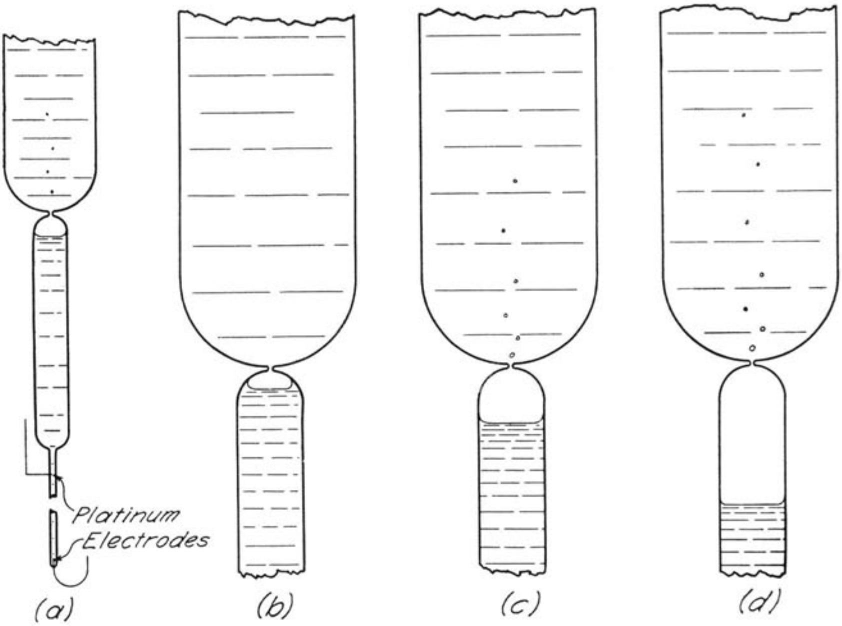


FIG. 43. METHOD BY WHICH CONCENTRATION TAKES PLACE IN CAPILLARY SPACES

solutions in the main body of the boiler. It has been assumed that the solutions penetrated the seams of the boiler and concentrated in the crevices between the plates. There has been much objection to this assumption, and the statement has been made that concentration will not take place in seams which do not leak. Laboratory tests have been run in order to determine whether or not concentration will take place in tight seams, and, if so, what the mechanism of such concentration is.

The apparatus used is shown in Fig. 42. A glass capillary tube with platinum electrodes sealed in was sealed into a large glass tube. The tube and capillary was fitted through a rubber stopper into a flask. The flask was filled about ⅔ full of water with salt in it in order to raise its boiling point. A dilute solution of NaCl of known concentration was put in the tube and the capillary. Reflux condensers were connected to the tube and the flask so that no concentration would take place in either through evaporation.

The platinum electrodes in the capillary tube serve to make a conductivity cell. The conductivity of sodium chloride solutions of various concentrations was determined at 98 deg. C. After the cell had

TABLE 31

CONCENTRATIONS ATTAINED IN CAPILLARY SPACES

Total Elapsed Time hr.	Concentration in Capillary grams per liter	Concentration of Solution Above Capillary grams per liter
0	2	2
6½	17	2
13	31	2
20	47	2
25	61	2
33	70	2
41	82	2
50	86	2
61	101	2
75	116	2
92	132	2
110	156	2

been standardized it was cleaned out and a solution of 2 grams per liter of NaCl added.

The flask was heated until the solution boiled. Sufficient salt had been added to the flask so that the boiling point was about 103 deg. C.

Soon after the solution in the flask started to boil a small bubble of steam formed in the capillary at the restricted portion between the capillary and the main tube. A bubble of steam soon forced its way upward through the restriction and slowly condensed as it traveled up through the solution in the tube. As the bubbles of steam traveled up through the restricted portion the volume occupied by the steam in the capillary increased. The steam leaving the capillary was slowly concentrating the solution in the capillary tube. Figure 43 illustrates the action of the steam forming and leaving the capillary. When the level of the solution reached the top of the smaller capillary tube a slight pressure was put on the condenser connected to the capillary tube. This forced the solution into the capillary due to the condensation of the steam under the increased pressure. As soon as the pressure was released a small steam bubble formed at the restricted portion and the previously described action again took place. From time to time the solution was cooled to 98 deg. C., the conductivity of the solution in the capillary tube determined, and the sodium chloride content calculated. The results of a few tests are given in Table 31. These show that the concentration takes place very easily and obviously the smaller the capillary the faster the concentration proceeds.

The restriction between the capillary and the tube acts as a valve which allows steam to go one way and solution the other. With steam constantly leaving the capillary the solution concentrates. The solution entering the capillary brings with it a small amount of salt. Thus concentrations of over 150 grams per liter have resulted while the strength of the solution in the main tube was still 2 grams per liter.

The crevices in the seam of a boiler may be compared to the capillary, the solution in the main body of the boiler to the solution in the tube. The variation in steam pressure allows the small steam bubbles to form in the seam and go into the boiler and in turn the boiler water penetrates the seam. In a manner directly comparable to the laboratory experiment the concentration slowly takes place in the seam. No leak to the outside is necessary. Well laid up seams in which the boiler water might penetrate would be in danger of having as high concentrations form as poorly laid up seams. If a free leak to the outside is present the danger of concentration taking place in the seam is much less. Of course, if there is no connection between the crevices in the seam and the boiler proper, such as in properly inside-caulked seams, one would not expect concentration to take place.

IV. Discussion of Results

29. *Causes of Embrittlement in Steam Boilers.*—The results that have been obtained from the investigation of actual cases of embrittled boilers and experimental work in the laboratory can be briefly summarized as follows:

(1) In the cases of embrittlement investigated, neither the design nor the workmanship of the boilers was the main cause of the trouble.

(2) No fault could be found with the material of the boiler plate, the quality of which was fully up to specification requirements.

(3) Apart from the nature of the feed water used the operation of the boilers was satisfactory.

(4) A caustic condition of the boiler water, with a low sulphate content, was found in all cases of embrittled boilers.

(5) The only material found in these boiler waters which has been shown to have the effect of embrittling stressed steel is sodium hydroxide. The concentration of sodium hydroxide necessary to produce embrittlement is higher than that found in the main body of the boilers.

(6) Increasing the sulphate content has been found to be effective in stopping or inhibiting embrittlement, both in laboratory experiments and in operating steam plants.

(7) As a result of the experimental work new embrittlement inhibiting agents have been developed.

All the data obtained from steam plants show that boilers crack in an intercrystalline manner only when operated on alkaline waters low in sulphates. This cracking has been stopped by increasing the sulphate or lowering the sodium hydroxide content. Plants free from it for years have suddenly encountered trouble when an alkaline water has been used. The laboratory results show that sodium hydroxide produces this type of cracking in stressed steel. A correlation of these observed facts shows conclusively that the offending agent has been the sodium hydroxide in the boiler. The only questions which arise are—how does the caustic act in the seams? and how does a stress exist of a magnitude sufficient to cause the caustic attack to start? It can be shown that boilers with a factor of safety of around 5 have a calculated theoretical stress of 11 000 to 12 000 lb. per sq. in. between the rivet holes. In this calculation it is assumed that the rivet holes are in line, that stresses are evenly applied, and that all the metal is perfectly homogeneous and has exactly the same physical properties. Allowing for the concentration of stress at the edge of a rivet hole due to the discontinuity of the metal, the actual stress in the plate at a rivet hole becomes nearly three times the average stress in the plate or about 33 000 lb. per sq. in., approximately equal to the yield point strength of the boiler plate. When there is added to this the concentration of stresses brought about by the fact that practically the holes cannot be absolutely in line, that the riveting pressure causes slight deformation, that caulking causes excess stresses, etc., there can be little doubt that a local stress of a magnitude about equal to that of the yield point strength exists. The tests conducted in the regular laboratory experiments represented steel under direct tension.

In the riveting of plates the rivet exerts an appreciable stress upon the metal immediately adjacent to the rivet hole due to the expansion of the rivet in the hole. Baumann* concludes that "even when riveting pressures barely sufficient to obtain properly formed and caulkable rivet heads are used, the material in the plates is still stressed beyond its yield point." To verify this samples of steel with small rivets forced into holes in the steel were put in caustic solution under steam pressure. When these were removed after three days small cracks were found radiating from the edges of the holes. The only stress in the steel was that produced by the action of the rivet filling the hole.

In some boilers a factor of safety as low as 3½ has been used, yet the high resulting stresses alone have not produced embrittlement. The

---

*Baumann, Forschungsarbeiten Verein Deutscher Ingenieurewessens, Heft 252, 1922.

factors of safety used have resulted from years of experience in boiler design and operation, and use of boiler plate. Many examples of evidence of stresses of a magnitude equal to the yield point strength of boiler plate in boilers are available.

The laboratory results show that the presence of a concentration of about 6000 grains per gallon of sodium hydroxide will cause embrittlement of a piece of stressed steel. It has also been demonstrated that if the solution be allowed to penetrate between two plates as a thin film the time required to produce embrittlement cracking and likewise the concentration necessary are reduced. The fact that cracking occurs in a shorter period of time when the solution penetrates between two plates is capable of two explanations. The first explanation is that, due to lack of circulation and reaction with the steel, the concentration increases locally. Analyses made of the coating on the iron after contact with the sodium hydroxide show it to be Fe_3O_4. The reaction to produce this is undoubtedly $3\ Fe + NaOH + 4\ H_2O = Fe_3O_4 + NaOH + 4\ H_2$. The sodium hydroxide merely acts as an accelerating agent by increasing the electromotive force of the solution with respect to the steel. The only materials actually entering into the reaction are iron and water. As the water is used it concentrates the caustic in the thin film of solution and increases the reaction.

The second explanation is that a thin film of liquid in immediate contact with two plates may have a higher activity than a large amount of solution surrounding a piece of steel. No statement can be made relative to the actual concentration in the seam. Baumann* has shown that concentration can take place in a theoretically constructed seam in which there was a possibility of diffusion but not an outside leak. If the diffusion possibility were reduced so as to simulate actual boiler operation no doubt exists as to the possibility of obtaining much higher concentrations than those obtained by Baumann. Berl† has reported the results of research on the possibility of concentration in seams and the effect of caustic soda solutions on iron at high pressures. He found that sodium hydroxide solutions of about 200 grams per liter readily attacked iron with the evolution of hydrogen at pressures around 100 atmospheres. He reported but little effect on steel of solutions of caustic of the concentration normally encountered in steam boilers. From these results he concluded that the caustic solutions would have to be concentrated before attacking the steel in boilers, and conducted experiments to determine

---

*"Zur Sicherheit des Dampfkesselbetriebes," Berlin, 1927. pp. 109-116.
†Forschungsarbeiten Verein Deutscher Ingenieurewessens, Hefte 295, 1927

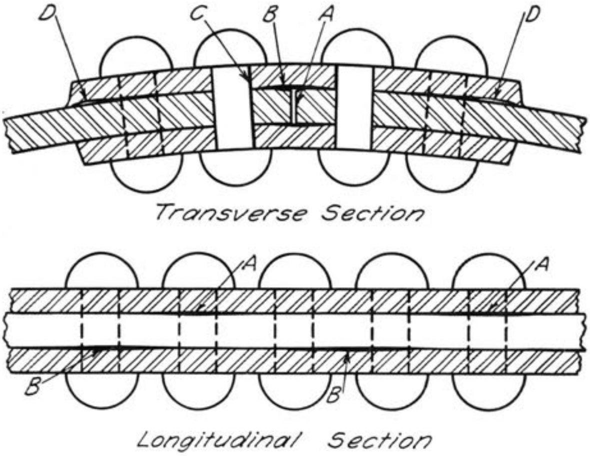


FIG. 44. SECTIONS THROUGH BUTT SEAM SHOWING POINTS OF POSSIBLE CONCENTRATION

whether or not the solutions would concentrate in the small crevices in the seams. He used capillary tubes sealed at one end and connected at the open end to larger tubes. Solutions of about one gram per liter of different salts were put into the tubes. The volume of solution in the capillary part was extremely small in comparison with that in the larger tubes. The capillary was heated, thus vaporizing the liquid in the capillary. The small amount of the liquid in the capillary adhered to the walls, and on vaporizing left a small amount of the salt on the walls. When the capillary was cooled the liquid from the larger tube forced its way into it. After the heating and cooling had been repeated a great many times the solution in the capillary slowly became concentrated, while the solution in contact with it, but in the larger tube, remained practically the same as at the start. By means of this procedure Berl caused the solutions in the capillary to reach their saturation point with the subsequent precipitation of the salt from solution, without producing concentration of the solution in the larger tube. He then proceeded to show that the seams in steam boilers have numerous capillary spaces in which the solutions could be concentrated in this manner. The raising and lowering of the steam pressure, the heating and cooling of the boiler, etc., all tend to favor slow concentration in these capillary spaces.

In these experiments diffusion was reduced to a minimum. If in addition the solution reacts with the steel, as caustic solutions do, the chemical reaction itself would cause an increase in concentration when

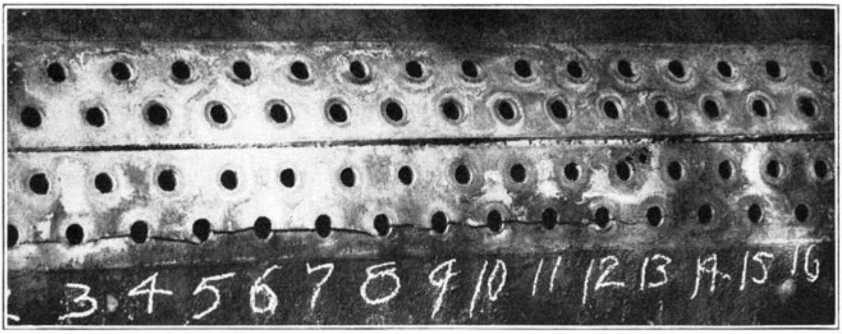


FIG. 45. EMBRITTLED SEAM WITH STRAP REMOVED TO SHOW POINTS OF POSSIBLE CONCENTRATION AND SALT DEPOSITS

full circulation was lacking. The laboratory tests reported in Section 28 illustrate further the mechanism of concentration in the capillary spaces in the seams. Figure 44 shows in an exaggerated manner these points of possible concentration in a riveted seam. Figure 45 shows an embrittled seam with the strap removed. The places where the solution has penetrated between the plates are clearly shown. Some of the deposit left by the solution is still on the plates.

Attention of the investigation was recently called to a large central power plant operating at a pressure of 225 lb. per sq. in. and using only 8 per cent make-up of zeolite-treated water. The ratio of the alkalinity as sodium carbonate to sodium sulphate was 6 to 1 instead of about 1 to 3. An examination of the boiler water showed that the percentage of hydroxide was about 3 times that of the carbonate, which is a condition common to boilers using this type of water at this pressure. When these boilers were down for inspection snow-like salt slowly formed on the inside of the drum where the plates and straps met. When this was scraped off new salt slowly formed. Tests showed this salt to be sodium carbonate. This indicated that the seams undoubtedly contained a concentrated solution of the boiler water high in hydroxide which was slowly seeping out, and when in contact with the carbon dioxide in the air formed the snow-like carbonate. It was estimated that at least two or three grams of this material was removed from a section of the seam only a few feet in length. Taking the maximum concentration reached in the boiler into account it was calculated that it would require about three liters of boiler water to give this amount of salt. It appears highly improbable, since this boiler is of recent design and manufacture, that this volume could exist in the seam; consequently, the only conclusion to be drawn is that the solution seeping out of the seam was much more concentrated than the boiler water ever had been. At the time of inspection the boiler had not given sufficient indication of trouble to justify the expense of a thorough examination for embrittlement cracking. It is being continued in operation under strict supervision.

The production of intercrystalline cracking in steel free from the action of caustic solutions is interesting, and should not be forgotten. It is known that under certain conditions of corrosion and stress nonferrous metals fail by intercrystalline corrosion. It is not unreasonable to presume that certain conditions of strain and corrosion will bring about intercrystalline weakness in boiler plate. The heating of steel in air at high temperatures (burning) causes an intercrystalline weakness. Strained steel in contact with certain molten metals fails by intercrystalline weakness, boiler plate has cracked in riveted areas of nitrate evaporators, etc. All these facts indicate that this type of failure can be produced in various ways by corrosion or attack of the grain boundaries.

If the mere occurrence of intercrystalline failure in a boiler were the only evidence available it would not be right to conclude that it was due to caustic merely because caustic produces such a crack in steel. But when in the hundreds of instances of this type of failure occurring in the United States it is shown that the only factor common to all the boilers affected is the presence of sodium hydroxide in the boiler water, and when it is shown that sodium hydroxide alone of all the chemicals encountered in the boiler water will crack steel in this manner, is it not logical to conclude that caustic soda was the contributing agent? Furthermore, it has been shown, both in plant and laboratory, that when the caustic action is prevented by the presence of sulphates, the embrittling action stops.

Before the presence of sodium hydroxide should be accepted finally as the contributing agent in these embrittlement failures, and the conclusion reached that all feed waters containing carbonate of soda without the presence of the required amount of sulphates should be treated to counteract the embrittling action, another question remains to be answered. This is, "why have some boilers operated on alkaline waters of this type for years without failure?" An attempt was made to investigate all available plants apparently operating successfully under these conditions. The first case examined was that of a local power plant using alkaline well water. The boilers were over seven years old and operated at a pressure of 160 lb. per sq. in. Analyses of the boiler water indicated that the A.S.M.E. recommended ratio had not been met. The hydroxide formed readily in the boiler. No reason for the lack of failure could be suggested. Six months later, however, the boilers in this plant were found to be badly embrittled. This leads one to conclude that, in default of evidence to the contrary, all boilers operating on this type of feed water, whether natural or produced as the result of water treatment, are in potential danger of embrittlement.

Recently two boiler plants were investigated which used a feed water containing about 12 grains per U. S. gallon of sodium carbonate and no sulphate. These plants operated at a pressure of about 125 lb. per sq. in. with a high make-up and a high rating. The percentage of sodium carbonate in the boiler waters was always at least three times, and in many cases as high as ten and fifteen times, that of hydroxide. The blow down was frequent, and the make-up carried in a large amount of carbonate. The only conclusion to be reached in these cases was that the decomposition of the carbonate had been retarded by the high partial pressure of the carbon dioxide and sufficient sodium carbonate remained undecomposed to prevent cracking.

Summing up all the evidence placed at the disposal of the investigation, and correlating it with the results of the laboratory research, it appears evident that the cases referred to as embrittlement have been brought about by the presence of boiler waters high in sodium hydroxide in which the sodium sulphate was correspondingly low.

30. *Mechanism of Laboratory Embrittlement.*—The results which have been obtained justify the opinion that mild steel is embrittled by sodium hydroxide. Stress and chemical attack now appear to be the predominating factors, neither of which can produce embrittlement in the absence of the other.

The action of sodium hydroxide of various concentrations on mild steel is illustrated in Fig. 46 which gives the e.m.f. of the steel to the solution. These curves show the potential of steel in respect to different concentrations of sodium hydroxide against normal NaOH, HgO, and Hg for different time intervals. The measurements were made by the regular compensation method. Figure 46 shows the e.m.f. of a steel which has been embrittled in the laboratory to ten normal NaOH. The e.m.f. of the same metal to the same solution after the outer coat has been ground off is also given.

The action of sodium hydroxide is to produce a thin, compact, and coherent coating of magnetic oxide of iron. Indicating the re-

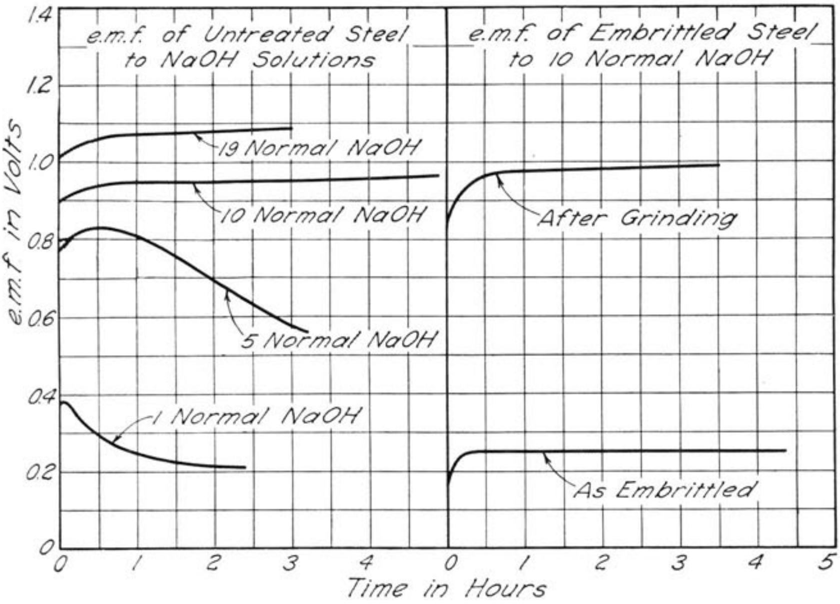


FIG. 46. E.M.F. OF MILD STEEL TO SODIUM HYDROXIDE SOLUTION

action with the hydroxyl ion only, it is $3\ Fe + 4\ OH = Fe_3O_4 + 4\ H$. If the concentration is kept in the range of 100 grams to the liter the action progresses slowly without any noticeable evolution of hydrogen. This coating makes the iron passive or resistant to further action of the hydroxide. If this coat is cut, removed, or penetrated, the fresh metal beneath is as active as the original surface. In a solution of ten normal sodium hydroxide (400 grams per liter) the e.m.f. between the fresh metal and the coated metal reaches 0.7 volt in the cold. This potential is sufficient to produce a slow electro-chemical action which would favor penetration toward the fresh metal. At higher temperatures lower concentrations of caustic would produce the same effect.

As long as the metal is subjected to a stress below the yield point, the chemical action progresses no further than the production of the outer coat of protective oxide. When the stress becomes greater than the yield point of the metal the outer coat appears to be broken in the strained areas, and the chemical attack progresses into the metal to embrittle it. This statement refers to short time laboratory tests.

The main essential is a solution which has an e.m.f. with respect to steel just sufficient to favor the reaction.

$$3\,\mathrm{Fe} + 4\,\mathrm{OH} = \mathrm{Fe_3O_4} + 4\,\mathrm{H}$$

The e.m.f. must not be any higher than necessary to start this reaction at the temperature involved. When the metal is in an unstrained condition a thin compact coat of oxide is formed which is slowly penetrated with the formation of a heavier coat, and eventually the entire metal will be changed to oxide. The attack is fairly even and penetrates the metal at an even rate at all points. If the metal is subjected to sufficient stress under these conditions the grain boundaries become active, first from the increased chemical activity brought about through the energy stored up there by the stress, and, second, by an increased e.m.f. produced at these points of high stress. If the e.m.f. is just sufficient to favor the action on the metal, this slight increase at the grain boundaries becomes sufficient to favor a much more rapid penetration at these points. The products of the action, $\mathrm{Fe_3O_4}$ and $\mathrm{H_2}$, both tend to favor further penetration. As already pointed out by Williams and Homerberg, the cathodic hydrogen will penetrate into the fine capillaries at the grain boundaries and reduce any oxides, with the formation of water and an increase in volume, thus increasing the stresses present at the boundaries. This product of chemical action does not plug the crevices and stop further chemical action, but, due to its e.m.f. relation to the solution and the fresh metal inside, acts as a stimulating agent and increases the action at these points.

If the e.m.f. is high, such as is produced by the action of an acid on a metal, the generation of $\mathrm{H_2}$ is general, and any slight difference in activity between the grains and the boundaries becomes negligible in the excess of e.m.f. produced by the acid. When too concentrated a solution of caustic is used at higher temperatures the test specimen is generally corroded, and even when under strain does not crack. Thus the attack has been so general and vigorous that the influence of the small grain boundary effect is lost.

To obtain a clear conception of the possible chemical attack taking place under stress above the yield point of the metal it becomes necessary to visualize what is taking place within the steel at the yield point. During a static test in which the load is applied at a definite rate it is found that at the yield point there is a marked increase in the elongation of the metal without any noticeable increase in load.

What takes place within mild steel to allow this permanent deformation is at present a matter of conjecture; undoubtedly it must be due to rearrangement within the metal.

The yield point can be said to be largely a function of the crystal strength. When the stress becomes greater than the crystal strength, slip takes place within the crystal. In an aggregate of grains, such as there is in mild steel, the slip is stopped partly by interference of adjacent grains and partly by resistance on the slip plane itself. The metal as it is stressed below the yield point is almost perfectly elastic, having an elastic stretch in this range of about one-tenth of one per cent of the length. As the stress reaches the yield point it becomes sufficient to start slip on the crystal faces. This initial slip is stopped by increase of strength along the slip plane as well as by "end thrust" against adjacent grains. Thus slip in one crystal allows distribution of the stress, which in turn increases the stress on the adjacent crystals. It may then be conceivable to think of the realignment of stresses within the metal at the yield point so as to bring more of the crystal planes and boundaries into a position to oppose the outer stress. After this "reorganization" within the metal there would be a permanent deformation, and further external stress would produce additional slip and drawing out of the crystals in the direction of pull. At the time of the realignment of stresses within the metal the stresses at the grain boundaries are undoubtedly of a great order of magnitude. The metal has stretched more than one per cent of its length. "It is to be assumed that the amorphous cement supposed to exist at the grain boundaries is electropositive to the crystal metal, and therefore has a high internal energy content. This would account for its greater susceptibility to chemical attack."* There must also be a storing up of energy when the grain boundaries are so highly stressed, and this in turn would make them still more chemically active than they were before stressing.

Once the penetration has started the chemical action follows the more chemically active path which is between the grain boundaries. As the boundaries are attacked the stresses are necessarily concentrated, and this favors still more intercrystalline penetration. Observation of the progression of cracks in embrittled steel shows that the cracks do not always start at grain boundaries. Often a crack starts by penetration through the outer grain, but once it reaches a grain boundary it progresses along the boundaries.

---

*Jeffries, "The Science of Metals," p. 78.

If another metal like nickel, which in small amounts is completely soluble in the crystal of ferrite, is added to steel the yield point is raised, since the solid solution of nickel in ferrite is stronger than ferrite, and slip starts at a higher stress value; this in turn retards the reorganization within the metal. If, on the other hand, the percentage of sulphur and phosphorus is increased, the strength of ferrite is increased, accompanied by a higher percentage of these elements in the boundaries. The yield point is raised, but chemical action starts before the yield point is reached, due to the fact that the grain boundaries are much more active.

In a metal which has been cold worked to a considerable degree the grains are completely changed, slips occur along various planes, the grains are elongated, the original crystal boundaries are almost entirely replaced, and the maximum stress is on the slip planes of the crystals. A higher stress would apparently be necessary here before the chemical action would progress. It would also appear probable that a small amount of cold work would have very little effect on the subsequent embrittling of the metal.

In the pearlitic areas of steel one would expect to find obstacles to the slip of the crystals, and as the carbon content increases the yield point should increase. The paths of embrittlement cracks should be such as to avoid passing across the lines of pearlite, and this is found to be almost invariably so.

The retarding influence of sodium sulphate is easily explainable on the basis suggested. The salt crystallizing on the immediate surface of the metal lowers the e.m.f. of the metal, and stops the action. It is not a plugging effect, as some have suggested, thus keeping the solution away, but, instead, the salt plays the role of a buffer solution, lowering the e.m.f. Any oxidizing solution like chromate will produce this effect. The phosphates, acetates, and tannates all act as buffers, and keep the e.m.f. too low for the action to take place.

V. CONCLUSIONS

31. *Summary of Conclusions.*—The general conclusions to be drawn from the results obtained in the investigation may be summarized as follows:

(1) Embrittlement in boiler plate is caused by the combined action of stress and chemical attack. The stresses are inherent in the construction and operation of the boiler, while the chemical attack is caused by the presence of sodium hydroxide in the boiler water.

(2) Certain methods of water treatment tend to convert some safe waters into the characteristic type which produces embrittlement.

(3) The presence of sodium sulphate in the boiler water tends to retard the embrittling effect of the sodium hydroxide and, if in proper proportions, will stop it entirely.

(4) The presence of phosphates, tannates, chromates, nitrates, acetates, etc., will also inhibit the embrittling action of caustic soda if these salts are present in the boiler water in proper amounts.

(5) Methods for the introduction of some of the newer inhibiting agents to feed waters have been worked out, and are in operation in large power plants.

(6) No steel suitable for boiler plate has been found which is resistant to the embrittling action of caustic soda.

APPENDIX A

BIBLIOGRAPHY

Bulletin No. **94** of the Engineering Experiment Station, University of Illinois, entitled "The Embrittling Action of Sodium Hydroxide on Soft Steel," issued in **1917**, contains a summary of the work conducted on this subject up to and including **1916**.

C. E. Stromeyer (The Eng. **124**, p. **496**, **1917**) studied the effect of caustic liquors on steel plate under compression and tension, and found that the metal under tension was brittle on subsequent bending, while the metal under compression was not affected.

Dr. E. B. Wolff (Holland) (The Eng. **124**, p. **456**, **1917**) investigated failures in marine boilers in which the cracks were typical of embrittlement. The chemical and physical properties of the steel were such as to meet the specifications. Wolff said the evidence pointed to a peculiar form of destruction of surface layers of otherwise very plastic material, and thought that this might be due to deformation during boring. He was not able to reproduce similar cracks in holes bored with a blunt drill or with excessive stress at the point of contact with the rivet, by slipping of the plates, or by the fatigue produced by heating and cooling. No study of water conditions was made.

Walter Rosenhain and D. Hansen (Jour. Iron and Steel Inst. **11**, p. **24**, **1920**) investigated several cases of cracked boiler plates similar to the embrittlement type and could find no general chemical or physical defects in the metal. The cracks were intercrystalline in nature. The investigators tried to develop similar cracks by prolonged stresses but were not successful. They suggest that this type of crack may be produced by stresses acting over a period of years. In their discussion they state that corrosion or chemical action may accelerate intercrystalline cracking, and point out that in the cases investigated corrosive influences had been at work, and may have accelerated the formation of the crack. No study was made of the water used.

Cecil Desch, in a paper on chemical influences in the failure of metals under stress (Eng'g. **111**, p. **418**, **1921**), states that chemical action frequently advances more rapidly along the surfaces which separate the crystal grains than through the mass of the metal, and is more likely to occur when the portion exposed to the reagent is in a state of tension than when it is in an unstrained condition. Strong acids are not selective. Passages of gases into the metals appear to follow the boundaries, and the same may be said of some weak electrolytes.

J. A. Jones, Research Department, Woolwich Arsenal, England (Trans. Faraday Soc., 17, p. 102, 1921), in investigating the failure of pans used in evaporating nitrates found the cracks to be of the embrittlement nature, and was able to reproduce these cracks by means of combining stress with the chemical action of various nitrate solutions. In a limited number of cases he produced intercrystalline cracks by using potassium hydroxide solution. He concluded that these cracks occur only when the stress is above a certain value, and is combined with chemical action.

H. J. French (Chem. and Met. Eng., 24, p. 1207, 1922) studied the effect of elevated temperature on boiler plate, and found an increase in the tensile strength up to 290 deg. C. (550 deg. F.), followed by a decrease. The normal strength was reached again at 370 deg. C. (700 deg. F.) At higher temperatures the strength decreased very rapidly.

R. S. Williams and V. O. Homerberg (Trans. Amer. Soc. Steel Treating, April, 1924) studied intercrystalline fracture in steel, and concluded that the impurities are located around the grain boundaries, and are attacked by the action of hydrogen and hot caustic solutions. This action is accelerated by stress.

L. R. Gray (Report of Prime Movers Committee N. E. L. A., 1926) described the system of sulphuric acid treatment used on natural sodium carbonate water at Dallas, Texas. The same publication contains a description of the embrittlement encountered by the Southern California Edison Co., as well as statements by the Babcock and Wilcox Co. and the Permutit Co. relative to embrittlement of boiler plate.

C. E. Stromeyer (Memorandum by Chief Engineer for the year 1925, Manchester Steam User's Association) in summing up the cases of boiler failures which have come to his attention in England, shows that a large number of cases of embrittlement attributed to other causes than caustic in the water are now readily seen to be due to caustic. He told of testing pieces of steel subjected to tension in caustic evaporators, and reported that they become brittle in a few months. The concentration of caustic solution was between 200 and 500 grams per liter.

During September, 1925 the Association of Large Boiler Owners, of Germany, held a session at Darmstadt and discussed the effect of boiler manufacture and feed water. The proceedings were published in a book called "Speisewasserpflege" (Boiler feed water treatment) published by the Association of Large Boiler Owners, Berlin, 1926. At this meeting Professor R. Baumann of Stuttgart reported his experience with intercrystalline cracking in caustic concentrators, and showed that the cracking occurred in parts under stress and in contact with caustic solutions. Chief Engineer Ries of Munich reported that he had been "able to prove that damage takes place only at such points which have been worked in one way or another, be it through riveting, drilling, fitting, cutting of threads, etc., or which have been stressed in some manner; and which come into contact with caustic soda solution." Prof. A. Thiel of Marburg discussed the possibility of caustic concentrating in the seams of boilers, and showed that if this were possible the steel would become embrittled. He compared seams to capillaries, and said sodium hydroxide would concentrate to 77.5 per cent NaOH at 200 deg. C. No experimental data were given to support these figures. He stated further that concentrated sodium hydroxide attacked steel to form hydrogen, and the hydrogen embrittled the steel. H. Kreigsheim commented on the sulphate-carbonate ratio as suggested in the United States by the A.S.M.E. code committee. He presented the experimental data from tests run at Columbia University to show that steel which was cracked in contact with hydrogen electrically generated in caustic solutions as well as with caustic and sulphate solutions, cracked in a transcrystalline manner. He tried to show that hydrogen brittleness was transcrystalline.

F. Korber and A. Pomp in their paper "Rissbildungen und Anfressungen auf Dampfkesselelementen" (Cracking and Corrosion of Steam Boiler Parts) (Zeitschrift des Bayerischen Revisions Vereins, Dec. 15, 1926, pp. 279, 301) discussed cracks in boilers. The cracking consisted entirely of that encountered in bent or strained parts in direct contact with the boiler water. The cracks were all corrosion cracks. He showed the presence of lines of stress, and how the corrosion followed the lines of stress.

Dr. Ing. Fry (The Behavior of Materials used in Boiler Construction when Subjected to Service Conditions) (Kruppsche Monatschefte, Vol. 7, Nov. 1926, pp. 185-196) reported a new type of steel called "Izett" which did not age after cold work. This steel could be cold worked and still have a high impact value. The older boiler steel would lose its impact strength after cold work. His theory for the use of this steel was that boiler plate is cold worked and highly stressed and then reheated to around 200 deg. C. which lowers the impact value of the steel.

A steel of low impact value would crack more easily; consequently, he concluded that the service cracks encountered in boilers are due to the aged steel. He also made the statement that the new steel would not become embrittled under steam and caustic attack and showed the results of tests where the new steel did not crack in caustic solution. (The results of tests conducted at the University of Illinois on this steel showed that it was not any more resistant to embrittlement than regular American boiler plate.)

Dr. Fry also reported a method of etching to bring out strain configurations in steel. His results in this respect confirm similar work done in various laboratories toward developing methods of detecting the effect of localized stresses.

Dr. R. Baumann ("Zur Sicherheit des Dampfkesselbetriebes," edited by the Union of Large Steam Boiler Users, published by Julius Springer, Berlin, 1927) has reported the results of his research to determine the possibility of concentration of solutions in seams. He showed definite concentration in pockets or seams built into test containers, even where there was the possibility of diffusion. His results showed that leaky seams caused the concentration to take place at a more rapid rate.

E. Berl ("Untersuchungen über die Einwirkung von Laugen und Verschiedenen Salzen auf Eisen," Forschungsarbeiten auf dem Gebiete des Ingenieurewessens, Heft 295, 1927) investigated the action of different salt solutions on iron at pressures up to 250 atmospheres. The results show that iron was not appreciably attacked by sodium hydroxide at the concentration occurring in the boiler, i.e., up to 5 grams per liter (about 300 grains per gallon) even at pressures of 50 atmospheres. When the caustic concentration reached 100 grams per liter the action was very active. The ductility of unstressed iron was also reduced. Berl compared the seams to capillaries, and he demonstrated that dilute solutions of salts could be concentrated to their saturation point by heating and cooling capillaries filled with a dilute solution in contact with a larger body of dilute solution. A glass tube was drawn out to a capillary at one end and enlarged at the other end. The end of the capillary was sealed and dilute solutions of various salts put in the tube. On the tube being held with the enlarged portion up and the capillary being heated, the solution in the capillary formed steam and condensed in the larger volume of solution in the large portion of the tube. Part of the salt remained behind on the inner surface of the capillary. The salt remaining caused the solution to become stronger. After many heatings and coolings the solution in the capillary became saturated while the solution in the larger portion was still dilute. He showed that in capillaries, diffusion, which entered into Baumann's tests and kept the concentration down, becomes almost negligible. He showed, further, that sodium sulphate in the ratios recommended in the United States for stopping embrittlement retards the action of even concentrated solutions of caustic.

R. E. Hall ("A Physico-Chemical Study of Scale Formation and Boiler-Water Conditioning," Bulletin 24, Mining and Metallurgical Investigations, Carnegie Institute of Technology, 1927) and his coworkers conducted a series of tests to explain scale formation from a physical-chemical viewpoint. He shows that a certain ratio of carbonate to sulphate ions must exist to prevent sulphate scale in the presence of calcium. This depends upon the steam pressure. He also states that a phosphate-sulphate ratio is more effective and less subject to the difficulty encountered by the decomposition of the carbonate. The results of his experiments indicate that organic materials apparently influence the end points of the regular methyl orange titration so that the reported carbonate is erroneous. He shows that the organic matter does not stop the decomposition of the carbonate, but merely affects the end point with methyl orange as an indicator.

D. J. McAdam, Jr. ("Stress-Strain Cycle Relationship and Corrosion Fatigue of Metals," Proc. A.S.T.M., Vol. 26, 1926, p. 269) reported the results of a series of corrosion fatigue tests, and showed that corrosion accelerated fatigue and lowered the endurance limit. In discussing failures he said, "their chief progress is probably along intercrystalline boundaries. Preliminary investigation of ingot iron indicates that, for this material, corrosion fatigue failure is at least partly intercrystalline." In his discussion he said "Microscopic examination of failed corrosion-fatigue specimens of a variety of steels has not revealed any purely intercrystalline fracture. In its path from one inclusion to another, however, a crack sometimes deviates and for a short distance follows intercrystalline boundaries." This substantiates the information given by F. F. Lucas ("Observations on the Microstructure of the Path of Fatigue in a Specimen of Armco Iron," Trans. Amer. Soc. Steel Treating, Vol. 11, 1927, p. 540) who concluded that grain boundaries do not appear to be a potential source of weakness.

H. S. Rawdon ("The Intercrystalline Corrosion of Metals," Indus. and Eng. Chem., Vol. 19, No. 5, pp. 613-619, 1927) concludes that "The corrosion of a metal while under tensile stress is a common cause of intercrystalline brittleness, although even here it is only by means of certain corrosive solutions, which are different for the different metals, that the result is accomplished.

In general, any practical remedy for the trouble must be along one of two lines. The stress acting on the metal, whether internally or externally applied, may be reduced considerably below the yield point. Most of the short-time laboratory tests have shown that in order to produce failure within a reasonable time in the laboratory the metal must be stressed close to its yield point. The practical solution of the problem of corrosion cracking in rough brasses and other copper alloys has been along this line. The other method is to reduce the corrosion attack either by protective coatings, as in the case of duralumin, or by the preventing so far as possible the formation and accumulation of caustic embrittlement." He states further, "While recognizing that the two factors, tensile stress and corrosion, are equally important in the failure of boiler steel by intercrystalline embrittlement, Parr and Straub have emphasized the importance of controlling the latter factor as being the only practical remedy. On the other hand, German investigators have minimized or discounted entirely the corrosive attack, and emphasized the importance of the results of the stressed condition upon the mechanical properties of the steel (Baumann, Fry). It has been shown that cold-working operations, followed by reheating at a relatively low temperature (200 deg. C.) reduce the shock resistance of mild steel enormously—for example in the ratio of 25 to 3. Such a condition is in itself a grave source of danger, and is not to be lightly passed over. However, its connection with embrittlement resulting from intercrystalline corrosion, the existence of which has been definitely established by experiment, has not been made clear."

A. H. White and J. H. Walker (American Water Works Association, 1927) reported on the acid treatment of zeolite-treated water in the Beacon Street heating plant of the Detroit-Edison Co. They gave the results of using sulphuric acid and sulphuric with phosphoric acid. The use of the latter acid allowed them to neutralize more sodium carbonate and reduce the carbon dioxide in the steam.

Pomp and Bardenheuer (Mitteilungen aus dem Kaiser Wilhelm Institut für Eisenforschung zur Dusseldorf. Ab. 128) (Engineer 148, Supplement (Metallurgist) 131-3, Sept. 27, 1929) discuss three cases of cracking of steel in boilers. In case one, rivet heads cracked off, and were found to have been overheated. In case two, failure took place in the bend in a flange. This was attributed to fatigue. In case three, rivet hole cracks occurred. Fry's reagent showed well marked strain lines. The plate showed good microstructure and the cracks were intercrystalline. The riveting pressure was not excessive. The failure was attributed to the action of alkaline water concentrating in the local crevices in contact with the highly stressed steel.

Rech (Mech. Eng. 51, 589-93, Aug. 1929) tells of the difficulty experienced by General Motors in various power plants. He showed that the typical embrittlement cracking took place only in power plants having low sulphates and high causticity in the boiler water. Other plants operating under identical conditions with higher sulphate in the boiler water did not encounter trouble. He also described similar cracking in tubes.

Fuller, T. S. ("Some Aspects of Corrosion Fatigue," Am. Inst. Mining and Metallurgical Engrs., Technical Publication 172, 1929, Abstracts of Articles on Fatigue of Metals, A.S.T.M., 1929) finds that while the effect of corrosion prior to the application of repeated stress, as has been established by McAdam and R. R. Moore, is known to produce corrosion pits which act as notches and thus vastly reduce the endurance limit of steel, the effect of absorbed hydrogen taken up during pickling or through any type of corrosion in which hydrogen is produced, is less well understood.

To study the effect of hydrogen, experiments were made with a 0.35-per-cent carbon, 3.5-per-cent nickel steel quenched and tempered to give a tensile strength of 110 000 lb. per sq. in., and a yield point of 80 000 lb. per sq. in. Rotating beam tests, made with a correctly designed Moore and Jasper type bar, but all run at a single nominal stress of 90 000 lb. per sq. in., that is, above the yield point of the material, were used as a criterion of the damage resulting from various treatments. Comparison was made on the basis of cycles to fracture at that stress, and it is admitted by the author that this tells nothing about the true endurance limit, and that the work only gives a rough preliminary indication.

The data obtained were:

Treatment	Number of Specimens	Life, Cycles Maximum	Life, Cycles Minimum	Life, Cycles Average
Uncorroded	4	141 000	105 000	120 000
1 hour in 10-per-cent H_2SO_4	2	66 000	62 000	64 000
1 hour in 10-per-cent H_2SO_4 heated	2	74 000	77 000	76 000
Cathode in 5-per-cent NaOH, 24 hours	1	78 000	......	80 000
Cathode in 5-per-cent NaOH, 48 hours	1	82 000	......	
1 month in steam and air	2	35 000	27 000	31 000
1 week in running tap water	2	51 000	36 000	43 000
1 week in running tap water, heated	2	42 000	38 000	40 000
Hot galvanized, 1 week in running tap water	2	34 000	30 000	32 000
Tin dipped, 1 week in running tap water	2	179 000	141 000	160 000

Since the specimens made cathode in NaOH showed no pitting, the reduction in life is assumed to be due to absorbed hydrogen, and the slightly better life of the acid pickled specimens after heating to 130 deg. C. for 4 hours is ascribed to the removal of hydrogen. The drop in the number of cycles required to break the pickled specimens from which hydrogen was removed is, of course, due to pitting. Pitting caused by exposure to steam for one month or to running tap water for one week produces much more damage than the more even attack resulting from pickling one hour in 10-per-cent H_2SO_4.

The conclusions as to effect of hydrogen absorption in acid pickling are in agreement with those of Langdon and Grossman, who, though not referred to by Fuller, had previously done more extensive work on the same problem and by much the same methods.* Langdon and Grossman, however, found no measurable brittleness due to cathodic cleaning in an alkaline cleaner, even though hydrogen was vigorously evolved at the surface.

The most interesting point in Fuller's work relates to the effect of hot-galvanized and hot-tinned coatings. The zinc-coated specimens, although not pitted by tap water, showed a shorter fatigue life than uncoated specimens that were badly corroded in tap water. The galvanized specimens developed cracks in the brittle $FeZn_3$ layer which extended themselves into the metal below.

The tin-coated specimens, on the other hand, after a week in tap water, had a fatigue life as good as, or better than, uncoated and uncorroded specimens.

Haigh, B. Parker ("Chemical Action in Relation to Fatigue of Metals," Transactions, The Institution of Chemical Engrs., Vol. 7, 1929. Abstracts of Articles on Fatigue of Metals, A.S.T.M., 1929) states that the process of fatigue was long regarded as wholly "mechanical" in nature; but in 1917 the author showed that the endurances

---

*Transactions, Am. Electrochemical Soc., Vol. 37, p. 305 (1920) and fatigue limits of certain metals are reduced when chemical reagents—even ordinary water—act on the surfaces of test specimens during the tests. A notable feature of this phenomenon is the importance of the simultaneous action of the chemical reagent and the cyclic stress. These results are in line with the extensive results of McAdam published somewhat later. The importance of chemical action was suggested to the author by failures of car axles in which the waste from the car lavatories struck the axle, and in failures of towing ropes used in salt water. An extensive discussion of the author's experiments and of those of McAdam is given. Tests are also quoted to show that metals which show discolored fractures when tested in air can have their fatigue strength raised appreciably by being covered with a heavy coating of grease or by being placed in baths of non-corrosive oil.

The author points out that the "source" of a fatigue fracture seems to be very slightly under the surface of a specimen. He develops a very interesting hypothesis that fatigue failure may start from a particle slightly below the surface of the specimen which is subjected to tension along each of the three principal axes of stress. This state of tension is called "fluid tension" or "triple tension." Under such conditions shearing stresses would be absent, or would be relatively small, and there would seem to be little chance to develop ductility, so that even materials regarded as ductile might fail in a brittle manner. Such a state of triple tension would exist in the center of a cooling ingot of steel, and the author believes that it may exist near points of stress concentration.

So long as mechanical fatigue was attributed to gliding of the kind that produces plastic strain, the influence of chemical action upon fatigue appeared inexplicable. It was impossible to fancy that chemical reagents acted as lubricants on the planes of gliding, facilitating slip. And direct experiment indicates that the conjoint chemical and mechanical action cannot be attributed simply to the pitting of the surface, although in many cases pitting may reduce the strength still further. These considerations, some years ago, forced the author to set aside the older theory that fatigue is directly associated with plastic slip, and to study other evidence of its action.

When fatigue is attributed to fluid tension, induced locally by contractions associated with changes of state from a meta-stable to some more stable form, the possibility of chemical influence is immediately evident. It is well known that gases and foreign reagents can penetrate metals, particularly through the films of amorphous metal between the grains; and it is reasonable to assume that the conditions of stress required to provoke changes from the meta-stable to a more stable state will depend on the chemical character of the amorphous films in contact with the crystalline grains. Not only will the range of stress required vary with the degree of saturation of the amorphous films, but the identity of the more stable state formed will often depend on the identity of the chemical reagent that is present.

McAdam, D. J., Jr. ("Corrosion of Metals as Affected by Stress, Time, and Number of Cycles," Technical Publication 175, Am. Inst. Mining and Metallurgical Engrs., 1929. Abstracts of Articles on Fatigue of Metals, A.S.T.M., 1929) finds that metals and alloys which corrode readily have their rates of corrosion increased by steady tensile stress. If the stress is released from time to time, that is, if the stress is intermittent, the rate of corrosion is still more markedly increased. Cycle stress of low frequency, for example, one cycle per day, accelerates corrosion pitting materially over that produced by stressless corrosion.

Increased time, increased stress, or increased stress-cycle frequency (at least up to the maximum speed, 1450 r.p.m. used), any two of the three remaining constant, accelerates corrosion. The relationship between corrosion-stress and either time or number of cycles necessary to cause constant damage is exponential. The damage due to corrosion is evaluated by determining the fatigue limit of the material in air after it has had preliminary corrosion under repeated stress. The fatigue limit falls as the corrosive attack increases, unless strengthening by understressing occurs at the bottoms of the corrosion notches. The stress imposed during corrosion and the stresses of the final fatigue test are only nominal since the actual endurance limit of the material does not change, the real change being in the stress concentration set up in the notches caused by corrosion.

Observed data may be plotted in various ways to represent the effect of the three variables, time, stress, and cycle frequency. Families of curves may be drawn to represent the way these variables affect the fatigue limit, one or more variables being held constant. Or, the stress, time, and frequency required to so damage the material that the fatigue limit falls to a definite value (constant damage) may be plotted. Cartesian or logarithmic coördinates may be used.

The increase in damage due to corrosion under repeated stress as compared with that under zero stress, may be plotted (constant net damage).

More than 70 graphs or families of graphs are utilized to show the inter-relation of the variables studied with the fatigue limit of seven steels, two of which were tested in two or more conditions of heat treatment, after stress-corrosion in (1) fresh (carbonate) water, (2) in Severn River water, which has one third the salinity of sea water. No data are given on specially corrosion-resistant steels, or on non-ferrous alloys. The materials used were ingot iron, 0.25 and 1.10-per-cent carbon; 0.50-per-cent carbon, 3-per-cent nickel, 1½-per-cent silicon; 0.30-per-cent carbon, 3½-per-cent nickel; 0.30-per-cent carbon, 1½-per-cent nickel, ¾-per-cent chromium; and 0.45-per-cent carbon, 2-per-cent nickel, 1-per-cent chromium steels. The endurance limits of the uncorroded materials ran from 24 000 to 108 000 lb. per sq. in. The type of corrosion encountered was by pitting, no materials tending to corrode in an intercrystalline manner were used. Work on corrosion-resistant steels and non-ferrous alloys is in progress.

On account of the extensive and detailed treatment of the subject in the paper the quantitative results and the discussion of the 11 methods of plotting must be sought in the original, as they are not readily abstracted.

McAdam, D. J., Jr. ("Some Factors Involved in Corrosion and Corrosion-Fatigue of Metals," Proceedings, A.S.T.M., Vol. 28, Part II, p. 117, 1928. Abstracts of Articles on Fatigue of Metals, A.S.T.M., 1929) in Part I gives a brief résumé of previous work, an outline of continued investigation, and a description of material and methods. The previous experiments had shown that even slight corrosion simultaneous with fatigue may cause failure at nominal stresses far below the ordinary endurance limit. Severe stressless corrosion prior to fatigue was much less damaging than even slight corrosion simultaneous with fatigue.

When the intial stress is below the endurance limit but above the corrosion-fatigue limit, the corrosion-fatigue process is divided into two stages. The first stage is the formation of pits. As the initial stress is below the endurance limit, such pit formation is assumed to be due to electrolytic solution pressure, not to fatigue. The electrolytic solution pressure that causes the pitting, however, is not the solution pressure of stressless corrosion, but is possibly an enhanced solution pressure due to cyclic stress. Whatever may be the reason, a metal in the first stage of corrosion-fatigue behaves as if its solution pressure were increased by the cyclic stress.

As the pit progresses, both the actual stress and the effective solution pressure are increased. The increase of actual stress is due to the usual stress concentration at an abrupt change of section. The increase of solution pressure is due to the increase of stress.

The mutual intensification of stress and solution pressure continues until the actual stress at the bottom of the pit surpasses the endurance limit of the metal. The second stage of corrosion-fatigue then begins. This second stage is merely fatigue accelerated by corrosion. In this stage the crack advances at a continually accelerated rate until the specimen breaks.

If the initial stress is above the endurance limit, the first stage of corrosion-fatigue is absent and the process is merely fatigue accelerated by corrosion.

Parts II and III of the paper cover an investigation of the effect of cyclic stress-range, time, and number of cycles on the corrosion of a variety of carbon and alloy steels.

The factors involved in corrosion of metals are: (1) nature of corroding agent, (2) temperature, (3) time, (4) cyclic stress range, (5) number of cycles, (6) corrosion resistance of the alloy, and (7) physical properties of the alloy. The investigation included the effect of (1), (3), (4), and (5), also a study of the effect of size of specimen, and of torsional corrosion-fatigue.

With carbonate water stressless corrosion of carbon and high-strength alloy steels lowers the second stage graph from one-half to two-thirds of the vertical distance from the endurance limit to the corrosion-fatigue limit. As the stress in stage one is increased from zero to the corrosion-fatigue limit, the second stage graph is lowered down to the corrosion-fatigue limit, but not uniformly or regularly.

With increase of stress in stage one there is a gradual and accelerated increase in depth of pitting up to a value called the "notching limit." With further increase of stress the depth and sharpness of notches change very little, until the stress approaches the corrosion-fatigue limit.

Stainless iron in carbonate water behaves somewhat differently in that pitting is evidently negligible at cyclic stresses below a certain "pitting limit" or "notching limit," with which the corrosion-fatigue limit coincides.

Carbonate water and soft water had practically the same effect on steels and on stainless iron.

For salt water the "notch-depth limitation" is less effective than for the other two waters, and the corrosion-fatigue limit is less.

Alloys of nickel, copper, and aluminum in fresh or salt water have notching limits not far from the corrosion-fatigue limits. Aluminum alloys show severe pitting even at zero stress.

Experiments on the effect of time per cycle indicate that the greater the time per cycle the greater is the stress concentration, and therefore the greater the indicated notch depth. The effect of number of cycles, when the time per cycle is constant, seems to be to decrease the notching limit.

Experiments on size of specimen indicated that a heat-treated chromium-nickel steel and low-carbon steel did not have their corrosion-fatigue limits increased by an increase of diameter from 0.5 to 2.3 in.

Experiments on torsional corrosion-fatigue indicated that chromium-vanadium steel had about the same corrosion-fatigue limit, whether in a hard or a soft condition. The cracks formed in this test made angles of 45 deg. with the axis of the specimen, and therefore were perpendicular to the direction of maximum tension.

McAdam, D. J., Jr. ("Fatigue and Corrosion-Fatigue of Spring Material," Transactions, A.S.M.E., Applied Mechanics Division, January-April, 1929, p. 45) gives data on 44 compositions or heat treatments of steels and on 37 non-ferrous metals. Many of the data have been previously published,* but some new data are included, and chief attention is paid to materials that might be used as springs.

A new terminology is introduced; the half stress range on properly polished and filleted specimens, below which, in completely reversed stress, failure will not occur, is, as usual, called the endurance limit. Nominal values of stress obtained in tests on notched specimens or those subjected to both corrosion and repeated stress are called fatigue limits.

There are indications that the low endurance limits of very hard material such as used for springs are due to internal stress. Cold-worked monel metal, annealed so as to relieve internal stress without materially dropping the tensile strength, can be obtained with an endurance limit over 50 000 lb. per sq. in. and a corrosion fatigue limit in fresh or salt water of 25 000 to 28 000 lb. per sq. in. Phosphor bronze (5 per cent tin), cold drawn and slightly annealed, has endurance and corrosion-fatigue limits (salt or fresh water) of 22 000 to 23 000 lb. per sq. in.; annealed stainless steel (0.38 per cent carbon, 14.50 per cent chromium) has an endurance limit of 52 000 lb. per sq.

---

*For example, Proceedings, A.S.T.M., Vol. 28, Part II, p. 117 (1928); Vol. 27, Part II, p. 102 (1927); Proceedings, Inst. Metals Division, Am. Inst. Mining and Metallurgical Engrs., p. 571 (1928); Internat. Congress Testing Mats., Amsterdam, 1927, Vol. 1, p. 305, and many earlier papers.

in. and corrosion fatigue limits (salt or fresh water) of 36 000 lb. per sq. in. A heat-treated nickel-silicon steel has an endurance limit of 108 000 lb. per sq. in., but a fresh water corrosion fatigue limit of only 12 000 lb. per sq. in.

Sharp notches so cut down the resistance of hard materials to repeated stress that the high endurance limit of materials often used for springs may be brought down to a notched fatigue limit no better than that for very soft materials. The importance of freedom from surface defects and internal flaws, as well as from internal stress in springs, is emphasized. It is suggested that cold-working without annealing may produce minute discontinuities within the metal which affect the fatigue limit without appreciably affecting static tensile properties.

The need for further information on the effect of varying the position of the endurance range (using other than completely reversed stresses) is brought out. Within the elastic range, it makes little difference what the position of the torsional endurance range is, but, especially for spring design, it would be useful to know certainly what the facts are in reversed tension and compression.

Corrosion-fatigue limits depend more upon the corrosion resistance of the material than upon its endurance limit. Stainless steel, high chromium low nickel, and especially the medium chromium high nickel austenitic steels appear promising for springs that are subject to corrosion. Corrosion of steels that are not essentially corrosion-resistant occurs with remarkable rapidity under repeated stress, even in fresh water. Cadmium plating of steel that is subject to corrosion has been found to double the corrosion-fatigue limit, and would be effective if exposure to corrosive conditions is not so long continued as to break down the coating. Chromium plating directly of steel has been found ineffective. Data are lacking on chromium coatings over a layer of copper or nickel.

Speller, F. N., McCorkle, I. B., and Mumma, P. F. ("Influence of Corrosion Accelerators and Inhibitors on Fatigue of Ferrous Metals," Proceedings, A.S.T.M., Vol. 28, Part II, p. 159, 1928. Abstracts of Articles on Fatigue of Metals, A.S.T.M., 1929) in this paper refer to fatigue tests made with sufficient inhibitor in the water to prevent general corrosion, and the effect of certain corrosion factors which tend to break down the protective influence of the inhibitor and cause pitting of the metal.

Corrosion of metals in water depends upon a number of conditions:

(1) Factors controlling the amount of free oxygen reaching the metal surface.

(2) Dissolved substances which act more or less independently of the dissolved oxygen present, such as acids and alkalies.

(3) Factors influencing localization of corrosion, such as internal stresses and electrolytic concentration cells of all kinds.

The experiments were made on an open-hearth steel of 0.35 per cent carbon. The fatigue tests included (1) specimens tested in air with a thin coating of unmedicated vaseline, (2) specimens tested under flowing water containing sodium chloride and sodium sulphate, and (3) specimens treated as in (2) but with the addition of sodium dichromate to the water as a corrosion inhibitor; and (4) specimens treated as in (3) but having a band of Duco $\frac{1}{16}$ in. in width painted on the specimen.

The endurance limits for cases (1) and (3) were alike, but the S-N diagram for the case of the water containing the inhibitor was moved definitely to the right of the specimens tested in air. The sodium dichromate was evidently sufficient to prevent the lowering of the endurance limit due to corrosion.

Case (2) showed the usual lowered endurance limit due to corrosion-fatigue.

For case (4) the conditions which tended to localization of corrosion had overcome the protection due to the sodium dichromate, with the result that the curve fell between cases (1) and (3).

A few tests like case (4), except that a rubber washer replaced the Duco, showed that the results practically coincided with case (2). Localization of corrosion had completely broken down the protective effect of the inhibitor.

APPENDIX B

EMBRITTLEMENT AT THE UNIVERSITY OF ILLINOIS POWER PLANT

In 1874 boilers were installed in one of the University buildings for furnishing steam heat. These boilers were fed surface water and operated intermittently at low pressures. In 1888 deep well (160 ft.) water was used for feed water. The boilers continued to operate at low pressures. During 1898 the steam pressure was increased and the boilers operated more continuously. Shortly after this, embrittlement started to manifest itself.

The official record of the occurrence of this type of difficulty in the University of Illinois boilers dates back to 1910. The boilers operating were as follows:

Nos. 1, 2, 4, 5, 6	long-drum water-leg boilers
3, 7, 8	bent-tube boilers

They were from 6 to 15 years of age—the bent-tube boilers being the newer ones.

The inspectors' reports indicate that difficulties as listed were noted at the stated times:

July, 1910—Boilers Nos. 4 and 5. Internally clean. Cracks in plate at corners of cross box in south drum of No. 5. One cracked header on rear end of No. 4 and leakage noted at one rear circulator and one girth seam on each drum.

December, 1912—The top middle drum No. 7 boiler has been replaced with a new one. (Old one installed 1904) No. 3 boiler cracked ligament in tube sheet in bottom drum, several tube ends leaking. In No. 6 the fifth rear header is cracked, should be renewed before boiler is used. One rear circulator and mud-drum nipple leaking. (During this time several blow-off flanges cracked and had to be replaced.)

In 1911 a new boiler plant was put in operation using two long-drum water-leg boilers operating at a pressure of 140 lb. per sq. in. This plant was to furnish power in addition to steam. The older plant was still kept in service for heating purposes. The inspectors' reports continue as follows:

Dec., 1912—Boilers Nos. 1 and 2, new plant; considerable leakage at girth seams should be caulked.

July, 1913—Boilers Nos. 1 and 2, new plant; girth seams still leaking.

April, 1914—Boilers Nos. 1 and 2, new plant; bad leaking at girth seams.

March, 1915—Cracking between rivets on drums in new plant. Advise replacing.

May, 1915—Old power plant, Boiler No. 1—Leaks between two rivets in front girth seam. Three leaky rivets in rear cross box.

Boiler No. 2—Leaky rivets in front cross box.
Boiler No. 3—Cracked plate bottom drum.
Leaky joint middle top drum.
Blow-off flange cracked and pieces of plate cracked off.
Boiler No. 4.—Renew six tubes.
Boilers Nos. 5 and 6—Out of service.
Boiler No. 7—Lap seam leaking, bottom drum.
Boiler No. 8.—Leak top middle drum.

In 1914 two new long-drum water-leg boilers (Nos. 3 and 4) had been installed in the new power plant.

In commenting on the difficulty experienced at the University of Illinois power plants the report of the Insurance Inspection read as follows:

"March 20, 1915—From our experience with the water used in your locality, it is evident to our mind that the cracks have started at all points where leaks have developed on these seams. This would mean that we consider that the girth seams as described in the drums of No. 1 boiler opposite where leakage has been shown, are fractured and it would be only a short time before the drums would have to be taken out and replaced with new ones."

"Wherever we have made any repairs to seams of this kind we have always found the cracks to extend considerably beyond the points where they could be noted before the plate was cut out. Therefore, we strongly advise and recommend that all four drums of these boilers be abandoned and replaced with new ones."

"In regard to the feed water used in operation of these boilers, it has been admitted that this brings about a change in the condition of the plates, which later develops into fractures."

When the difficulty became apparent in 1912, and it was noted that similar cracking had occurred in other plants using water of a type similar to that used at the University, attempts were made to treat the water to neutralize the effect of the caustic alkalinity. A letter written July 11, 1913 reads as follows:

Mr. H. D. Oberdorfer,
114 Engineering Hall.
Dear Sir:—

The investigation on brittleness of boiler plates has been reported on so far as our experiments here are concerned, and covers the time up to the first of July. I can say that all our experiences so far are in accord with the report of the superintendent for the Babcock and Wilcox Company, which is returned herewith.

The effect of sodium hydrate can be neutralized by any salt which will react with that substance to form a new compound which will not hydrolize in the boiler. Magnesium sulphate is a good material to use for this purpose. The only point to be guarded is an excess of the material over the chemical equivalent necessary to neutralize the sodium hydrate.

> Since magnesium salts are corroding it is necessary to avoid an excess of this reagent. However, this is a matter easily controlled and I would endorse the recommendation under proper observations as indicated.
>
> Very truly yours,
> S. W. PARR
> Professor of Applied Chemistry

Early in 1915 the suggestion was made to add sulphuric acid to neutralize the sodium carbonate in the feed water. Under the date of July 15, 1915, Mr. I. Harter, Jr., then superintendent of the Babcock & Wilcox Co., wrote to Professor C. R. Richards, then Acting Dean of the College of Engineering, as follows:

> I have your letter of July 12th stating that Prof. Parr has recommended the elimination of the sodium carbonate present in the feed water by treatment with sulphuric acid.
>
> I do not feel that the sulphuric acid method will in practice be satisfactory. I am assuming of course that the treatment will be external to the boiler so that the formation of CO_2 will not result in its being carried into the boiler itself, and I am also assuming that the treatment will be checked by continual titrations, so that by no possibility can any free acid go over into the boiler.

On February 10, 1916, Mr. W. L. Abbott wrote to Professor S. W. Parr in regard to the proposed acid treatment:

> I thank you for your letter of February 7th with attached charts descriptive of the results obtained in reducing the alkalinity of the water in the boilers by feeding the boilers with magnesium sulphate.
>
> I note your suggestion to substitute sulphuric acid for magnesium sulphate. This is a proposition which a chemist would naturally make and from which a boiler user would naturally shrink: not that the results would not be exactly as you predict so long as the treatment is wisely administered, but rather as to what results might be if the treatment is bungled. On the whole, I would like to see the acid treatment tried out, provided it can be arranged for in a way which will reasonably preclude the possibility of damage to the boiler or piping by contact with acid of considerable strength.

About March 1916 the use of sulphuric acid to partially neutralize the sodium carbonate was substituted for that of magnesium sulphate which had been used since early in 1914. This treatment was carried on in two 40 000 gallon tanks under close chemical supervision. This treatment has been continued and is still in use. After 10 years of operation the boilers were thoroughly examined, test rivets removed, holes cleaned, etc., and no indication of embrittlement or corrosion was evident. The boilers after 15 years are still free from leaks or indications of embrittlement.

A few abbreviated reports of the insurance inspectors in regard to the results of inspection of boilers in the new plant are given below, to indicate the change brought about in the boilers after the sulphate treatment was started. These, when compared with the reports issued previous to treatment, clearly show the results of the treatment.

Internally		*Externally*	
Nov., 1918—4 Boiler	light scale	1, 2, 3, 4	good order
Sept., 1919—1, 2, 3, 4	good order	1, 2, 3, 4	good order
Sept., 1921—1, 2, 3, 4, 5, 6	good order	1, 2, 3, 4, 5, 6	good order
Aug., 1922—1, 2, 3, 4, 5, 6	good order	1, 2, 3, 4, 5, 6	good order
Sept., 1923—5, 6	light scale	1, 2, 3, 4, 5, 6	good order
Oct., 1924—3, 4	light scale	1, 2, 3, 4, 5, 6	good order
Oct., 1925—1, 2, 3, 4, 5, 6	light scale	1, 2, 3, 4, 5, 6	good order
Mar., 1926—1, 2, 3, 4, 5, 6	light scale	1, 2, 3, 4, 5, 6	good order
Nov., 1926—3, 4	light scale	1, 2, 3, 4, 5, 6	good order
June, 1927—1, 2, 5, 6, 7, 8	light scale	1, 2, 3, 4, 5, 6, 7, 8	good order
Nov., 1928—3, 4	light scale	1, 2, 3, 4, 5, 6, 7, 8	good order
Feb., 1929—3, 4	light scale	1, 2, 3, 4, 5, 6, 7, 8	good order
July, 1929—1, 4, 5, 6, 7, 8	light scale	1, 2, 3, 4, 5, 6, 7, 8	good order
Dec., 1929—2	light scale	1, 2, 3, 4, 5, 6, 7, 8	good order

APPENDIX C

DATA FROM EMBRITTLED BOILERS

The following is a summary of the data gathered with regard to boilers which have been embrittled, to 1929. The names of the operating companies are on file, but, since some request that no mention be made directly, it has been deemed expedient not to give the specific sources of information.

The instances of embrittlement are divided into three classes, depending upon the source of water used:

(1) Those occurring with natural alkaline water.
(2) Those occurring with water made alkaline by treatment with soda ash.
(3) Those occurring with water made alkaline through zeolite treatment.

(1) Cases of embrittlement occurring with natural alkaline water:

Illinois

Belden, 1924. Horizontal tubular boiler, 54 inches in diameter, five years old, found cracked for more than 39 rivets.

Big Foote Prairie. Horizontal tubular boilers, eight years old, rivets cracked off.

Bloomington, 1912. Long-drum water-leg type boiler exploded, others found to be badly embrittled. The water was changed and no further trouble occurred.

Bloomington, 1921. Long-drum water-leg type boiler, seven years old, embrittlement cracks for 27 rivet holes.

Bloomington, 1921. Long-drum water-leg type, eleven years old, cracked girth seam.

Champaign, 1899. Tubular boiler, 60 inches in diameter, exploded.

Champaign, 1925. Four 500 h.p. bent-tube boilers found embrittled; one drum cracked for 27 rivet holes, not 3 per cent of metal found to be effective.

De Kalb, 1901. Vertical tubular boiler cracked and was removed.

De Kalb, 1900-1904. Long-drum water-leg boilers, 5 drums embrittled; replaced with bent-tube boilers, which later had cracked drum and head.

De Kalb, 1911. Long-drum water-leg boilers, drums cracked.

De Kalb, 1924. Bent-tube boiler, blow-off flange and shell cracked.

Hartland, 1919. Horizontal tubular boiler, five years old, headless rivets found on boiler; straps removed, no cracks found; straps replaced and riveted by hand.

Hartland, 1924. Same boiler, rivet heads cracked off; cracks found from head to girth seam.

Hoopeston. Several cases of tubular boilers with leaks and cracks.

Paxton, 1901. Two-sheet tubular boiler, cracks found; boiler later exploded.

Paxton. Tubular boiler, cracked, did not explode.

Sycamore. Tubular boiler, cracked seams.

Sycamore. Several cases of tubular boilers in creameries in this district with cracked seams.

Urbana, 1915. Long-drum water-leg boilers, 500 h.p., five years old, four drums replaced due to embrittlement cracks; trouble experienced with older bent-tube boilers since 1910.

Watseka, 1897. Tubular boiler, 72 inches in diameter, 18 feet long, leaking, followed by explosion.

Wisconsin

Appleton, 1920. Horizontal tubular boiler, 78 inches in diameter, 20 feet long, 9 years old, found cracked over two-fifths of circumference of boiler. Replaced with long drum water-leg boilers, which later encountered trouble with cracking.

Appleton. Three separate explosions of tubular boilers due to ripping along longitudinal seam.

Southern California

Los Angeles, 1924. Seventeen drums in 770-h.p. bent-tube boilers replaced due to embrittlement.

Texas

Dallas, 1922. Six bent-tube boilers, 300 h.p., 15 years old, butt-strap construction, condemned.

Dallas, 1924. Long-drum water-leg boilers, 12 years old, also experienced trouble.

Houston, 1919. Long-drum water-leg boilers, 520 h.p., three drums replaced.

Houston, 1921. Long-drum water-leg boiler, 520 h.p., replaced drum 9 years old. The replaced drum cracked after one year of service.

Houston, 1922. Long-drum water-leg boiler, 600 h.p., replaced drum four years old.

Waco, 1923. Long-drum water-leg boiler, 600 h.p., 225-pound steam pressure, drums 7 years old replaced. These drums had double riveted girth seams.

Colorado

Denver, 1923. Bent-tube type boilers, 750 h.p., 4 years old, replaced.

The waters used in all these plants came from deep wells.

(2) Cases of embrittlement occurring with water made alkaline by treatment with soda ash:

Torpedo boat destroyers, 1916. One White-Foster express-type oil-burning boiler burst drum; embrittlement cracking; run 3 per cent normal alkalinity using boiler compound, found to be sodium hydrate and sodium carbonate.

Revenue cutters. Two sets of long-drum water-leg marine boilers were made in the shops at the same time, went into service at the same time, and had approximately the same service. After 18 months one cutter had both boilers embrittled. Embrittled boilers had used 3300 lb. boiler compound, the other, which had used 300 lb., experienced no trouble. Boilers were constructed under navy specifications, which required all holes to be drilled from solid, and workmanship, as well as materials, of drums to be the best.

Four central stations developed embrittlement. They carried high soda ash alkalinity with little sulphate. Plants were surface condensing, and carried high excess alkalinity as a precaution against magnesium chloride which might reach boilers. One plant replaced fifteen drums.

A railroad running through pure water district used soda ash to prevent corrosion and stop light scale: had more than one hundred locomotive boilers embrittled in twelve years.

(3) Cases of embrittlement occurring with water made alkaline through zeolite treatment:

The zeolite or base exchange system of water softening is one in which the calcium and magnesium bicarbonates are replaced by sodium bicarbonate and the calcium and magnesium sulphates by sodium sulphate. When this softener is used on a water free from or low in sulphates the sodium carbonate becomes present in large excess.

Indiana

Auburn, 1925. 350-h.p. bent-tube boiler embrittled, used water low in sulphate; water softener in operation about two years.

Oklahoma

Lawton, 1926. Long-drum water-leg type boiler, two years old, steam pressure 255 lb. per sq. in.; old plant operated 30 years on lake water without embrittlement; new plant used zeolite softener on same water from 1925.

New York

Buffalo, 1926. Bent-tube boilers operating on 200 lb. per sq. in. steam pressure embrittled after five years; Lake Erie water with zeolite softener used entirely.

Instances of embrittlement which have been collected since 1927, are given as follows:

Arkansas

A boiler operating at 215-pound steam pressure exploded in 1929. The boiler was about six years old. The boiler next in line was badly damaged as a result of the explosion. Two other boilers were found to be badly cracked. All the cracking took place in the riveted areas. During the first two years of operation the make-up water was taken from a pond and received no treatment. Because of dirty steam and some scale, a system of treatment was started using a deconcentrator in connection with soda ash. Daily analyses were made on the boiler waters for alkalinity, but no attention was paid to the sulphate content. This method of treatment had been in use about four years when the explosion took place.

California

(1) An electric power plant supplying power and light used untreated water for twenty-five to thirty years without encountering embrittlement. In 1922 new boilers were added to the installation, the older ones still being retained in service. The operating pressure was from 200 to 250 lb. per sq. in. A zeolite water softener was installed in 1922. In 1927 it was found that cracks had developed in four boilers, both old and new boilers being affected.

(2) Two boilers installed in 1922 operating at a pressure of 250 lb. per sq. in. were found cracked in 1927. The water supply was river water zeolite treated.

The boilers of an excursion boat of cross-drum water-leg type were operated about two years at a pressure of 225 lb. per sq. in. using a well water high in sodium carbonate content. Four boilers developed cracking.

Colorado

Serious cracking was detected in a 1300-h.p. boiler operating at 380-pound pressure. The boiler was three years old. A fairly pure make-up water was used and soda ash treatment was given. At times sodium sulphate, phosphate, and tannin were used. A composite sample of four boilers had been analyzed weekly. The results of these analyses gave the following information:

Ratio $\frac{Na_2SO_4}{\text{Total alkalinity}}$	Portion of the three years
Below 1	14 per cent
Between 1 and 2	32 per cent
Between 2 and 3	32 per cent
Above 3	22 per cent

The phosphate content was zero at times, and high at other times. The cracks were found to be intercrystalline, and could be readily classed as embrittlement cracks.

Illinois

(1) A boiler operated at a pressure of 200 lb. per sq. in., used untreated Lake Michigan water for three years. A zeolite softener was then installed, and twenty months later cracks were found to have developed.

(2) Two 200-h.p. long-drum water-leg boilers operating at 175-lb. pressure operated four years and were found to be badly embrittled. Cracks were found in circumferential seams. A well water high in sodium carbonate and low in sulphate was used for two years. Deposits formed in the feed water heater and feed lines, and leaks occurred in the seams of the boiler. A zeolite softener was installed apparently to overcome these difficulties. The seam leakage continued, and after four years total operation the boilers were replaced due to the cracking.

(3) During 1929 serious cracking was detected in a boiler operating at 140-lb. steam pressure. The boiler was about fifteen years old. A triple-riveted butt-strap construction was used, and the cracking took place at the second row of rivets. A well water containing sodium carbonate and only a small amount of sulphate was used for boiler feed water.

(4) Rivets cracked off and cracks were found in two 500-h.p. bent-tube boilers which had operated at 250-lb. pressure for about ten years. A river water treated by the lime-soda process had been used during this period of time. A high causticity and low sulphate resulted in the boiler water.

Indiana

Four 25 000 feet capacity firebox heating boilers operating at a pressure of 30 lb. per sq. in. using zeolite treated water developed extensive embrittlement cracking in the summer of 1927, after having been in service under these conditions for less than four years. The boilers were designed for 100-lb. pressure. New boilers were installed, and the operators were instructed to modify the water treatment. No change was made in the water conditions. Late in 1929 the replacement boilers encountered embrittlement.

Louisiana

Rivets were found cracked off from bent-tube boilers after operating for four years at 200-lb. pressure. No straps were removed, and no cracking in the drums could be detected by means of an external examination of the boilers. The water in use was a well water practically free from sulphate and containing sodium carbonate.

Michigan

(1) Late in 1929 trouble was experienced in large bent-tube boilers operating at 250-lb. pressure in an industrial plant. Serious cracking was found in the drum heads and horizontal seams. The make-up water was treated so as to produce a boiler water high in causticity, and with the sulphate about equal to the total alkalinity.

(2) Four 722-h.p. cross-drum water-leg boilers operating at 175-lb. pressure were found badly embrittled. The boilers were from two to four years old. The water treatment used during the later two years gave a boiler water high in causticity and low in sulphate.

(3) Three 300-h.p. bent-tube boilers operating at 175-lb. pressure encountered cracking after three years of operation. The water supply at this plant was from the city mains and was zeolite treated. The sulphate content of the boiler water was low in respect to the alkalinity.

(4) Trouble was experienced in the drums, headers, and tubes of four 722-h.p. cross-drum water-leg boilers, operating at 175-lb. pressure, which were seven months old. The water used was well

water, zeolite treated, and did not meet the A.S.M.E. recommendations.

Minnesota

Boilers operating at a pressure of 150 lb. per sq. in. used untreated water until 1913, and the same water treated with a lime soda ash softener subsequently. The water was low in sulphate. Two drums were found to be cracked during 1927.

One 500-h.p. bent-tube boiler operating at 200-lb. pressure had been in operation on zeolite-treated river water for about seven years. The insurance inspector notified the operators about the danger of embrittlement because of the high causticity in the boiler water at least two years before the cracking occurred. The operators asked the water-treating company about the possibility of danger and were told that no trouble would result from the use of their treatment. Consequently no attention was paid to the sulphate content. The boiler developed serious cracking in a mud drum and a top drum and only timely examination by the cautious inspector prevented an explosion. The cracking was found to be typical of embrittlement cracking.

New York

Two 500-h.p. bent-tube boilers were in operation at this plant. The steam pressure was 175 pounds. One boiler had been in use one year on hard water before the second boiler was installed. At the time the newer boiler was installed, a hot-process lime softener was put in operation. The resulting boiler water was low in sulphate and high in causticity. After seven years in operation, sixteen rivet heads were found cracked off from the inside of one of the seams of the newer boiler. When the butt straps were removed they were found to be badly cracked. The cracking was typical of embrittlement cracking.

Ohio

At this plant four 722-h.p. cross-drum water-leg boilers operating at 160-lb. pressure were found to be badly cracked after operating only one year. The cracks occurred in practically all the seams of the drums. Tubes were found cracked where they were rolled into the headers. The boilers were in a dangerous condition when the cracking was detected.

A well water was used for make-up, and it was zeolite treated before being fed to the boilers. The sodium carbonate content was high in respect to the sulphate. A high caustic alkalinity resulted in the boiler water.

Pennsylvania

Long-drum water-leg boilers ten years old operating at a pressure of 265 lb. per sq. in. used Lake Erie water treated by the lime-soda process and over-treated with soda ash. One boiler developed cracks.

Wisconsin

In a heating boiler five years old, operating at a pressure of 70 lb. per sq. in., using zeolite treated well water, the rivets became embrittled and cracked off.

The boilers of a steam plant operated for many years at a steam pressure of 150 lb. per sq. in., using untreated river water, and no difficulty was experienced from embrittlement. Zeolite water treatment was introduced in 1924, and two years later trouble from cracking was experienced. Boiler No. 1, a horizontal return tubular boiler built in 1914, gave no trouble until the winter of 1926, when a crack developed in a circumferential seam for about one-third the circumference of the boiler. This was repaired by cutting out the damaged portion all the way around the boiler and replacing it with a new plate about a foot wide, making two seams. About nine months later the new rivet heads became embrittled and cracked off. Boiler No. 2, a bent-tube boiler installed in 1909, developed a crack in a horizontal lap-jointed seam in the top rear drum early in 1927. Boiler No. 5, a bent-tube boiler, installed in 1920, developed cracks in a horizontal butt-jointed seam in a mud drum during the summer of 1927.

Virginia

Three 500-h.p. cross-drum water-leg boilers operating at 425-lb. pressure cracked after two years of operation. A crack opened up in one boiler for a length of over 7 feet from rivet hole to rivet hole. Rivet heads cracked off and cracks were found in all three boilers.

APPENDIX D

DETERMINATION OF PHOSPHATE IN BOILER WATER

In boiler water treatment it is often advisable to use phosphate. In order to control the use of phosphate, it is also advisable to be able to determine rapidly, and with a fair degree of accuracy, the soluble phosphate in the boiler water at frequent intervals. The application of this method is intended for use on boiler water samples, although, if organic matter is present in sufficient amounts to cause a marked coloration of the water, or if the silicate content is high, the method connot be used.

The test is dependent upon the fact that molybdenum present as phospholybdic acid may be reduced in the presence of an excess of molybdic acid. The reducing agent used is hydroquinone. If hydroquinone is added to an acid solution of molybdic acid, no phosphate being present, the solution will be colorless when treated with alkaline sulphite; but if phosphate is present, phospholybdic acid is formed and reduced, giving a blue color. As small an amount as 5 parts per million of phosphate gives a distinct blue color in this test.

Apparatus and Solutions

(1) Glass funnels and filter paper.
(2) Three 250 cc. volumetric flasks.
(3) 10 cc. and 5 cc. pipettes.
(4) 50 cc. graduated cylinder.

Molybdic Acid Solution

This solution is made from 125 grams of pure ammonium molybdate dissolved without heat in about 2 liters of phosphate-free distilled water to which 75 cc. of sulphuric acid (H_2SO_4) are slowly added and the volume made up to, roughly, 2½ liters. A slight blue coloration does not hinder the use of this solution.

Hydroquinone Solution

To prepare this solution 50 grams of pure hydroquinone are dissolved in about 2½ liters of phosphate-free distilled water and 3 cc. of concentrated sulphuric acid (H_2SO_4) added.

Carbonate-Sulphite Solution

To 6 liters of distilled water add 1500 grams of commercial soda ash. Dissolve 225 grams of sodium sulphite in 1500 cc. of water and add to the soda ash solution.

Stock Solution of Phosphate

Pure mono-potassium phosphate is finely ground, dried at 105 deg. C. for three hours, cooled, and kept in desiccator. Of this salt 0.1432 grams are dissolved in distilled water, 5 cc. of concentrated sulphuric acid (H_2SO_4) added, and the volume made up to one liter in a volumetric flask with distilled water. One cubic centimeter of this solution contains one-tenth of a milligram of phosphate (PO_4).

Sulphuric Acid Solution

Sulphuric acid solution mentioned later is made by adding 300 cc. of concentrated sulphuric acid (H_2SO_4) to about 2200 cc. of distilled water. This is labeled H_2SO_4.

Determination of Phosphate

Three 250 cc. volumetric flasks are required. Into the first, measure 50 cc. of the filtered sample of boiler water. By a pipette, 10 cc. of the standard phosphate solution are delivered into the second flask and 20 cc. of the phosphate solution are delivered into the third flask. Add to each flask in succession, 10 cc. of sulphuric acid, 5 cc. of molybdic acid and 5 cc. of hydroquinone solution. Allow the reactions to proceed for 5 minutes, then add to each flask 15 cc. of the carbonate sulphite solution, agitate each flask to mix the reagents, and fill each flask to the 250 cc. mark with distilled water.

Place the flask containing the sample of boiler water between the two flasks containing the standard solutions and compare colors. If the color is lighter than the flask containing the 10 cc., the PO_4 content is less than 20 parts per million. If the color is between that of the one containing the 10 cc. and that of the one containing 20 cc., the content is between 20 and 40 parts per million. If the color is darker than that of the one containing 20 cc., the content is over 40 parts per million.

Different maximum and minimum values may be established by changing the amount of standard phosphate solution used, and the PO_4 content should be within a possible error of about 10 per cent.

RECENT PUBLICATIONS OF THE ENGINEERING EXPERIMENT STATION†

Bulletin No. 171. Heat Transfer in Ammonia Condensers, by Alonzo P. Kratz, Horace J. Macintire, and Richard E. Gould. 1927. *Thirty-five cents.*

Bulletin No. 172. The Absorption of Sound by Materials, by Floyd R. Watson. 1927. *Twenty cents.*

Bulletin No. 173. The Surface Tension of Molten Metals, by Earl E. Libman. 1928. *Thirty cents.*

**Circular No. 16.* A Simple Method of Determining Stress in Curved Flexural Members, by Benjamin J. Wilson and John F. Quereau. 1928. *Fifteen cents.*

Bulletin No. 174. The Effect of Climatic Changes upon a Multiple-Span Reinforced Concrete Arch Bridge, by Wilbur M. Wilson. 1928. *Forty cents.*

Bulletin No. 175. An Investigation of Web Stresses in Reinforced Concrete Beams. Part II. Restrained Beams, by Frank E. Richart and Louis J. Larson. 1928. *Forty-five cents.*

Bulletin No. 176. A Metallographic Study of the Path of Fatigue Failure in Copper, by Herbert F. Moore and Frank C. Howard. 1928. *Twenty cents.*

Bulletin No. 177. Embrittlement of Boiler Plate, by Samuel W. Parr and Frederick G. Straub. 1928. *None Available.*

Bulletin No. 178. Tests on the Hydraulics and Pneumatics of House Plumbing. Part II, by Harold E. Babbitt. 1928. *Thirty-five cents.*

Bulletin No. 179. An Investigation of Checkerbrick for Carbureters of Water-gas Machines, by C. W. Parmelee, A. E. R. Westman, and W. H. Pfeiffer. 1928. *Fifty cents.*

Bulletin No. 180. The Classification of Coal, by Samuel W. Parr. 1928. *Thirty-five cents.*

Bulletin No. 181. The Thermal Expansion of Fireclay Bricks, by Albert E. R. Westman. 1928. *Twenty cents.*

Bulletin No. 182. Flow of Brine in Pipes, by Richard E. Gould and Marion I. Levy. 1928. *Fifteen cents.*

Circular No. 17. A Laboratory Furnace for Testing Resistance of Firebrick to Slag Erosion, by Ralph K. Hursh and Chester E. Grigsby. 1928. *Fifteen cents.*

Bulletin No. 183. Tests of the Fatigue Strength of Steam Turbine Blade Shapes, by Herbert F. Moore, Stuart W. Lyon, and Norville J. Alleman. 1928. *Twenty-five cents.*

Bulletin No. 184. The Measurement of Air Quantities and Energy Losses in Mine Entries. Part III, by Alfred C. Callen and Cloyde M. Smith. 1928. *Thirty-five cents.*

Bulletin No. 185. A Study of the Failure of Concrete Under Combined Compressive Stresses, by Frank E. Richart, Anton Brandtzaeg, and Rex L. Brown. 1928. *Fifty-five cents.*

**Bulletin No. 186.* Heat Transfer in Ammonia Condensers. Part II, by Alonzo P. Kratz, Horace J. Macintire, and Richard E. Gould. 1928. *Twenty cents.*

**Bulletin No. 187.* The Surface Tension of Molten Metals. Part II, by Earl E. Libman. 1928. *Fifteen cents.*

**Bulletin No. 188.* Investigation of Warm-air Furnaces and Heating Systems. Part III, by Arthur C. Willard, Alonzo P. Kratz, and Vincent S. Day. 1928. *Forty-five cents.*

Bulletin No. 189. Investigation of Warm-air Furnaces and Heating Systems. Part IV, by Arthur C. Willard, Alonzo P. Kratz, and Vincent S. Day. 1929. *Sixty cents.*

**Bulletin No. 190.* The Failure of Plain and Spirally Reinforced Concrete in Compression, by Frank E. Richart, Anton Brandtzaeg, and Rex L. Brown. 1929. *Forty cents.*

---

*A limited number of copies of the bulletins starred are available for free distribution.

†Copies of the complete list of publications can be obtained without charge by addressing the Engineering Experiment station, Urbana, Ill.

Bulletin No. 191. Rolling Tests of Plates, by Wilbur M. Wilson. 1929. *Thirty cents.*

Bulletin No. 192. Investigation of Heating Rooms with Direct Steam Radiators Equipped with Enclosures and Shields, by Arthur C. Willard, Alonzo P. Kratz, Maurice K. Fahnestock, and Seichi Konzo. 1929. *Forty cents.*

Bulletin No. 193. An X-Ray Study of Firebrick, by Albert E. R. Westman. 1929. *Fifteen cents.*

**Bulletin No. 194.* Tuning of Oscillating Circuits by Plate Current Variations, by J. Tykocinski-Tykociner and Ralph W. Armstrong. 1929. *Twenty-five cents.*

Bulletin No. 195. The Plaster-Model Method of Determining Stresses Applied to Curved Beams, by Fred B. Seely and Richard V. James. 1929. *Twenty cents.*

**Bulletin No. 196.* An Investigation of the Friability of Different Coals, by Cloyde M. Smith. 1929. *Thirty cents.*

**Circular No. 18.* The Construction, Rehabilitation, and Maintenance of Gravel Roads Suitable for Moderate Traffic, by Carroll C. Wiley. 1929. *Thirty cents.*

**Bulletin No. 197.* A Study of Fatigue Cracks in Car Axles. Part II, by Herbert F. Moore, Stuart W. Lyon, and Norville J. Alleman. 1929. *Twenty cents.*

**Bulletin No. 198.* Results of Tests on Sewage Treatment, by Harold E. Babbitt and Harry E. Schlenz. 1929. *Fifty-five cents.*

**Bulletin No. 199.* The Measurement of Air Quantities and Energy Losses in Mine Entries. Part IV, by Cloyde M. Smith. 1929. *Thirty cents.*

**Bulletin No. 200.* Investigation of Endurance of Bond Strength of Various Clays in Molding Sand, by Carl H. Casberg and William H. Spencer. 1929. *Fifteen cents.*

**Circular No. 19.* Equipment for Gas-Liquid Reactions, by Donald B. Keyes. 1929. *Ten cents.*

Bulletin No. 201. Acid Resisting Cover Enamels for Sheet Iron, by Andrew I. Andrews. 1929. *Twenty-five cents.*

Bulletin No. 202. Laboratory Tests of Reinforced Concrete Arch Ribs, by Wilbur M. Wilson. 1929. *Fifty-five cents.*

**Bulletin No. 203.* Dependability of the Theory of Concrete Arches, by Hardy Cross. 1929. *Twenty cents.*

**Bulletin No. 204.* The Hydroxylation of Double Bonds, by Sherlock Swann, Jr. 1930. *Ten cents.*

**Bulletin No. 205.* A Study of the Ikeda (Electrical Resistance) Short-Time Test for Fatigue Strength of Metals, by Herbert F. Moore and Seichi Konzo. 1930. *Twenty cents.*

**Bulletin No. 206.* Studies in the Electrodeposition of Metals, by Donald B. Keyes and Sherlock Swann, Jr. 1930. *Ten cents.*

**Bulletin No. 207.* The Flow of Air Through Circular Orifices with Rounded Approach, by Joseph A. Polson, Joseph G. Lowther, and Benjamin J. Wilson. 1930. *Thirty cents.*

**Circular No. 20.* An Electrical Method for the Determination of the Dew-Point of Flue Gases, by Henry Fraser Johnstone. 1929. *Fifteen cents.*

Bulletin No. 208. A Study of Slip Lines, Strain Lines, and Cracks in Metals Under Repeated Stress, by Herbert F. Moore and Tibor Ver. 1930. *Thirty-five cents.*

**Bulletin No. 209.* Heat Transfer in Ammonia Condensers. Part III, by Alonzo P. Kratz, Horace J. Macintire, and Richard E. Gould. 1930. *Thirty-five cents.*

Bulletin No. 210. Tension Tests of Rivets, by Wilbur M. Wilson and William A. Oliver. 1930. *Twenty-five cents.*

**Bulletin No. 211.* The Torsional Effect of Transverse Bending Loads on Channel Beams, by Fred B. Seely, William J. Putnam, and William L. Schwalbe. 1930.

**Bulletin No. 212.* Stresses Due to the Pressure of One Elastic Solid Upon Another, by Howard R. Thomas and Victor A. Hoersch. 1930. *Thirty cents.*

**Bulletin No. 213.* Combustion Tests With Illinois Coals, by Alonzo P. Kratz and Wilbur J. Woodruff. 1930. *In press.*

**Bulletin No. 214.* The Effect of Furnace Gases on the Quality of Enamels for Sheet Steel, by Andrew I. Andrews and Emanuel A. Hertzell. 1930. *In press.*

**Bulletin No. 215.* The Column Analogy, by Hardy Cross. 1930. *In press.*

**Bulletin No. 216.* Embrittlement in Boilers, by Frederick G. Straub. 1930. *Sixty-five cents.*

---

*A limited number of copies of the bulletins starred are available for free distribution.

UNIVERSITY OF ILLINOIS

THE STATE UNIVERSITY

URBANA

HARRY WOODBURN CHASE, Ph.D., LL.D., President

THE UNIVERSITY INCLUDES THE FOLLOWING DEPARTMENTS:

The Graduate School

The College of Liberal Arts and Sciences (Curricula: General with majors, in the Humanities and the Sciences; Chemistry and Chemical Engineering; Pre-legal, Pre-medical, and Pre-dental; Pre-journalism, Home Economics, Economic Entomology, and Applied Optics)

The College of Commerce and Business Administration (Curricula: General Business, Banking and Finance, Insurance, Accountancy, Railway Administration, Railway Transportation, Industrial Administration, Foreign Commerce, Commercial Teachers, Trade and Civic Secretarial Service, Public Utilities, Commerce and Law)

The College of Engineering (Curricula: Architecture, Ceramics; Architectural, Ceramic, Civil, Electrical, Gas, General, Mechanical, Mining, and Railway Engineering; Engineering Physics)

The College of Agriculture (Curricula: General Agriculture; Floriculture; Home Economics; Landscape Architecture; Smith-Hughes—in conjunction with the College of Education)

The College of Education (Curricula: Two year, prescribing junior standing for admission — General Education, Smith-Hughes Agriculture, Smith-Hughes Home Economics, Public School Music; Four vear, admitting from the high school—Industrial Education, Athletic Coaching, Physical Education. The University High School is the practice school of the College of Education)

The School of Music (four-year curriculum)

The College of Law (three-year curriculum based on a college degree, or three years of college work at the University of Illinois)

The Library School (two-year curriculum for college graduates)

The School of Journalism (two-year curriculum based on two years of college work)

The College of Medicine (in Chicago)

The College of Dentistry (in Chicago)

The School of Pharmacy (in Chicago)

The Summer Session (eight weeks)

Experiment Stations and Scientific Bureaus: U. S. Agricultural Experiment Station; Engineering Experiment Station; State Natural History Survey; State Water Survey; State Geological Survey; Bureau of Educational Research.

The Library collections contain (May 1, 1930) 836,496 volumes and 221,800 pamphlets.

For catalogs and information address

THE REGISTRAR
Urbana, Illinois