AQUEOUS SOLUTIONS OF ETHYLENE GLYCOL, GLYCERIN AND SODIUM SILICATE AS QUENCHING MEDIA FOR STEELS

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ABSTRACT

The quenching characteristics of aqueous solutions of ethylene glycol, glycerin, and sodium silicate were studied by means of temperature-time cooling curves on small cylinders of a 0.96 per cent carbon steel quenched in solutions of various concentrations and temperatures. Center cooling curves are given for cylinders one-half inch in diameter by 2 inches long, quenched in aqueous solutions of ethylene glycol and glycerin at atmospheric temperature. Surface and center cooling curves are given for aqueous solutions of two lots of sodium silicate having different soda-to-silica ratios, namely, 1:4 and 1:2.5. These two silicates are designated in this report by these ratios. The effect of increasing the temperature of solutions of the 1:4 sodium silicate from 20° to 80° C. was also studied. The characteristics of these cooling curves and a study of the hardnesses and structures produced suggest that these sodium silicate solutions would be useful for obtaining cooling rates from slightly less than that obtained with water to that of oil.

Four concentrations of the 1:4 sodium silicate having specific gravities corresponding to 4.6°, 9.5°, 13.2°, and 16.7° B. and two of the 1:2.5 sodium silicate, 12.4° and 28.8° B., were found which gave intermediate cooling rates between those obtained with water and with oil at atmospheric temperature.

Some trouble was experienced with the instability of certain of the aqueous solutions of the 1:4 sodium silicate. The stability of these solutions was greatly increased by the addition of 2 per cent by volume of a solution of sodium hydroxide of specific gravity 1.065.

The wide variations in cooling produced by check tests on aqueous solutions of ethylene glycol and of glycerin indicate that these solutions may not be particularly useful as media for the quenching of steels.

Quenching experiments with "stepped" bars of a 1.06 per cent carbon steel indicate that sodium silicate solutions can be used at atmospheric temperature to provide coolants with graded cooling speeds between those of water and oil.

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I. INTRODUCTION

The structure and properties of a quenched steel depend upon both the critical cooling rate of the particular steel in question and the cooling characteristics of the media in which the steel is quenched. In recent years plain carbon steels have been supplemented by alloy steels in which the alloying additions have changed the critical cooling rates. The simplest and most widely used quenching media are water and oil. The cooling characteristics of these two media have been modified by adding salts, alkalis, acids, or other chemical compounds to water, by using water or aqueous solutions at temperatures below or above room temperatures, and by employing emulsions of oil and water.

With quenching solutions available giving a complete graded series of cooling rates, the control of the results to be obtained from quenching both plain carbon and alloy steels is obviously made much more simple. Oil-water emulsions, concentrated sulphuric acid, and hot aqueous solutions have been used in the attempt to supply this need.

Experiments previously made at the National Bureau of Standards on emulsions of water and machine oil showed that the addition to water of only 0.1 per cent of oil, by volume, decreased the cooling rate of the water almost to that of the oil alone. The extreme accuracy that apparently is required in preparing and maintaining emulsions of this type in order to secure quenching solutions of known cooling rates appears seriously to limit the usefulness of such emulsions.

Concentrated sulphuric acid has been used successfully to give cooling rates between those obtained with oil and water.¹ Its disadvantages are its hygroscopic nature, making maintenance of its concentration difficult, and the very great danger to workmen from splashing.

Hot water and hot aqueous solutions are sometimes used to give cooling rates intermediate between those of oil and water.² Such solutions require good circulation and accurate control of temperature and concentration.

Solutions of glycerin also have been used as quenching media. Scott³ reported that glycerin-water solutions "effectively bridge the gap between oil and water."

The present investigation was directed chiefly toward a study of solutions of sodium silicate as quenching media which it was expected might give cooling rates intermediate between those of oil and of water. Some attention was also given to the behavior of solutions of ethylene glycol and of glycerin when used as quenching media.

II. EXPERIMENTAL METHODS AND MATERIALS

The experimental method employed in the present investigation was based on the classical work of LeChatelier,⁴ who first succeeded in devising means for recording photographically the temperature changes taking place over the period of a few seconds in small speci-

¹ H. J. French and O. Z. Klopsch, Quenching Diagrams for Carbon Steels in Relation to Some Quenching Media for Heat Treatment, *Trans. Am. Soc. Steel Treating*, **3**, p. 284; 1924.

² H. J. French and T. E. Hamill, Hot Aqueous Solutions for the Quenching of Steels, *B. S. Jour. Research*, **3** (RP103), p. 399; 1929; *Trans. Am. Soc. Steel Treating*, **16**, p. 711; 1929.

³ H. Scott, Quenching Properties of Glycerin and its Water Solutions, *Trans. Am. Soc. Steel Treating*, **6**, p. 31; 1924.

⁴ H. LeChatelier, "Etudes sur la trempe de l'acier," *Revue de Métallurgie*, **1**, p. 473; 1904.

mens of steel quenched in various coolants. LeChatelier's method was further developed by Benedicks⁵ and employed in studying the influence on quenching rates of the surface of the steel, the rate of motion of the steel, the dimensions, mass, and chemical composition of the specimen, the temperature of the quenching bath, and other factors.

In the present work determinations were made of surface and center cooling curves of steel cylinders one-half inch diameter by 2 inches long; quenched from 875° C. in several coolants at various temperatures from 20° to 80° C. The quenching media were moving with a velocity of 3 feet per second. The time-temperature curves were obtained on a moving photographic film by a method previously described in detail⁶ in which thermocouples suitably mounted at the center or on the surface of the steel specimen were connected to an Einthoven "string galvanometer."

In addition to the determination of cooling curves on the plain cylindrical specimens, hardness determinations was made on the steel at the surface and at the center of the specimens. A study was also made of the hardness and microstructure developed in cylindrical "stepped" bars (fig. 13) which were machined to have abrupt changes in diameter from one-fourth to one-half inch to 1 inch.

The surface hardness of the quenched cylinders was taken as the average of six determinations made along the length of the cylinder on the side meeting the direct flow of the liquid during quenching. These tests were made after removing about 0.01 inch of metal from the surface by wet grinding to form a narrow flat strip along the length of the cylinder. The center hardness was determined from tests made after cutting the cylinders in half (transversely) under a water spray.

Two steels were used in the preparation of specimens, one for the plain cylindrical specimens for cooling curves and second for the "stepped" bars. They differed but slightly in composition both being practically a 1 per cent plain carbon steel.

TABLE 1.—Chemical composition of steel specimens

	Carbon	Manga- nese	Silicon	Phos- phorus	Sulphur
Plain cylinders.....	0.96	0.23	0.18	0.016	0.028
"Stepped" bars.....	1.06	.24	.18	.014	.016

Commercial sodium silicate from two sources was used in the preparation of the silicate quenching solutions. The two lots differed in soda-to-silica ratios. One contained approximately 6 per cent Na₂O, 25 per cent SiO₂ by weight, and the other approximately 11 per cent Na₂O, 27 per cent SiO₂, the balance being water in each case. The ratios of soda to silica were thus nearly 1:4 and 1:2.5. The two solutions are referred to in this report by these ratios. While the 1:4 silicate was cloudy the 1:2.5 silicate was quite clear, apparently due to its higher proportion of Na₂O.

The diluted solutions of sodium silicate, ethylene glycol, and glycerin were prepared in the concentrations shown in Table 2. The

⁵ C. Benedicks, The Cooling Power of Liquids, Quenching Velocities, J. Iron and Steel Inst., 2, p. 153; 1908.

⁶ See footnote 1, p. 556.

thoroughly stirred solutions were allowed to stand for several hours and again stirred in order to cause complete solution before they were used in the quenching experiments.

The prepared quenching oil was the same commercial quenching oil that has been used in previous studies on quenching at the National Bureau of Standards and designated there as No. 2 oil. Its physical properties have been given in a previous publication.⁷

TABLE 2.—Concentrations and specific gravities of the sodium silicate, glycol, and glycerin quenching solutions

SOLUTIONS OF 1:4 SODIUM SILICATE

Per cent by volume		Specific gravity at 20° C./15.6° C.	° B.
Sodium silicate	Water		
10	90	1.030	4.6
20	80	1.070	9.5
30	70	1.100	13.2
40	60	1.130	16.7
60	40	1.190	23.2
100	0	1.300	33.5

SOLUTIONS OF 1:2.5 SODIUM SILICATE

20	80	1.093	12.4
60	40	1.248	28.8
100	0	1.405	41.8

ETHYLENE GLYCOL SOLUTIONS

Ethylene glycol	Water	Specific gravity at 20° C./15.6° C.	° B.
20	80	1.033	-----
60	40	1.083	-----
100	0	1.113	-----

GLYCERIN SOLUTION

Glycerin	Water	Specific gravity at 20° C./15.6° C.	° B.
60	40	1.165	

III. QUENCHING EXPERIMENTS WITH GLYCOL AND WITH GLYCERIN SOLUTIONS

The center cooling curves of the one-half by 2 inch cylinders of the 0.96 per cent carbon steel quenched in ethylene glycol and aqueous solutions of 20 and 60 per cent glycol and of 60 per cent glycerin are shown in Figure 1. The velocity of the quenching medium was 3

⁷ See footnote 2, p. 556.

FIGURE 1.—Center cooling curves of 0.96 per cent carbon steel cylinders quenched into aqueous solutions of glycol and glycerin at 20° C.

feet per second in the tests with glycol and the glycol solutions and 1 foot per second in the tests with the glycerin solution.

The curves of Figure 1 show clearly very considerable variations in the cooling rates and the characteristics of the cooling curves between duplicate quenching tests. The greatest variations occur in the middle portions of the cooling curves, between 300° and 700° C. Most of the curves, however, coincide rather well at 200° C. It is thus evident that the total time of cooling from 875° C., the quenching temperature in all cases, to 200° C. can not be taken as a characteristic of the coolant which will indicate the constitution and properties of a steel quenched in that solution. The structure of a quenched steel is controlled by the cooling rates at the Ar' and Ar'' transformation points. For this particular steel these points lie in the neighborhood of 675° and 375° C., respectively. They are thus in the very region of the greatest variations in the cooling curves of check tests. Consequently, large variations are to be expected in the structures and hardness of duplicate specimens of a given steel quenched in any of these solutions.

It is to be kept in mind, however, that the variations in the temperature-time curves representing duplicate quenching tests are not solely the result of variations in the cooling rate of the solution. When the cooling rate is so slow as to permit the Ar^1 transformation the heat effect of this transformation acts to decrease still further the cooling rate of the specimen and magnifies the decreased cooling rate of the solution as represented in the curves of Figure 1.

The center and surface hardness values of these same quenched specimens, Table 3, give evidence of this expected variation in properties of steel quenched in these solutions under identical conditions. In specimens quenched in glycol solutions observed variations in hardness (Rockwell "C" scale) were 10 to 20 points on both surface and center. In specimens quenched in the 60 per cent glycerin solution, the variations in hardness were somewhat less.

TABLE 3.—Center and surface hardness of 0.96 per cent carbon steel quenched in aqueous solutions of glycol and glycerin

Test No.	Quenching medium	Rockwell hardness, "C" scale	
		Center ¹	Surface ²
2483	100 per cent glycol.....	44.1	45.2
2484	do.....	46.6	55.1
2487	do.....	43.0	50.7
2493	do.....	52.8	53.6
2496	do.....	42.6	46.4
2497	60 per cent glycol.....	66.2	66.4
2499	do.....	45.4	66.0
2501	do.....	46.0	47.8
2503	do.....	63.1	63.9
2498	20 per cent glycol.....	57.1	55.0
2500	do.....	44.1	48.6
2502	do.....	64.4	64.4
2504	do.....	65.0	66.2
1097	60 per cent glycerin.....	58.8	63.8
1106	do.....	56.9	63.4
1107	do.....	62.2	64.3
1114	do.....	58.3	61.5
1121	do.....	63.2	63.6

¹ Average of 3 tests.

² Average of 6 tests.

IV. QUENCHING EXPERIMENTS WITH SODIUM SILICATE SOLUTIONS

1. EFFECT OF VARYING CONCENTRATIONS OF SODIUM SILICATES

(a) COOLING TIMES AND COOLING RATES

The surface and center cooling curves obtained on the 0.96 per cent carbon steel cylinders quenched into various concentrations of the 1:4 and the 1:2.5 sodium silicates at 20° C. are shown in Figures 2 and 3. Cooling curves obtained on quenching in water and in oil at 20° C. are also given for comparison.

FIGURE 2.—Surface and center cooling curves of 0.96 per cent carbon steel cylinders quenched into solutions of the 1:4 sodium silicate, water, and oil at 20° C.

Each curve is the average of two or three tests.

Increasing the concentration of solutions of both the 1:4 and 1:2.5 sodium silicates lowered the cooling rates. The cooling times increased from slightly less than that of water to greater than that of oil. The comparison between the cooling times and cooling rates of oil and one of the more concentrated sodium-silicate solutions is more readily seen in Figure 4 which shows the surface and center cooling curves of the oil and the 23.2° B. solution of the 1:4 sodium silicate.

FIGURE 3.—Surface and center cooling curves of 0.96 per cent carbon steel cylinders quenched into solutions of the 1:2.5 sodium silicate, water, and oil at 20° C.

Each curve is the average of two or three tests.

FIGURE 4.—Replot of surface and center cooling curves of Figure 2, comparing the cooling curves of the oil and 23.2° B. solution of the 1:4 sodium silicate at 20° C.

The surface cooling in the 23.2° B. solution is much slower than in the oil, while the center cooling was about the same for both quenching media.

Figures 2 and 3 also show that three concentrations of the 1:4 sodium silicate and two of the 1:2.5 sodium silicate gave cooling rates intermediate between water and oil. These were the 9.5°, 13.2°, and 16.7° B. solutions of the 1:4 sodium silicate and 12.4° and

FIGURE 5.—Center cooling rates and center and surface cooling times and hardness of 0.96 per cent carbon steel cylinders quenched into different times and concentrations of sodium silicates at 20° C.

28.8° B. solutions of the 1:2.5 sodium silicate. The 4.6° B. solution of the 1:4 sodium silicate also gave slightly slower cooling than water at the center, but at the surface both cooled about the same except at lower temperatures.

The decrease in center cooling rate and increase in surface and center cooling times with increasing concentrations of the sodium silicate solutions is better shown in Figure 5. The relation between

the center cooling rate and the concentration of the 1:4 sodium silicate is almost linear up to concentrations of approximately 20° B. At higher concentrations the cooling rate changes relatively little with increasing concentration. On the other hand, the 1:2.5 sodium silicate containing the higher soda to silica ratio shows quite different results. With solutions of the 1:2.5 silicate the center cooling rate and surface and center cooling times are very little affected by increasing concentrations up to approximately 28° B. Higher concentrations, however, produced rapid changes in both the center cooling rates and surface and center cooling times.

Surface cooling rates were not calculated from any of the surface cooling curves in as much as these curves are so steep and contain so many fluctuations in temperature that the cooling rate at 720° could not be measured accurately.

(b) HARDNESS AND MICROSTRUCTURE

The center and surface hardness of the 0.96 per cent carbon steel quenched in the several concentrations of the 1:4 and 1:2.5 sodium silicates are shown in Figure 5. The steel was fully hardened at the center (Rockwell C65) on quenching in the 4.6° and 9.5° B. solutions of the 1:4 sodium silicate.

The steel quenched in these two solutions (fig. 6, *A* and *B*) was almost completely martensitic in structure with small amounts of troostite. With increasing concentrations of the 1:4 silicate there was an abrupt decrease in center hardness and in surface hardness at concentrations of 9.5° and 13.2° B., respectively. Increasing amounts of troostite and finally sorbite and pearlite, in the structures shown in Figure 6, *C*, and in Figure 7, *D*, *E*, and *F*, correspond with these changes in hardness.

The center cooling rate at 720° C., corresponding to the highest concentration of the 1:4 silicate giving practically complete center hardening, was 115° C. per second. The center cooling rates in solutions of the 1:2.5 sodium silicate, as indicated in Figure 5, exceeded this critical rate in all concentrations up to approximately a 34° B. solution. Consistent with this are the center hardness values which show complete hardening on quenching in 28.8° B. solution of the 1:2.5 silicate. The structures at the center of the specimens quenched in solutions of the 1:2.5 silicate are shown in Figure 8.

It appears possible that the relatively slow cooling rates obtained with sodium silicate solutions may be explained by the deposits of silica which formed on steel quenched in such solutions. The decrease in cooling rate with increase in concentration of sodium silicate may be due to the increase in thickness of the layer of silica that deposits on the steel during quenching. While no definite measurements were taken, it was observed that cylinders quenched in low concentrations of sodium silicate had a much thinner layer of silica than those quenched into highly concentrated solutions. Photographs of quenched "stepped" bars (fig. 14) verify this observation.

The only known difference between the two sodium silicates used in these experiments is that of the soda-to-silica ratios, the 1:2.5 silicate having the higher ratio—a greater proportion of alkali. This may account for the greater cooling rates observed in the lower

FIGURE 6.—Microstructures at the center of 0.96 per cent carbon steel cylinders quenched from 875°C . into different concentrations of the 1:4 sodium silicate at 20°C .

Etched in 2 per cent nitric acid in alcohol. Magnification, left $\times 100$ and right $\times 1,000$. A, quenched into 4.6% B. solution; B, quenched into 9.5% B. solution; C, quenched into 13.2% B. solution.

FIGURE 7.—Microstructures at the center of 0.96 per cent carbon steel cylinders quenched from 875°C . into different concentrations of the 1:4 sodium silicate at 20°C . Magnification left $\times 100$ and right $\times 1,000$

Etched in 2 per cent nitric acid in alcohol. D, quenched into 16.7° B. solution; E, quenched into 23.2° B. solution; F, quenched into 33.5° B. solution.

FIGURE 8.—Microstructures at the center of 0.96 per cent carbon steel cylinders quenched from 875°C . into different concentrations of the 1:2.5 sodium silicate at 20°C . Magnification, left $\times 100$ and right $\times 1,000$
Etched in 2 per cent nitric acid in alcohol. A, Quenched into 12.4°B . solution; B, quenched into 23.8°B . solution; C, quenched into 41.8°B . solution.

concentrations of the 1:2.5 silicate in that such solutions may exhibit to a greater degree than solutions of the 1:4 silicate, the rapid cooling of which is characteristic of aqueous caustic alkali solutions. It may also be assumed that solutions of the 1:2.5 silicate made up to specific gravities of between 30° and 42° B. will give cooling curves intermediate between those of water and of oil corresponding to the intermediate rates obtained with solutions of the 1:4 silicate of specific gravities between 10° and 24° B.

2. EFFECT OF VARYING THE TEMPERATURE OF SODIUM SILICATE SOLUTIONS

The effect of temperature on the cooling characteristics of the various concentrations of the 1:4 sodium silicate was studied, chiefly in order to determine what variation in temperature of the quenching media could be allowed without producing excessive variations in the properties of the quenched steel.

FIGURE 9.—Center cooling curves of 0.96 per cent carbon steel cylinders quenched into solutions of the 1:4 sodium silicate at different temperatures

Figures 9 and 10 show the center and surface cooling curves obtained with the various concentrations of the 1:4 sodium silicate (4.6° to 23.2° B.), when heated to temperatures between 20° and 80° C. The center cooling rates and surface and center cooling times, taken from the curves are given in Figure 11. Increasing the temperature of the sodium silicate solutions from 20° to 80° C., decreased the center cooling rates and increased the surface and center cooling times in all concentrations investigated. (Fig. 9 and 10.) This change is smaller, however, between 20° and 50° C. than between 50° and 80° C. This behavior is a distinct advantage, since it indicates that some increase in temperature of the media can be

allowed without expecting large changes in the properties of the quenched steel.

The fact that this temperature increase from 20° to 50° C. had less effect on cooling rates and times than from 50° to 80° C. is more readily seen in Figure 11. If the slopes of the cooling rate curves are compared, it is obvious that for all concentrations the slope is greater between 50° and 80° C. than between 20° and 50° C. and is greater for the lower concentrations than for the higher concentrations. This means that when using solutions of low concentration the variation in the temperature of the medium must be kept to a minimum if no variation in the quenched sample is to be expected. When using higher concentrations the cooling rate is much less affected by changes in temperature, but the cooling times change considerably.

FIGURE 10.—Surface cooling curves of 0.96 per cent carbon steel cylinders quenched into solutions of the 1:4 sodium silicate at different temperatures

If the center cooling rates of the high concentrations are compared with their respective center cooling times, the cooling rate is the more important factor because slow cooling at the A_r' will cause a partial transformation of the austenite while variations in cooling rate below this point will not produce large variations in hardness.

It will be noticed that considerable importance has been attached to the center cooling rate at 720° C., but it is well realized that the final structure and hardness of a quenched specimen depends on other factors of equal importance. The cooling times from the quenching temperature down to 100° C. and the cooling rates at the A_r'' point are also of considerable importance. However, the cooling rate just preceding the A_r' point determines whether austenite will change into martensite, troostite, sorbite, or pearlite. If the center cooling rate at this point does not exceed the "critical cooling rate" of the

steel, a combination of two or more of the following structures, martensite, troostite, sorbite, or pearlite, will be formed depending on that rate. If the center critical cooling rate is exceeded, the austenite remains stable until the Ar'' transformation is reached where either all or part of it is transformed into martensite. When the latter change occurs, it will be accompanied by an increase in volume which sets up internal stresses if the change does not occur simultaneously throughout the entire specimen. Thus, when the critical cooling rate at the Ar' transformation is exceeded, the cooling rate at the Ar'' point would then determine the final structure provided the cooling below this latter point is not too slow.

Some rather peculiar results are seen on close examination of certain of the center and surface cooling curves of Figures 9 and 10. Some of the surface cooling curves cross the center cooling curves at temper-

FIGURE 11.—Center cooling rates and center and surface cooling times of 0.96 per cent carbon steel cylinders quenched into solutions of the 1:4 sodium silicate at different temperatures

atures of 500° C. or lower. It is impossible that the center of the cylinder actually could cool faster than the surface, since the cooling of the cylinder in contact with the quenching medium must take place through the surface. It must be remembered that these surface and center cooling curves were obtained by using different samples and that each cooling curve represents the average of two or three different curves, or two or three different samples. Also, the cooling at the surface of the quenched cylinder was measured by spot welded thermo-couple wires on the cylinder approximately one-quarter inch apart. This thermocouple, therefore, measures only the temperature of the area where it is spot welded to the cylinder, whereas the actual cooling of the cylinder takes place through the whole surface in contact with the quenching medium. A second and more probable explanation is that this slow cooling of the surface at

the lower temperatures may be due to the formation of silica around the thermocouple wires at the point where they were spot welded to the cylinder. This layer of silica appears to be thicker at this point of contact of the thermocouple wires than the layer left on the smooth sample after quenching.

The effect of temperature on the concentrated sodium silicate solution (33.5° B.) was not investigated. The undiluted sodium silicate showed no promise of practical application as a quenching medium. Its very high viscosity hinders circulation of the coolant and movement of the quenched piece and also leaves a rather heavy coating of silica on the quenched steel.

3. STRUCTURE AND HARDNESS OF "STEPPED" SPECIMENS QUENCHED IN SODIUM SILICATE SOLUTIONS

The effect of various concentrations of the 1:4 sodium silicate and of water and oil on the hardness of "stepped" bars is shown in Figure 12. The form and dimensions of the "stepped" bars are

FIGURE 12.—Center and surface hardness of the different sections of stepped bars quenched in the coolants indicated in Figure 13

Area between surface and center curves shows range of hardening of each section.

shown in Figure 13. They were machined from a 1.06 per cent carbon steel having the chemical composition given in Table 1.

It was expected that some of these bars, with their sharp corners and large variations in size, would crack when quenched in some of the cooling media used. Such cracking frequently occurs on rapid cooling caused by the high internal stresses set up as a result of the volume changes which accompany the structural changes during the hardening of steel.

The material from which the "stepped" bars were machined was first given a preliminary heat treatment in order to secure an even carbide distribution and proper grain refinement. The bars were normalized by heating to 850° C., holding for one hour and cooling in air. They were then annealed at 760° C. for one hour and cooled in the furnace.

FIGURE 14.—Stepped bars after quenching in different concentrations of the 1:4 sodium silicate, water, and oil at 20° C.

The "stepped" bars so prepared for quenching were placed in an electric muffle furnace at a temperature of $800^{\circ}\text{C}.$, held at this temperature for one hour, and then quenched (two bars each) into the various media. The quenching was carried out by gripping the end of the bar at *A* (fig. 13) in tongs and rapidly lowering it vertically into the desired medium. All quenching media were at a temperature of $20^{\circ}\text{C}.$ and moving at a velocity of 3 feet per second. The floor of the furnace was covered with a layer of granular carbon about $1\frac{1}{2}$ inches deep to reduce oxidation. The bars were laid on bricks in the furnace and did not touch the carbon. Figure 14 shows the bars after quenching.

It was rather surprising that none of the bars cracked immediately on quenching. However, specimens for hardness tests and microscopic examination cut from the bars that were quenched into the two fastest quenching media; that is, water and the $4.6^{\circ}\text{B}.$ solution did crack later.

The tendency of these bars to distort and crack could no doubt have been somewhat reduced if the bars had been moved rapidly up and down in a vertical position during the quenching instead of keeping the bar still while the quenching medium was flowing past the bar. The latter method was used, however, because it had been used in the previous experiments and it was desired to keep the conditions approximately the same.

FIGURE 13.—Design of the stepped bar used in quenching experiments

The rapid movement of the specimen vertically during quenching would also doubtless have reduced the thickness of the layer of silica which formed on the sample, especially when quenching in the higher concentrations of sodium silicate. These layers appear to be rather thick (see fig. 14), but were never found to be over 0.005 to 0.01 inch, and then only when quenching in solutions of the highest concentrations.

Hardness tests were made on specimens, one-fourth inch thick, cut from the middle of each section, as indicated by the dotted lines in Figure 13. Figure 12 shows the results of the hardness tests taken at the center and surface of these samples.

A surface hardness of over 65 Rockwell was obtained on the one-fourth and one-half inch diameter samples, that had been quenched in water, and in 4.6° , 9.5° , and $13.2^{\circ}\text{B}.$ sodium silicate solutions. Approximately the same surface hardness was also obtained on the 1-inch samples quenched in water and in the $4.6^{\circ}\text{B}.$ sodium silicate solution. On the other hand, a center hardness of over 65 was obtained only on the one-fourth inch diameter samples that had been quenched in water, and in 4.6° and $9.5^{\circ}\text{B}.$ sodium silicate solutions. Increase in concentration of the sodium silicate solutions or change in size to one-half or 1 inch produced a rapid decrease in hardness at the center. This rapid decrease was accompanied by changes in structure from martensite with a small amount of primary troostite,

to martensite with a large amount of troostite, then to troosto-sorbite with some lamellar pearlite, and finally to sorbite with large amounts of lamellar pearlite. Free carbides were also evident in all of these microstructures.

The one-fourth inch sections of the bars that had been quenched in water and in the 4.6° B. sodium silicate solution were the only sections that hardened completely throughout; that is, whose structure was martensite free from troostite. These samples had a center hardness of about 66.

It is evident from the hardness tests and their corresponding microstructures that samples having a martensitic structure with some primary troostite had practically the same hardness as those samples having a martensitic structure free from primary troostite. It may be concluded, therefore, that hardness tests alone can not be used as a means of determining whether the steel is completely martensitic or not. Microscopic or other tests are also necessary.

V. STABILITY OF SODIUM SILICATE QUENCHING SOLUTIONS

Sodium silicate solutions like nearly all quenching solutions have advantages and disadvantages. Among their advantages are their low cost and the fact that they do not readily corrode the steel.

The chief disadvantages of sodium silicate solutions as quenching media are the formation of a thin coating of silica on the surface of the quenched piece and the instability of some of the solutions. The thin coating of silica that forms when using high concentrations of sodium silicate can be removed slowly by dissolving it in water or by boiling in a dilute sodium hydroxide solution. In most cases it should not be necessary to remove this coating.

Some trouble was experienced with the instability of certain of the solutions of the 1:4 sodium silicate. A flocculent precipitate formed in the 9.5°, 13.2°, and 16.7° B. solutions on standing from six weeks to two months. However, solutions of these same concentrations made up with the addition of 2 per cent of sodium hydroxide of specific gravity 1.065 at 20° C. showed no evidence of instability and breaking down after three months. The addition of sodium hydroxide was without effect on the cooling rates of these solutions. Sodium silicate solutions of 4.6° and 23.2° B. remained stable for more than three months, even without additions of sodium hydroxide. The stability of solutions of the 1:2.5 sodium silicate was not investigated. Presumably these solutions are more stable than solutions of the 1:4 sodium silicate on account of the higher soda content.

A test was also made to determine the stability of solutions of the 1:4 sodium silicate at temperatures of from 20° to 60° C. This test consisted of adding 2 per cent of a solution of sodium hydroxide of the concentration given above to the sodium silicate solutions. The solution was then allowed to stand in a closed container for about three weeks. No precipitate had formed at the end of this time. A definite amount of red-hot steel was quenched in these solutions so that their temperature was raised from 20° to 60° C. This test was repeated eight times on each solution. The solutions were then allowed to stand for three more weeks. No precipitate had formed in any of them.

The cooling rates of the solutions were then tested and found to be unchanged thus showing that no breakdown had occurred. This test indicates that these solutions are fairly stable up to 60° C.

VI. SUMMARY

1. Center cooling curves were obtained and hardness tests made on cylinders of 0.96 per cent carbon steel, one-half inch in diameter and 2 inches long, when quenched from 875° C. in 20, 60, and 100 per cent glycol-water and 60 per cent glycerin-water solutions at 20° C. The results obtained are believed to justify the conclusion that these solutions can not be used successfully as quenching media for intermediate cooling between the rates obtained with water and with oil.

2. Similar cooling curves were determined for solutions of two sodium silicates having ratios of Na₂O to SiO₂ of 1:4 and 1:2.5, respectively. Concentrations ranging from 4.6° to 23.2° B. for the 1:4 silicate and 12.4° to 41.8° B. for the 1:2.5 silicate were used. Increasing the concentration and the temperature of the 1:4 sodium silicate and the concentration of the 1:2.5 sodium silicate lowered the cooling rates and increased the cooling times. The changes in cooling rates and times of the 1:4 sodium silicate were smaller at temperatures between 20° and 50° C. than between 50° and 80° C.

3. Sodium silicate solutions can be used successfully to obtain intermediate cooling rates between those obtained with water and with oil at 20° C. Three concentrations of the 1:4 sodium silicate and two of the 1:2.5 sodium silicate were found which gave intermediate cooling. These were the 9.5°, 13.2°, and 16.7° B. solutions of the 1:4 sodium silicate and the 12.4° and 28.8° B. solutions of the 1:2.5 sodium silicate. However, there is very little difference in cooling between the latter two solutions.

4. No correlation was found between the results obtained with the various concentrations of the 1:4 and the 1:2.5 sodium silicates.

5. The stability of solutions of the 1:4 sodium silicate was considerably increased by the addition of 2 per cent of a solution of sodium hydroxide (specific gravity of 1.065 at 20° C.) without changing the cooling speeds of the silicate solutions.

6. Quenching experiments on "stepped" bars of a 1.06 per cent carbon steel were made to determine the relation between the hardness and microstructures produced by the various concentrations of the 1:4 sodium silicate, water and oil at 20° C.

7. It is possible that the aqueous solutions of other sodium silicates having different soda-to-silica ratios may be more stable and give better results than the ones used in the present investigation.

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