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HYDROGEN IN STEELMAKING

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INTRODUCTION

FOR many years steel producers have been concerned with the problem of hydrogen in steel. The presence of hydrogen in excess of its solubility at the melting point may cause bleeding and unsoundness in ingots and castings. In fully-killed steels the hydrogen content which causes such unsoundness depends on the alloy content, and may range from 6 to 12 parts per million.* It is also recognized that even smaller contents of hydrogen, down to 1 or 2 parts per million, may play a part in causing other defects such as flakes and hair-line cracks, and generally lowered ductility. Table 1 and Fig. 1 show typical data on these effects of hydrogen in steel.^{1,2} Small amounts of hydrogen pose a problem of special importance in such products as large forgings where maximum properties are desired.

It is possible to remove hydrogen from solid steel by suitable heat treatment because of its relatively high rate of diffusion in steel. However, the effectiveness of heat treatment dimin-

* Parts per million = PPM; 1PPM = 0.0001 wt. per cent = 1.11 cc. per 100 grams = 0.0873 Relative Volumes (volume of hydrogen per volume of metal).

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ishes rapidly as the cross-section of the steel part treated increases. The time required to reduce the hydrogen content to an acceptable level increases approximately as the square of the diameter of the section. If heating for 4 days is required for a section 10 inches in diameter, heating for about 16 days will be required for a 20-inch diameter section. Thus, large forgings may require excessively protracted heating periods. For this reason the importance of keeping the hydrogen content of the steel as low as possible while it is still liquid becomes evident.

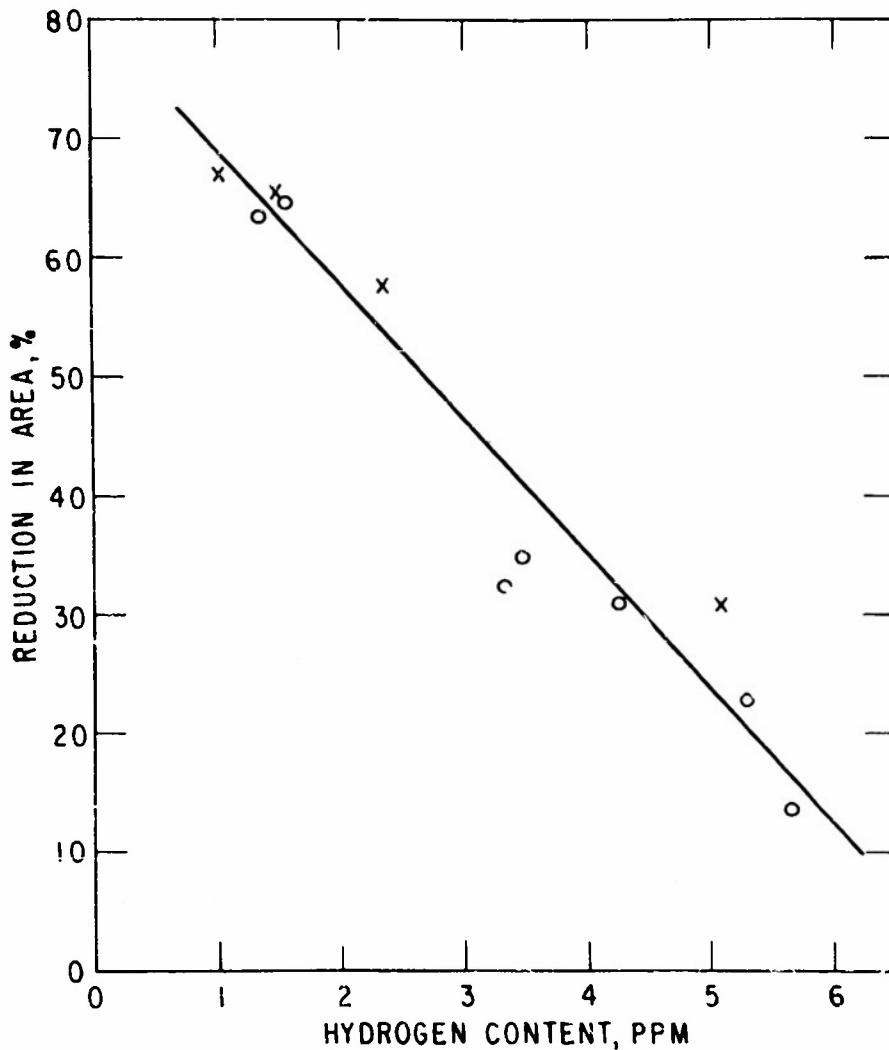


Fig. 1 — Effect of hydrogen content on ductility of killed AISI 1010 steel.
(From S. Marshall, et al²)

TABLE 1

Approximate Hydrogen Content in Liquid Steel Expected to Produce Porosity and Wildness in Fully Killed Basic Electric Steel
(from Barraclough¹)

Type of Steel	Hydrogen Content, parts per million		
	Sound Ingots	Porous Ingots	Wild Ingots
Carbon Steel	up to 6.0	6.0 — 7.5	over 7.5
Low-Alloy Steel	up to 6.5	6.5 — 8.0	over 8.0
Chromium Stainless	up to 9.0	9.0 — 11.0	over 11.0
Austenitic Stainless	up to 11.0	11.0 — 12.5	over 12.5

The purpose of this paper is to discuss what is known about the effects of steelmaking operations on the hydrogen content of the liquid steel. The discussion emphasizes the following points:

The main source of hydrogen input is from moisture — in the furnace atmosphere, in the slag, in slagmaking and bath additions, and in ladle and runner refractories. In normal practice the only way by which hydrogen can be removed from the bath is through the flushing action provided by the evolution of CO gas during the "boil." A balance is set up between the hydrogen input from the above sources and its removal by the flushing action of the boil. Thus, to keep the hydrogen content of the bath at a low level, a vigorous boil must be maintained. If the flushing action diminishes or is stopped, as when a heat is blocked in the furnace, the hydrogen content of the bath will increase as hydrogen continues to be supplied from the slag and furnace atmosphere. Hydrogen pick-up under reducing conditions will be slower in the electric furnace since the concentration of water vapor in the furnace atmosphere is much smaller than in fuel-fired furnaces.

SOLUBILITY OF HYDROGEN AND OF WATER VAPOR IN IRON

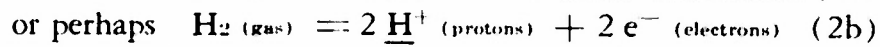
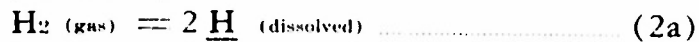
Several laboratory groups have studied the solubility of hydrogen and water vapor in iron.

Solubility of Hydrogen

Gaseous hydrogen dissolves in iron according to the relationship

$$\text{PPM} = k (\text{pH}_2)^{1/2} \quad (1)$$
 where PPM = parts per million of dissolved hydrogen,
 pH_2 = the partial pressure of gaseous hydrogen,
 k = an empirical constant dependent on the temperature and alloy content of the metal.

This equation, known as Sievert's Law, indicates by the square-root relationship that hydrogen dissociates in order to enter iron — i.e., dissolved hydrogen is present in iron in the form of atoms, or perhaps as protons.



The solubility increases with temperature³ and is plotted for

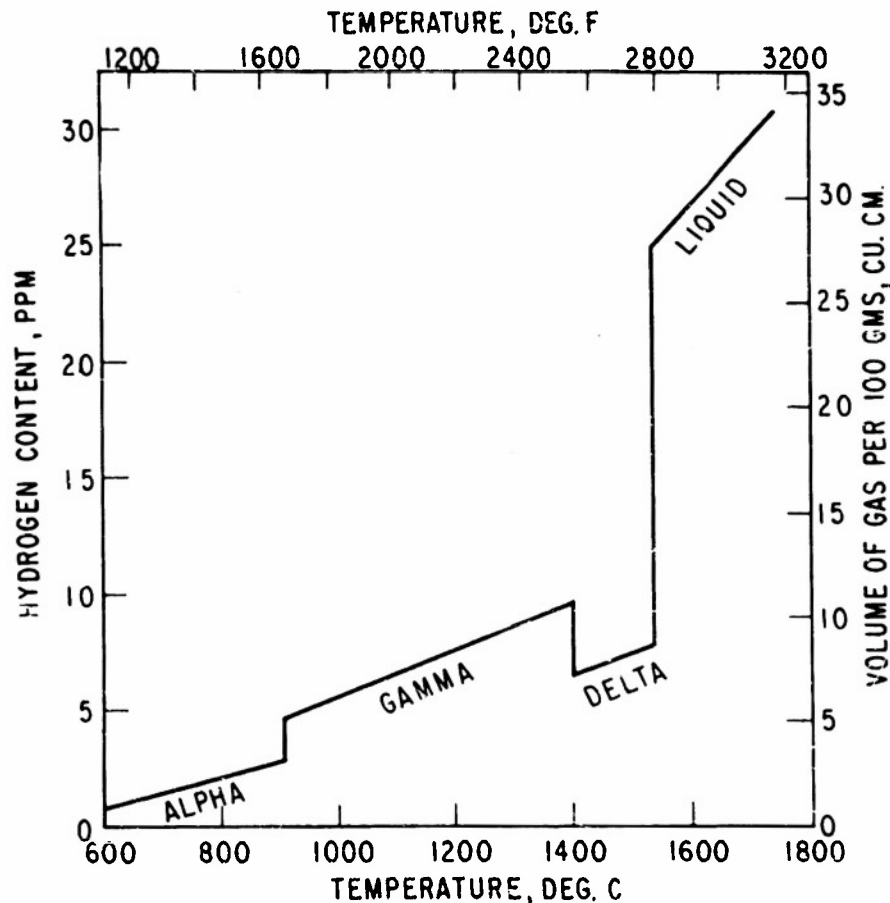


Fig. 2-- Effect of temperature on the solubility of hydrogen in iron at one atmospheric pressure. (From "Basic Open Hearth Steelmaking," AIME, p. 624, 1951)

pure iron in Fig. 2. This curve shows the large decrease in solubility upon solidification of liquid iron, and that hydrogen is more soluble in the face-centered cubic (gamma) structure than in the body-centered cubic (alpha and delta) structure. It may be mentioned that the diffusion rate of dissolved hydrogen is greater in the body-centered structure than in the face-centered structure.⁴ For this reason, heat treatments to diminish the hydrogen content are best carried out just below the critical temperature. Gaseous hydrogen, as such, can scarcely be a cause of difficulty in steelmaking operations, since hydrogen is never

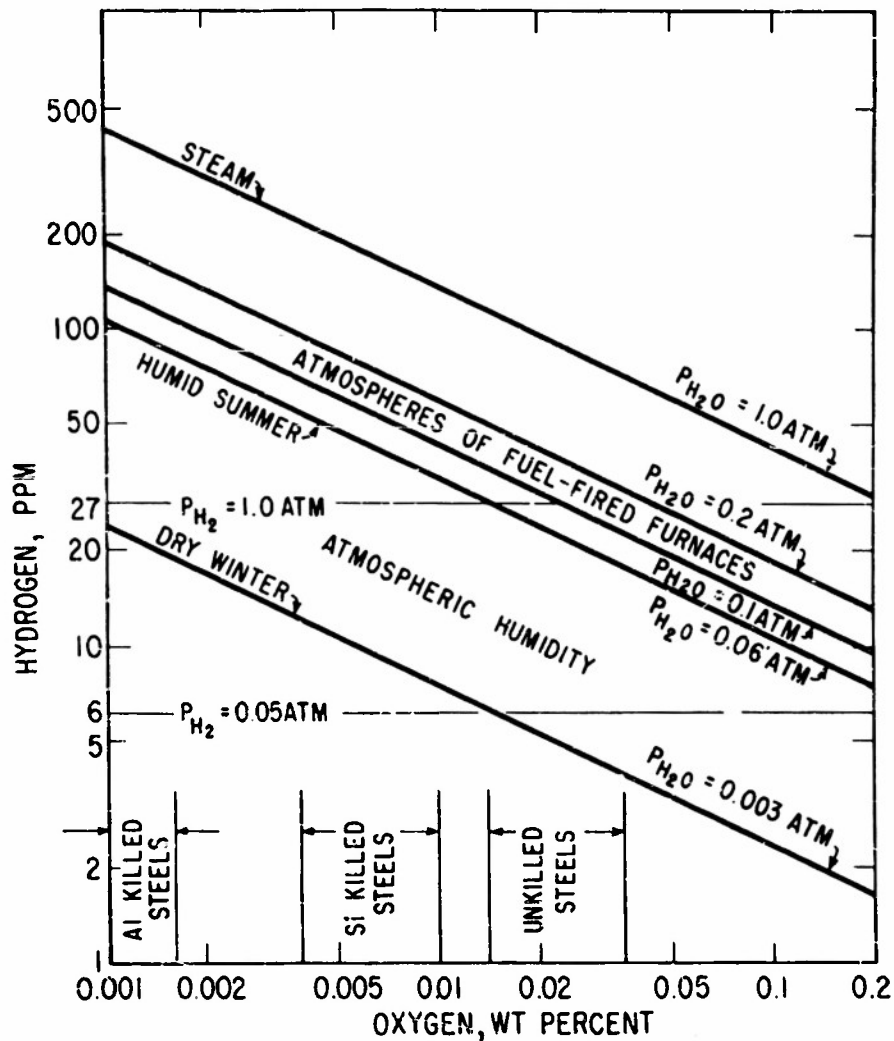


Fig. 3—Equilibrium hydrogen and oxygen contents of liquid iron under various water vapor pressures. (From Carney, Chipman and Grant⁵)

present in significant amounts. The most important source of hydrogen is undoubtedly from water and water vapor. Water is present in the combustion products of fuel-fired furnaces and in lesser amounts in slagmaking additions and refractories, and in air.

Solubility of Water Vapor

Iron can reduce water to hydrogen according to the following reaction.

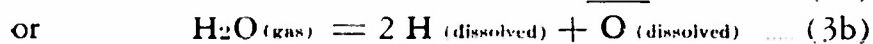
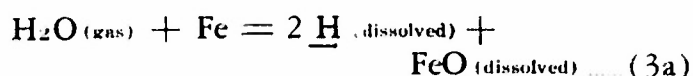


Fig. 3 is a plot of the equilibrium hydrogen and oxygen contents of liquid iron under atmospheres containing varying amounts of water vapor.⁵ At low oxygen concentrations steels may pick up more hydrogen from a humid atmosphere than from pure dry hydrogen. For example, liquid iron will pick up 6 parts per million of dissolved hydrogen under a hydrogen pressure of 0.05 atm.; but a water pressure of only 0.003 atm. is sufficient to put in more than 6 parts per million of hydrogen, provided the oxygen concentration is less than 0.015 weight per cent, as it is in killed steels.

Since the hydrogen content of steel is measured in parts per million, the amount of water necessary to supply this hydrogen is very small. Even the amount of water contained in 100 cubic feet of air on a dry winter day is sufficient to raise the hydrogen content of one ton of steel by 1 part per million.

SAMPLING OF LIQUID STEEL FOR HYDROGEN

To obtain reliable figures for the hydrogen content of liquid steel, special sampling techniques are essential. The great mobility of hydrogen in liquid steel and in solid steel, even at room temperature, makes it difficult to retain in the solid sample all the hydrogen present in the liquid. The greatest danger of loss during the sampling occurs in the transition from liquid to solid because of the sharp drop in solubility. Two general types of approach to the problem of retaining the hydrogen have been employed: (1) the sample is taken in a device which allows for collection of escaping hydrogen, (2) the

sample is drastically quenched to prevent the escape of any hydrogen.

Two devices utilized by a German and a British group respectively are shown in Fig. 4. The German device used most recently by Piper et al⁶ is of the first type. The sample is sucked

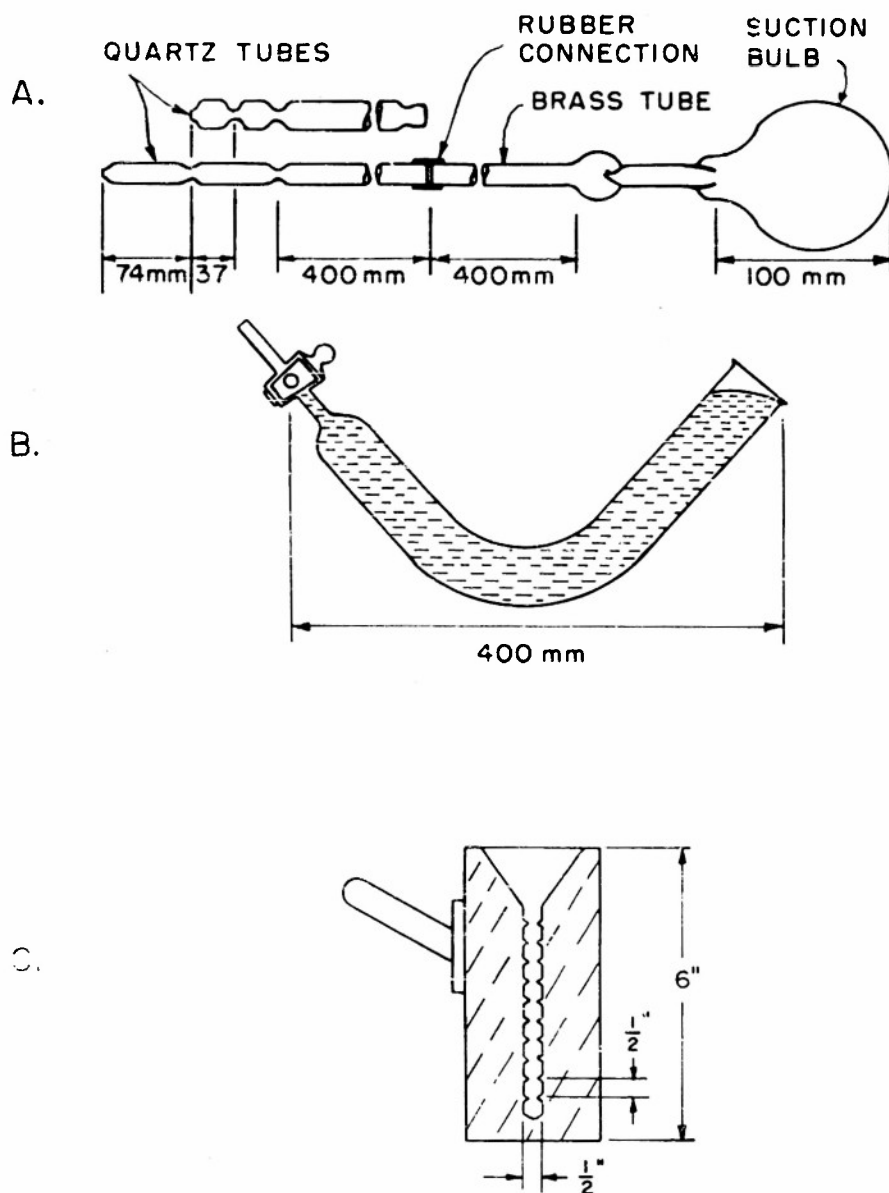


Fig. 4.—Devices for sampling liquid steel for hydrogen. German sampler showing (A) quartz suction tube, and (B) mercury filled storage vessel. (Piper, et al⁶) (C) British notched pencil mold constructed of copper. (Barraclough¹)

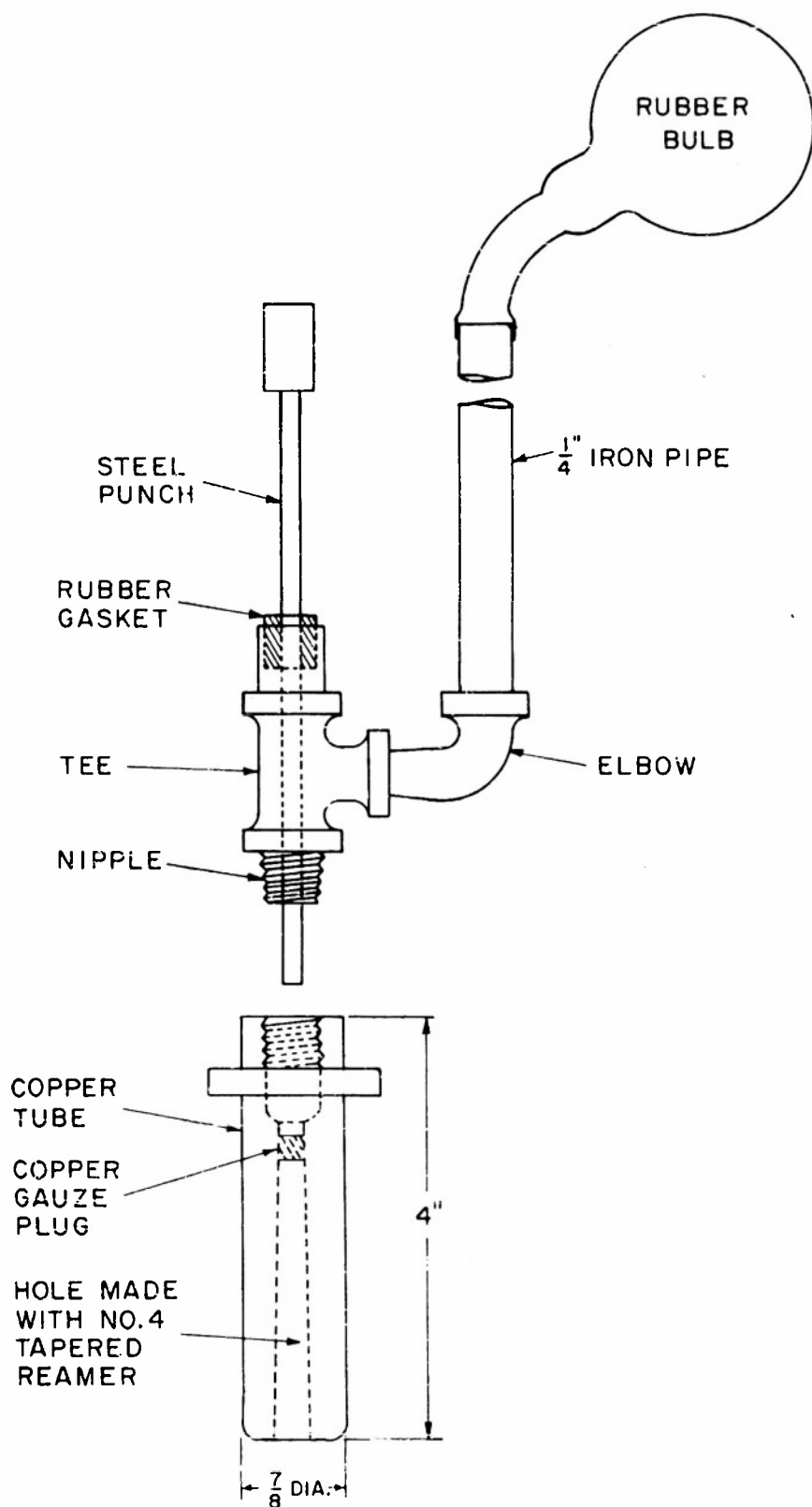


Fig. 5 -- Device for sampling liquid steel for hydrogen developed at Massachusetts Institute of Technology.

up into a quartz tube and is rapidly immersed under a mercury-sealed container. Both the sample and the evolved gas are analyzed. The British device is of the second type and consists of a notched-pencil mold constructed of copper.⁷ The steel is poured into the mold where it rapidly solidifies and the sample is then broken out of the mold and quenched in water.

The sampler used by the authors is also of the second type. It is similar to that described by Carney⁸ and in its latest modification is illustrated in Fig. 5. The sample is drawn up into a tapered copper cylinder by suction applied from a rubber bulb. A punching mechanism is provided so that the solidified sample can be immediately ejected into a quenching bath of ice-water from which it is then transferred to a liquid nitrogen bath for storage. This sampler combines the suction feature of the German device with the rapid solidification obtained in the copper mold. Less than five seconds are required to draw the sample and punch it out into the quenching bath. After about ten seconds agitation in the ice-water quench the samples are placed in liquid nitrogen which is at a temperature low enough to prevent any diffusion losses. The overall operation of this device has been tested by sampling steel melted in the laboratory under controlled hydrogen pressures. The hydrogen content of the bath is thus fixed in accordance with equation (1) and analysis of the samples has shown that little hydrogen is lost on sampling a killed bath.

All three devices require killed steel to prevent losses due to boiling. When sampling industrial heats, the usual procedure is to take the sample from a slagged spoon to which 0.1 to 0.2 per cent aluminum has been added.

Analysis of samples of these types for hydrogen content has been performed by various methods. These include collecting the gas by hot extraction,^{1, 9} vacuum fusion,¹⁰ and vacuum tin fusion.¹¹ The particular merits of the various systems are discussed in the references given. It has been the authors' experience that uncertainties due to sampling are generally greater than errors in analysis.

Change of Hydrogen Content during the Course of the Heat

Several investigations of the change of hydrogen content during the course of commercial heats have been in good

agreement as to the direction and magnitude of the changes effected by various normal furnace operations. Figs. 6, 7, and 8 present selected data from the literature and from our own work which are considered typical for open hearth and electric practice. Study of these heat logs indicates that there are several factors which have a major effect on the final bath hydrogen content.

Effect of Boil

It will be observed that, in all practices, the hydrogen content of the bath reaches its lowest value at some stage of the carbon boil. During the boil the hydrogen content is considered to be a balance between the flushing action of CO evolution and the rate of supply of hydrogen to the bath. Hydrogen is available to the bath from the furnace atmosphere, the slag and refractories, and from slag and bath additions. Apparently the low level in hydrogen content is not materially affected by the hydrogen content prior to the onset of the boil, provided a vigorous boil is obtained. Thus, rusty scrap, limestone, and ore of high moisture content, charged early in the heat, will not necessarily result in a high hydrogen content. In several instances it has been found that the hydrogen content of the bath increases somewhat in the later stages as the boil slackens off even though no additions have been made. It would seem, therefore, that hydrogen is continually supplied to the bath from the furnace atmosphere and slag. Hence a relationship should exist between the strength of the boil and the lowest hydrogen value obtainable. The flushing action of the boil is the only mechanism by which the bath can be brought down to and maintained at a low level in usual practice. Consequently, the importance of maintaining a vigorous boil cannot be over-estimated. A theoretical calculation of the flushing action of the boil is presented in a later section.

Effect of Additions

Slag-shaping additions such as lime or ore may contribute somewhat to the hydrogen of the bath if added in the later stages of the boil. Even with reasonable precautions, these additions contain considerable water. The effect is probably negligible except in the case of lump materials which sink to the slag-metal

interface. Lighter materials reacting at the slag surface tend to give up the bulk of their associated water to the furnace atmosphere.

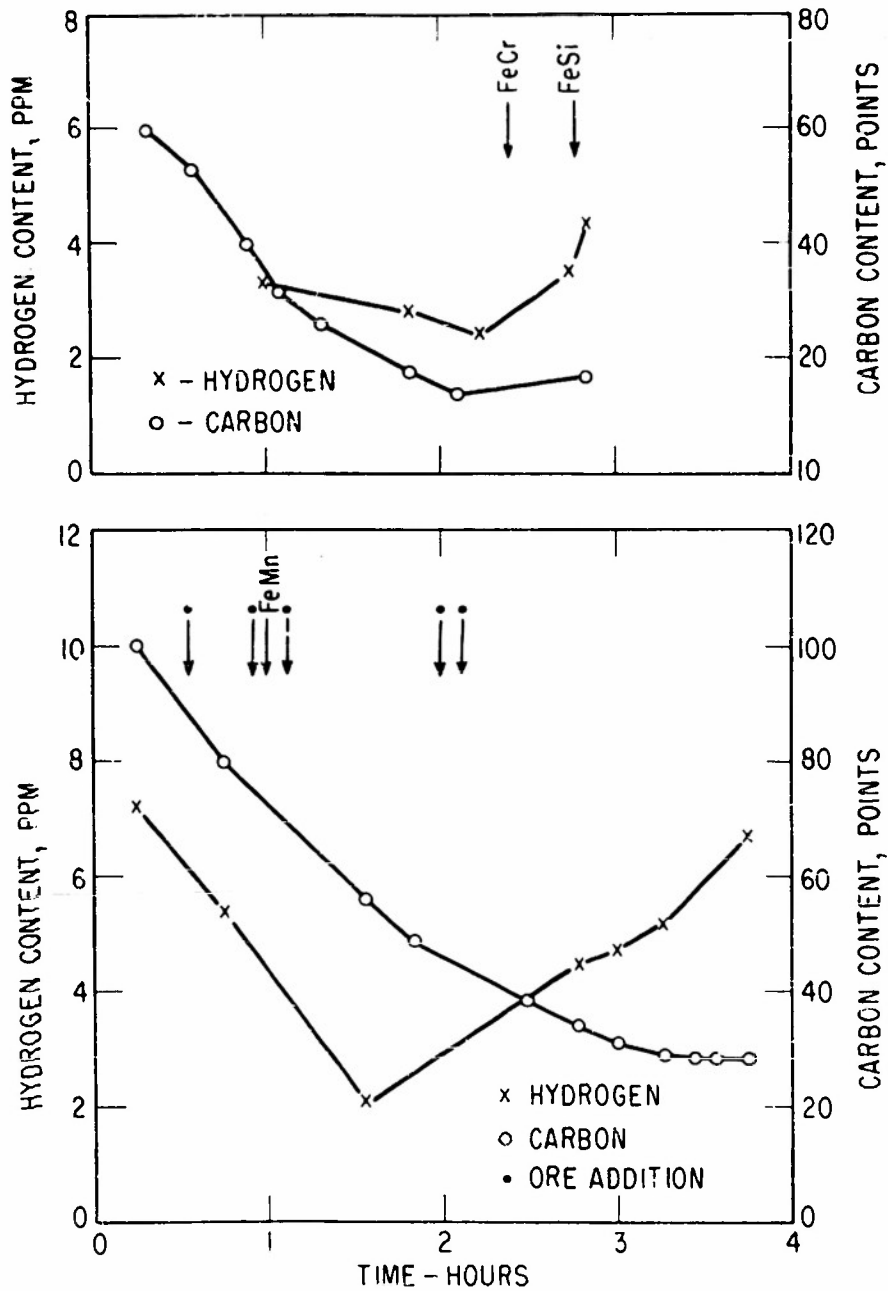


Fig. 6 — Typical hydrogen and carbon heat logs for acid open hearth steels. (Top log from authors' work; bottom log from Wentrup, et al¹²)

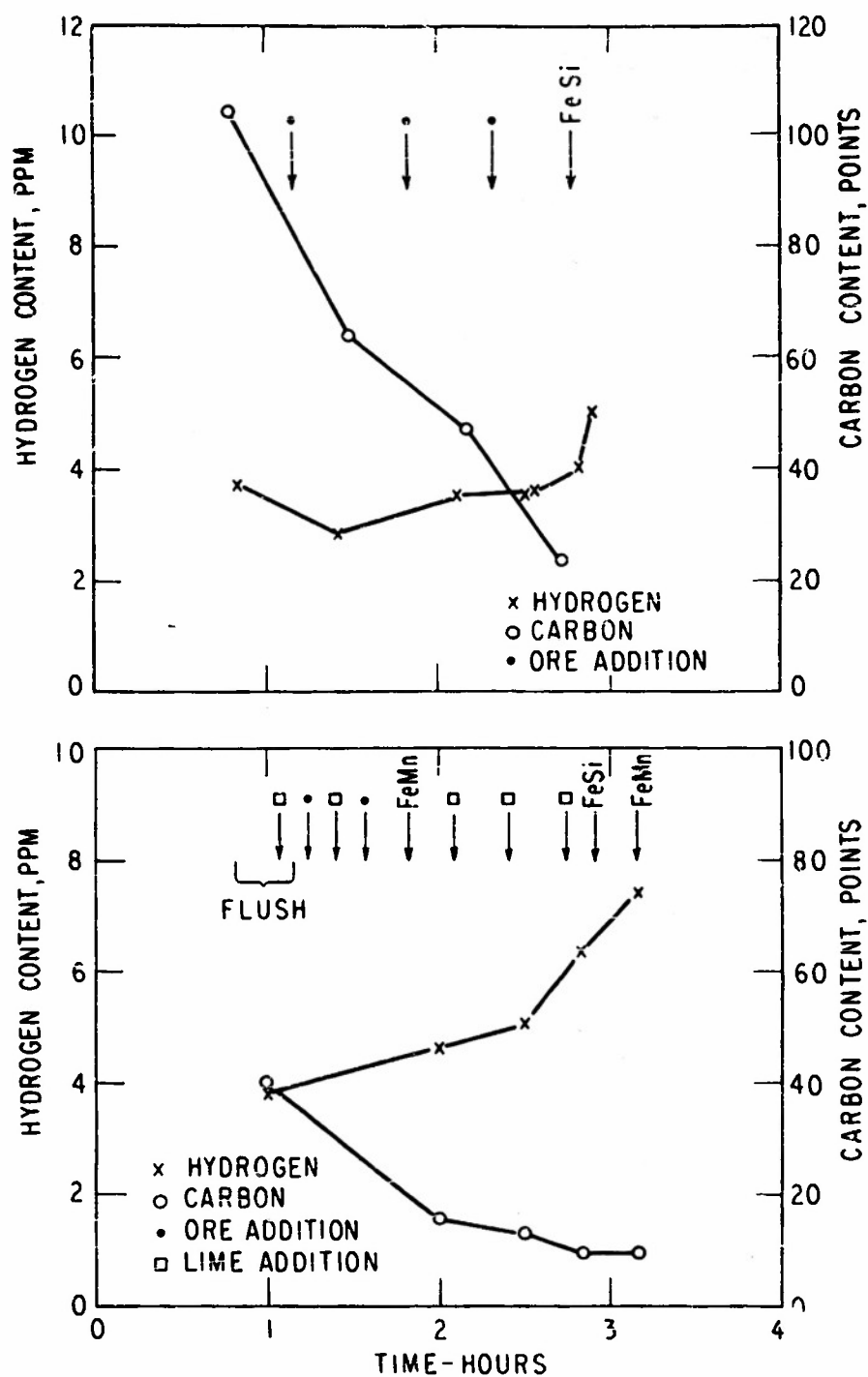


Fig. 7 — Typical hydrogen and carbon heat logs for basic open hearth steels.
(Top log from authors' work; bottom log from Piper, et al⁶)

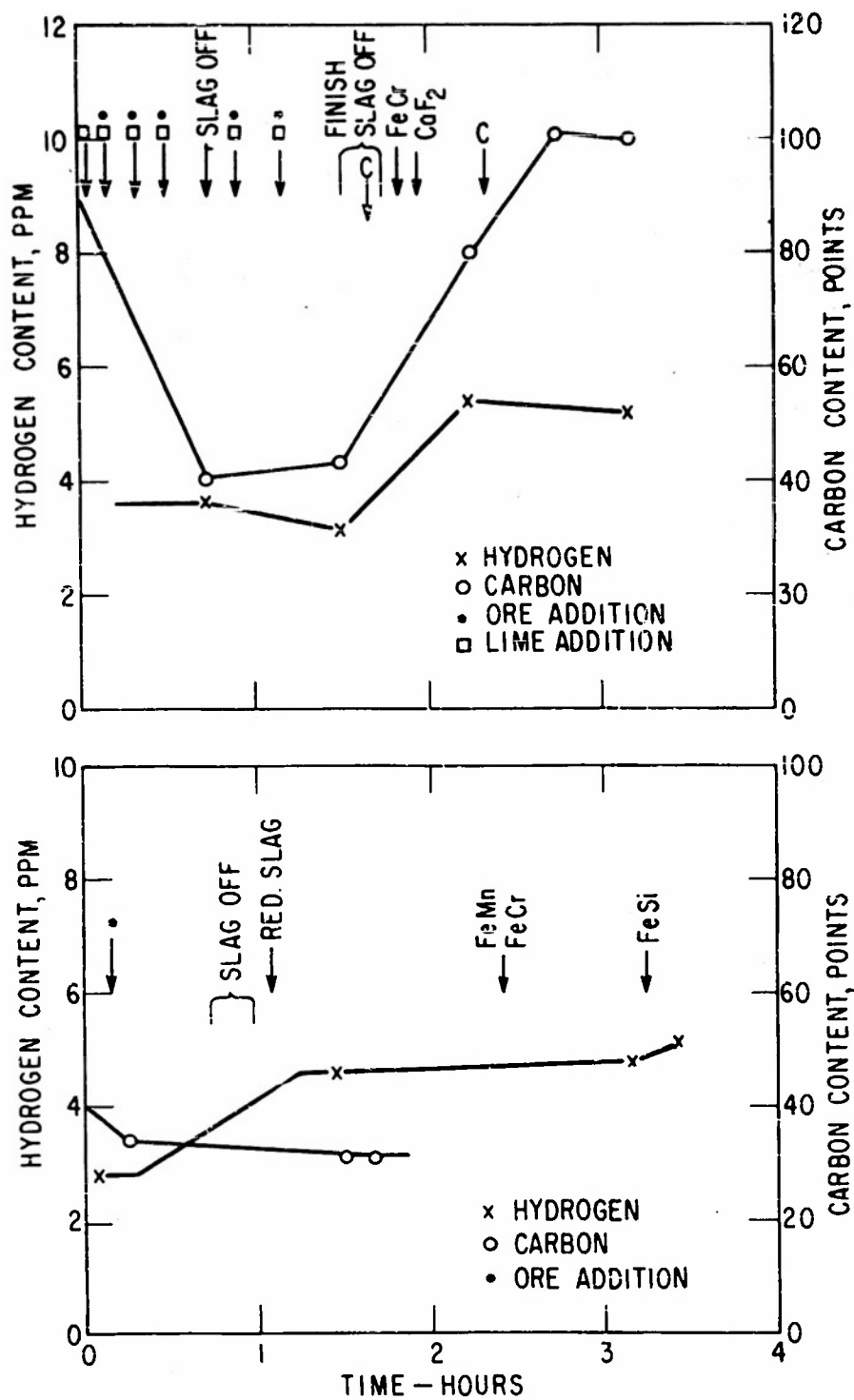


Fig. 8 — Typical hydrogen and carbon heat logs for basic electric furnace steels. (Top log from Piper, et al;⁶ bottom log from authors' work)

Deoxidizing additions such as manganese and silicon, added to control the carbon content by slowing the boil, may cause a measurable increase in hydrogen content. Hydrogen associated with the ferroalloy additions either as dissolved hydrogen or absorbed water will tend to dissolve in the bath. Furthermore, the deoxidizing nature of these additions may raise the hydrogen content by impairing the rate of CO flushing. Analyses performed on several ferroalloys by Piper et al⁶ show fairly high hydrogen contents as indicated in Table 2. However, unless the maximum values are greatly raised by poor handling and storage under wet conditions, the small weight of the usual addition indicates that the slowing of the boil is the paramount cause of the hydrogen increase noted.

TABLE 2
Hydrogen Content of Ferroalloys and
Nonferrous Metals
(from Piper, et al⁶)

		Average Content of Alloy per cent	Hydrogen Content, ppm	
			Average	Range
FeSi	Si	76.3	13.7	10.2 — 16.0
FeSi	Si	91.8	9.3	9.0 — 9.6
FeCr	Cr	69.2	6.1	2.8 — 10.6
FeMn	Mn	82.7	24.5	13.4 — 34.0
FeW	W	84.7	3.4	2.6 — 5.0
FeMo	Mo	61.4	2.9	2.0 — 4.1
FeV	V	74.6	26.8	18.0 — 34.2
FeTi	Ti	37.5	33.6	—
FeCb	Cb	63.3	31.2	—
Pure Ni	Ni	98.0	6.9	3.0 — 13.9
Pure Co	Co	99.6	6.8	6.1 — 7.9
Al Sheet	Al	99.5	1.5	—
Al Pig	Al	93 — 95	5.3	—

Effect of Block

Blocking the heat in the furnace brings the flushing action of the boil to a halt. Under these conditions the hydrogen content of acid and basic open hearth steel rises rapidly. Drying out the blocking material by pre-heating is a procedure many operators use. This is no doubt helpful but, even with such precautions, rises from 0.5 to 1.0 PPM have been observed

during the period from block to tap. It would be expected that under an extended block the hydrogen content would continue to rise as hydrogen is supplied to the dead bath from the slag and furnace atmosphere. When a furnace block is necessary, the best procedure is to tap the heat as quickly as possible; ladle blocking offers an alternative procedure provided, of course, the ladle is dry.

In electric furnace two-slag practice, where the second stage of the heat is carried out under a reducing slag with no CO evolution, a jump of from 1 to 2 PPM is usually found on replacing the oxidizing slag by the reducing slag. The jump is largely due to the reduction of water contained in the slagmaking materials and may be kept to a minimum by preheating the additions. If further additions are well dried, the hydrogen content does not rise appreciably during the reducing period. This might be expected since the electric furnace atmosphere is relatively dry.

Effect of Tapping and Teeming

The problem of following the hydrogen content on tapping the furnace is complicated by additions made in the ladle and by the ladle refractory itself. Hydrogen associated with wet runner refractories and additions, such as anthracite coal, may raise the hydrogen content considerably. Increases of as much as 2PPM have been reported from these causes.^{1,13} Newly lined ladles, even though preheated in a careful fashion, are also dangerous and may still retain appreciable moisture after two or three heats. For example, one test showed that a newly lined ladle caused a hydrogen increase in the metal of 1.0 PPM on the first use, and a rise of 0.3 PPM on the third use. Repairs to ladles using wet materials should be followed by careful drying.

There is some disagreement in the literature as to whether hydrogen is gained or lost on tapping when the runner has been well dried and the ladle used for several heats. Barraclough¹ reports that a hydrogen loss of 0.3 to 0.7 PPM is noticed repeatedly and accounts for this by the exposure of the liquid metal to the atmosphere in the pouring stream. It should be pointed out that it is unlikely that hydrogen can be lost by oxidation, since Fig. 2 shows that even so-called dry atmospheres are hydrogenating to the metal. However, it is possible

that some hydrogen can be lost by diffusion; in addition, semi-killed steels may lose hydrogen from continuing CO evolution. The authors have found, as have others, that killed steels show a characteristic rise of the order of 0.5 PPM.

Similar conditions hold for teeming of the ingots or castings. Table 3 indicates the effect of the mold condition. Five castings were teemed from the same ladle; castings 1 and 3 were teemed into clean steel molds, casting 2 was teemed into a heavily tarred steel mold, casting 4 was teemed into a dry sand mold, and casting 5 into a green sand mold. The heavily tarred mold caused a large increase in hydrogen content whereas the dry sand mold showed about the same hydrogen content as the clean steel mold. The green sand mold casting contained only slightly more hydrogen than the castings in the clean steel molds.

TABLE 3
Effect of Mold Condition on Hydrogen Content
of Killed Steel

Casting No.	Description	Hydrogen Content ppm
1	Clean steel mold 6" diam., 10" depth	4.0
2	Heavily tarred steel mold 6" diam., 15" depth	8.6
3	Clean steel mold 6" diam., 10" depth	4.1
4	Dry sand mold 10" x 15" x 12"	4.1
5	Green sand mold 10" x 15" x 12"	4.6

Note: All molds poured from same ladle.

Role of the Slag

Table 4 is a compilation of the average values, obtained by several investigators,^{1, 7, 8, 12} of the hydrogen content at tap characteristic of different practices. These results are in agreement in showing that acid open hearth steels generally have the lowest hydrogen content at tap. Basic steels have higher hydrogen contents with the basic open hearth steels generally slightly higher than similar grades made in the electric furnace. The differences in the absolute values within a given practice

TABLE 4
Average Values of Hydrogen Content at Tap
for Acid and Basic Open Hearth and Basic
Electric Steels

<u>Acid</u>	<u>Basic Electric</u>	<u>Basic</u>	<u>Author</u>
3.7 (40) *	4.1 (40)	—	Barracclough ¹
5.9 (10)	8.1 (8)	8.5 (19)	Wentrup et al ¹²
3.8 (11)	5.6 (14)	—	Sykes et al ⁷
3.1 (3)	2.8/5.0 (2)	4.6 (1)	Carney, Chipman and Grant ⁸
3.8 (3)	4.4 (6)	5.6 (3)	Authors

* Number of heats in brackets.

are probably due to variations in the operating procedures already discussed; however, all investigators agree as to the relative position of the three practices. Since the atmospheres of the basic and acid open hearth furnaces have almost the same water vapor content, and as other variables affecting the hydrogen content are essentially the same, the difference in the final value is most likely due to the difference in the nature of the slag. The special characteristics of the electric furnace will be discussed later.

While the presence of hydrogen in steelmaking slags has only recently attracted interest, it has been known for some time that hydrogen is present in such slag-like materials as glasses¹⁴ and geologic magmas.¹⁵ The form in which hydrogen is dissolved in slag is not as yet known, but it may be present as hydroxyl ion. Wentrup¹² first reported slag analyses for hydrogen content in terms of both water and hydrogen using a vacuum extraction technique. Piper⁶ later used a modification of this method in which the extracted gases were passed over ferromanganese to reduce any water vapor to hydrogen, and then the analyses were reported as total hydrogen. The authors used high temperature vacuum extraction under reducing conditions and likewise reported the analyses in terms of total hydrogen. Typical analyses of acid and basic open hearth slags and of oxidizing period basic electric slags are given in Table 5. It was found that hydrogen could be quite rapidly extracted in laboratory analysis, which suggests that hydrogen in the slag is readily available to the bath in practice.

TABLE 5
Hydrogen Content of Slags

<u>Type of Slag</u>	Range of Total Hydrogen ppm	
	<u>Authors</u>	<u>Wentrup¹²</u>
Basic Open Hearth	50 — 75	36 — 184
Acid Open Hearth	10 — 35	27 — 89
Basic Electric (oxidizing period)	40 — 70	

The results indicate that the concentration of hydrogen in the slag is large as compared to the concentration in the steel so that the total quantity of hydrogen in the slag may exceed that in the bath, with the usual proportions of slag and metal. Basic slags show a higher concentration of hydrogen than acid slags, and this may well account for the difference in the hydrogen content between acid and basic open hearth steels.

On the other hand, the concentration of hydrogen in the liquid slag in the furnace is small compared to what is usually found in the slagmaking constituents as charged (such as limestone). Thus it would be expected, as Wentrup¹² reports, that the hydrogen content of the slag would fall during the early part of the heat as some of the water from the relatively moist lime and ore additions is driven off.

Preliminary studies of the equilibrium between slag and different water vapor atmospheres show that, as expected, the hydrogen content increases with the partial pressure of the water vapor. For the same slag at 1550 C a hydrogen content of from 90-110 PPM was obtained under a steam atmosphere while in air values from 10-20 PPM were obtained. The drier atmosphere of the electric furnace and the special character of the second slag may therefore account for the fact that basic electric steels show slightly lower hydrogen contents than basic open hearth steels. Normal two-slag practice, however, prevents the attainment of very low hydrogen contents at tap because of the jump which occurs when the reducing slag is made up.

FLUSHING CALCULATION

The text has emphasized the importance of CO evolution in reaching and maintaining a low hydrogen value in the steel.

Since it is known that CO bubbles are nucleated on the hearth of the furnace and rise through the metal, this flushing action is likely to be highly efficient. The following calculation is presented assuming that equilibrium between the escaping gas bubbles and the hydrogen content of the bath is reached, i.e., theoretical efficiency.

Consider any bubble of gas which is evolved at the surface of the bath; the bubble contains CO and hydrogen, the volume dv of each being proportional to the partial pressure.

$$\frac{dv_{H_2}}{dv_{CO}} = \frac{p_{H_2}}{p_{CO}} = \frac{p_{H_2}}{P - p_{H_2}}$$

where p_{CO} = partial pressure of CO gas in the bubble

p_{H_2} = partial pressure of hydrogen in the bubble

P = total pressure = $p_{CO} + p_{H_2}$

Taking $P = 1$ atm. and noting that p_{H_2} is very much smaller than P

$$1/p_{H_2} \times dv_{H_2} = dv_{CO} \quad (4)$$

Each bubble of gas evolved containing dv_{CO} and dv_{H_2} depletes the bath of dC points of carbon and $dPPM$ parts per million of hydrogen. Hence, with a bath weight W ,

$$dv_{CO} = -dC \times W \times 359 / (12 \times 10^4)$$

and $dv_{H_2} = -dPPM \times W \times 359 / (2 \times 10^6)$

substituting in equation (4),

$$1/p_{H_2} \cdot dPPM = 1.66 dC$$

then, obtaining the solubility relationship from equation (1) and substituting for p_{H_2}

$$1/PPM^2 \cdot dPPM = 1.66/k^2 \cdot dC$$

Expressing carbon drop as a function of time,

$$1/PPM^2 \cdot dPPM = 1.66/k^2 \cdot (dC/dt) \cdot dt$$

Referring to Fig. 2, k has a value of 27 at 1600 C in pure liquid iron

$$1/PPM^2 \cdot dPPM = 2.3 \times 10^{-3} (dC/dt) \cdot dt \quad (5)$$

Integration of this equation between limits, for constant values of dC/dt results in the relation between hydrogen content and time plotted in Fig. 9.

Fig. 9 indicates that the rate of hydrogen elimination under a strong boil (greater than 20 points per hour) is considerable even when the hydrogen content of the bath is relatively low. For example, if the hydrogen content of the bath is 3 PPM under a boil rate of 50 points per hour, the theoretical rate of hydrogen removal is equal to about 0.1 PPM per minute. If this boil rate is maintained and the hydrogen content is not found to drop, then hydrogen must be entering the bath at a similar rate. In open hearth practice, hydrogen contents during the boil of lower than 3 PPM are difficult to achieve, indicating that the rate of hydrogen input to the bath is substantial.

Equation 5 may also be used to indicate the effect of flushing

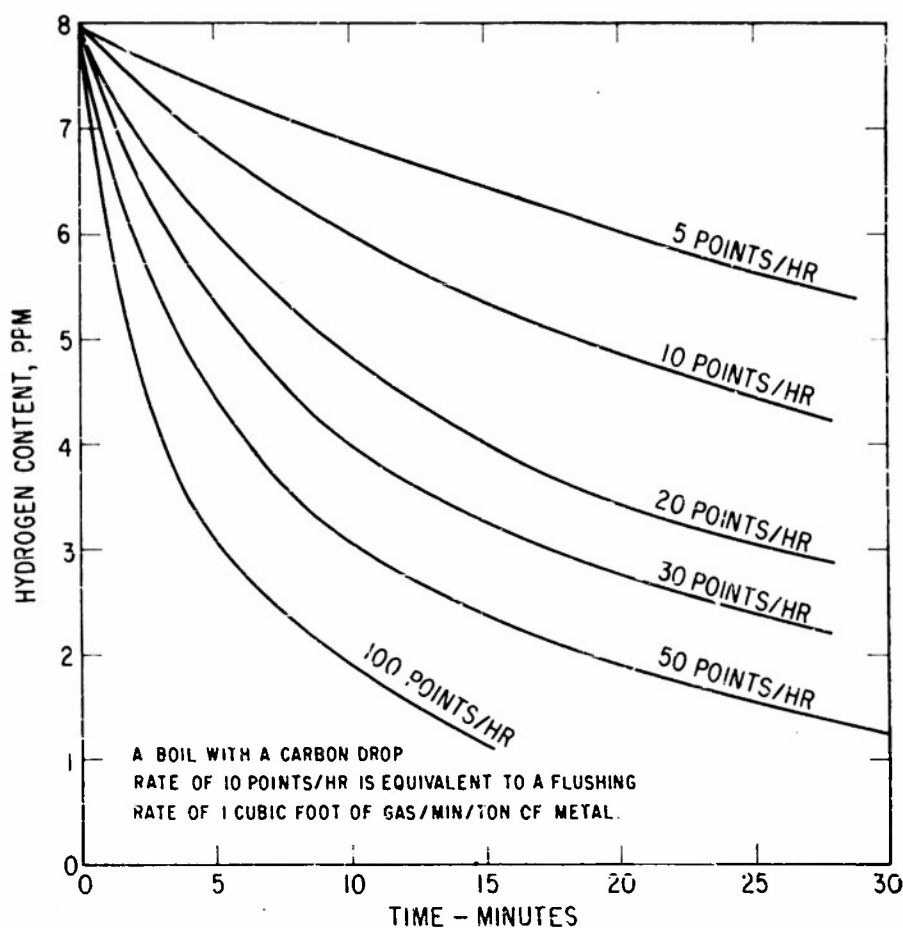


Fig. 9 — Theoretical flushing curves showing effect of carbon boil rate on the hydrogen content of liquid iron.

with any inert gas by converting dC/dt to gas volumes. It is apparent that large flow rates must be used, if effective flushing is to be accomplished in a reasonable time.

CONCLUSIONS

The following measures for limiting the hydrogen content have been suggested by this discussion and are listed in the order of their apparent importance.

(1) A vigorous boil should be maintained in order to flush the hydrogen content of the bath to a low value.

(2) After blocking, acid and basic open hearth heats should be tapped as soon as possible.

(3) Good ladle, runner, and mold practice are necessary to prevent excessive hydrogen pickup on tapping and teeming killed steels.

(4) Additions made after the completion of the boil should not have been stored under wet conditions.

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