CANADA

DEPARTMENT OF MINES AND TECHNICAL SURVEYS

OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 62-89

THE SAMPLING AND DETERMINATION OF HYDROGEN IN LIQUID PIG IRON FOR QUEBEC IRON AND TITANIUM CORPORATION

by

G. SMELSKY & N. S. SPENCE

PHYSICAL METALLURGY DIVISION

OCTOBER 17, 1962

Mines Branch Investigation Report IR 62-89

THE SAMPLING AND DETERMINATION OF
HYDROGEN IN LIQUID PIG IRON
FOR QUEBEC IRON AND TITANIUM CORPORATION

by

G. Smelsky[*] and N. S. Spence[**]

— — — — —

SUMMARY OF RESULTS

Hydrogen analyses obtained on samples taken during two visits to Quebec Iron and Titanium Corporation are reported, together with the results of analyses of the iron produced here in the intervening and later periods.

The sampling techniques and analytical methods used in the investigation are described.

---

[*]Technician and [**]Section Head, Nuclear Metallurgy Section, Physical Metallurgy Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

INTRODUCTION

The work described in this report was carried out in connection with a study of pig iron (Sorelmetal) quality at Quebec Iron and Titanium Corporation, Sorel, Quebec, the object being to establish the hydrogen content at the time of pig casting.

Samples were taken during production and casting of a number of thirty-five to fifty ton heats in the Sorel plant. Additional heats produced in the Mines Branch laboratory were used for comparative evaluation.

The determination of the hydrogen content of liquid iron is difficult due to the problems of obtaining a representative sample and control of conditions such that an accurate analysis can be made. Hydrogen, because of its high diffusivity in iron, will readily escape during and after sampling and, conversely, can be readily picked up from the atmosphere or other sources. In addition, contamination of samples (e.g., slag) and gaseous segregation make analysis more difficult.

Although a number of sampling techniques are available (1) the choice of any technique must be made bearing in mind that reliable comparison of sampling methods are rare, and since hydrogen analyses can be significantly affected by the sampling method, comparison of results with other analyses on iron or steel is rendered unsatisfactory. This is also true for certain methods of analysis and for these reasons the sampling and analytical procedures are dealt with in considerable detail in this report.

The standard routine used by this laboratory for determination of hydrogen in liquid steel was used so that comparison with other hydrogen analyses could be made and the results readily evaluated.

SAMPLING

A completely satisfactory method for sampling liquid iron for hydrogen has not yet been devised. However, Geffner pin tube samples (2) (the pin tube is simply a small $\frac{1}{4}$ in. by 4 in. long evacuated pyrex tube) are admirably suited to this purpose. The pin tube method is becoming a generally accepted technique, because of its reliability and simplicity, coupled with the fact that it provides a convenient analytical sample.

Although the hydrogen content of a pin sample may be somewhat lower than the hydrogen level of the parent molten bath from which the sample was taken, the relative accuracy of analysis is quite good ($\pm$ 0.2 ppm for steel) and is probably directly proportional to the absolute value. As a result, the final hydrogen analysis can be affected to a greater degree by the manner in which the parent material is made available for sampling rather than by the means of sampling. This is shown in recent literature (3) in the course of investigation of various sampling methods for hydrogen in liquid steel whereby sampling was carried out by (a) sampling in the bath (inside the furnace), (b) from a sampling spoon (after removing metal from the furnace with a

sampling spoon), and (c) from moulds (metal is removed from the furnace in a
sampling ladle and poured into a mould).

Sampling procedure

Since the method of sampling is a significant factor in evaluating
hydrogen results, a description of the procedures used in this investigation
is outlined below. Geffner pin tubes were used exclusively in the work.

Pin samples were obtained by immersing the tip of the tube about
2 cm into the molten iron so that the tip melted and the metal was drawn into
the tube. The sample was then immediately quenched in water, held for about
ten seconds and then tagged and placed into liquid nitrogen for storage.
(Cold storage is necessary to avoid loss of hydrogen by diffusion at room
temperature.) Actual sampling time was held to within five seconds before
quenching. After quenching no significant loss of hydrogen will occur with
samples containing less than 4 ppm for short periods (e.g., steel samples
have been held in water for as long as one minute without significant loss of
hydrogen).

Samples obtained from pig iron in the mould were taken directly
from the molten iron about ten seconds after pouring, whereas the "at tap",
"runner" and "ladle" samples were taken from a sampling spoon, the metal in
the spoon being killed with aluminum. The sampling time in the latter
instances was also approximately ten seconds.

Samples were prepared for analysis by cutting to size with a rod
cutter (they may be broken to size using hammer and vise) and then filed
clean. No further preparation was necessary and the rinsing of samples in
solvents was avoided because of the danger of entrapment contamination. Total
sample preparation time was three to five minutes.

ANALYSIS FOR HYDROGEN

The most widely used methods for determination of hydrogen in metals
are the vacuum fusion and sub-fusion (or hot extraction) procedures. For
hydrogen analysis the vacuum fusion principle may be employed in two ways.
The first and most common procedure requires the melting of the sample in a
graphite crucible in which an iron bath is used to assist gas extraction.
Although complete extraction of hydrogen is assured, the accuracy and speed of
analysis suffers because of the large amounts of other gases liberated and the
complexity of the operation. In pig iron the total gas content is usually
high and heterogeneous within the sample. Therefore, this method is not
suitable for routine analysis. The other method involves the use of a tin
bath held in a silica crucible in which the sample is melted at lower tempera-
tures. By this method hydrogen is completely extracted, whereas only a
fraction of the other gases are liberated and, mainly for this reason, this
technique is considered best suited for highest absolute analytical accuracy.
The tin fusion method is well documented in the literature (4).

- 3 -

Although the procedures outlined above have been used in this laboratory, experience has indicated that considerable time and expense would be involved for routine analysis of pig iron by vacuum fusion, and because of this the sub-fusion method seemed preferable.

SUB-FUSION ANALYSIS

The sub-fusion method is now commonly used for hydrogen analysis. Although the method can be successfully applied to certain iron and steel materials, care must be exercised in order to avoid erroneous results.

It is well known that the amount of hydrogen that can be extracted from solid iron or steel is dependent upon a number of variables. The extraction temperature, extraction time, sample size and composition, as well as the hydrogen content of the sample affect the rate which hydrogen will diffuse from the metal and hence the completeness of extraction.

To develop a suitable analytical procedure, a series of tests was carried out to determine whether hydrogen behaviour was similar to that of cast iron in work done elsewhere (5). The completeness of extraction was determined by measurement of hydrogen evolution by means of a thermal conductivity gauge specifically developed for this purpose.

Gas evolution was monitored during analysis at 950°C (1740°F), 900°C (1650°F), 800°C (1470°F), 750°C (1380°F), 700°C (1290°F) and 650°C (1200°F), and indicated that hydrogen extraction was essentially complete in fifteen minutes at temperatures of 650°C (1200°F) or above 900°C (1650°F). Analysis at intermediate temperatures indicated lower hydrogen recovery. Unfortunately, due to the porous and heterogeneous nature of the samples available for testing purposes, the amount of hydrogen extracted was found to vary considerably even in samples taken from the same pin.

Similar difficulties were encountered in vacuum fusion analysis due to wide variation in total gas content and the effects of condensable vapours (most likely originating from the porous areas), which tended to contaminate the apparatus, thereby requiring further conditioning before analysis could proceed.

These difficulties discouraged further work by vacuum fusion and to minimize this problem the lowest suitable extraction temperature, namely 650°C (1200°F), was used in all further work.

The hydrogen analyses were carried out in the Hot Extraction apparatus described in Physical Metallurgy Division Internal Report PM-I-58-15. The procedures outlined in this report were used in the present work.

RESULTS

The following results are shown in the same sequence as the sampling of the iron, which was carried out over a period of several months. It will be noticed that in the order of presentation, comments are made to clarify sampling and analytical results.

The various types of iron analysed are shown in Table 1. In the manufacturing process of the iron, gas (usually nitrogen) was used as the transport medium for injection of calcium carbide and graphite. Although figures on the amount of material injected are not available here, injection time is given with some of the results since gas injection may be significant with regard to resulting hydrogen content of the iron.

In the tables, calcium carbide injection is shown as the first injection and graphite as the second injection.

The results shown in Table 2 were obtained on samples taken at Quebec Iron and Titanium Corporation on June 26, 1962. This series of samples consists solely of mould samples. In Table 5 results are shown for samples taken at tap, from the ladle, runner, and mould. This was done in order to determine whether there was hydrogen loss or pick-up at these stages. These samples were taken on August 9, 1962.

TABLE 1

Composition of Iron (Sorelmetal)

Iron type	C, %	S, %	P, %	Si, %	Mn, %
F1	4.1-4.6	0.035 max.	0.035 max.	0.25 max.	0.015 max.
D1	2.2-2.6	0.040 max.	0.035 max.	0.50 max.	0.015 max.
D3	1.8-2.99	0.040 max.	0.035 max.	0.50 max.	0.015 max.
S100	3.85 min.	0.035 max.	0.035 max.	0.75-1.25	0.015 max.
M225	3.6 min.	0.035 max.	0.035 max.	2.25-2.49	0.7-1.0

Typical analysis of the residual elements is as follows:

Al 0.015%, Co 0.038%, Cr 0.023%, Cu 0.033%, Ni 0.080%, Ti 0.019%, V 0.024%.

TABLE 2

Results of Hydrogen Analysis on Samples Taken From the Mould

(Quebec Iron and Titanium Corporation Limited)

Identification	Sampling Time After Beginning Of Pour (min)	Hydrogen Content, Wt %	Nitrogen Injection Time (min)
F1 iron			
Tap 8-2839	15	0.00023, 0.00029 (0.00046)☆ (0.00063)	60
Tap 4-7220	35	0.00015, 0.00045, 0.00053	43
Tap 6-3909	40	0.00042, 0.00043	40
Tap 2-1363	10	0.00013	40
Tap 2-1363	30	0.00010, 0.00015	as above
D1 iron			
Tap 5-6800	15	0.00020, 0.00024 (0.00068)	5
Tap 6-3940	18	(0.00019), 0.00026, 0.00056	15
Tap 6-3940	40	0.00058, 0.00065	as above
D3 iron			
Tap 1-6758	25	0.00029 (0.00053)	15
Tap 5-6801	40	0.00019, 0.00021 (0.00062)	20

The results shown in brackets are questionable but no obvious reason for the discrepancies could be found.

☆ Vacuum fusion analysis.

The results show that large amounts of hydrogen were present in some samples. Considerable variation in hydrogen content was found and apparently this is due to the nature of the samples. The poor relative accuracy of analysis strongly suggests that this is attributable to inherent characteristics of the iron and probably is representative of actual gas conditions, indicating gas segregation.

Evaluation of the analytical procedure may be made by comparing these results with the results shown in Table 3.

TABLE 3

Results of Hydrogen Analysis on Samples
Taken At Various Times During Production

(Heat No. A-1960 D3 Iron, Mines Branch)

Description of Sampling	Hydrogen Content, Wt %
before first injection (calcium carbide)	0.00025, 0.00028
after first injection	0.00035, 0.00044
after injection (repeat calcium carbide)	0.00038, 0.00041
after second injection (graphite)	0.00019, 0.00021
mould	0.00046, 0.00049, 0.00052, 0.00056

In previous analyses (Table 2), samples taken from the mould were found to contain a relatively high degree of porosity and non-uniformity (in the gas content sense) and considerable difficulty was encountered in analysis.

The samples described in Table 3 appeared to have little or no porosity and this is reflected in the consistency in hydrogen results. Identical procedures were used (15 min extraction at 650°C) and it was not considered necessary to check by vacuum fusion analysis. The mould samples were taken with and without aluminum addition. The killed mould samples gave 0.00046 and 0.00052 wt % hydrogen and the unkilled samples 0.00049 and 0.00056 wt % hydrogen. These results are within the normal deviation and although it is recognized that aluminum addition to certain pig iron may result in porosity, no apparent detrimental effects were noted in the present work due to its use. For this reason and because of previous difficulty in obtaining sound samples, small amounts of high purity aluminum wire were added at the sampling spoon and mould immediately prior to taking pin tube samples in later work. (Tables 4 to 6)

TABLE 4.

Results of Hydrogen Analysis of D3 Iron
Produced at the Mines Branch

Heat Number	Before 1st Injection	After 1st Injection	Before 2nd Injection	After 2nd Injection	Before Tap	Mould
A-1960	0.00025 0.00028	0.00035 0.00044	0.00038 0.00041	0.00019 0.00021	–	0.00046 0.00049 0.00052 0.00056
A-1967	0.00025	0.00040 0.00047	0.00021 0.00024	0.00021 0.00024	✱(0.00025) (0.00049) (0.00069)	0.00048 0.00051
A-1968	0.00016 0.00018	0.00021 0.00023	–	–	–	–
A-1969	0.00029 0.00028	0.00076 0.00073	0.00027	0.00052	–	0.00037
A-1972	0.00045 0.00058	0.00051 0.00070	–	0.00036 0.00046	–	0.00033
A-1973	0.00024 0.00031	0.00040 0.00052	–	–	–	0.00027 0.00059
A-1974	0.00034 0.00047	0.00052	–	–	0.00047 0.00042	0.00024 0.00026

✱ poor sample

TABLE 5

Results of Hydrogen Analysis of Various Irons
Produced at Quebec Iron and Titanium Corporation

Identification	Tap Sample	Ladle Sample	Runner Sample	Mould Sample
D1 iron				
Tap 4-7358	-	0.00008 0.00009 0.00019 0.00033	0.00018 0.00017	0.00018 0.00018
Tap 6-4051	-	-	0.00016 0.00013	0.00026 0.00026 0.00028 0.00029
Tap 7-4335	0.00024 0.00039	0.00036 0.00041	0.00026 0.00025	0.00057 0.00065
D3 iron				
Tap 2-1492	-	-	0.00021 0.00041 0.00041	0.00031 0.00034
Tap 5-6936	-	-	0.00033 0.00042	0.00026 0.00038 0.00055
Tap 8-2964	0.00033	-	0.00021 0.00033	0.00035 0.00042
S100				
Tap 3-6982	-	-	0.00011 0.00009	0.00009 0.00019 0.00019
M225				
Tap 4-7357	-	-	0.00011 0.00012	0.00024 0.00014

TABLE 6

<u>Results of Hydrogen Analysis Using Propane Injection</u>

<u>Heat No. A-1994 D3 Iron, Mines Branch</u>

Description of Sampling	Hydrogen Content, Wt %
before first injection (calcium carbide)	0.00018
after first injection	0.00039
before second injection (graphite)	0.00024
after second injection	0.00031 (0.00062)ᴂ
mould	(0.00065)ᴂ

ᴂ questionable sample, possibly porous

CONCLUSION

     Suitable methods of sampling and analysis have been developed for the routine determination of hydrogen in pig iron. The results obtained give reasonable values when compared with steel analyses. The accuracy of analysis appears to be mainly dependent upon the quality of the sample and before definite conclusions may be drawn on the basis of the results available, considerably more work would be necessary to determine the corresponding relationships with manufacturing processes.

REFERENCES

1. T.B. KING - "Sampling of Liquid Metals" - The Determination of Gases in
   Metals, Special Report No. 68, The Iron and Steel Institute
   1960.

2. J.G. BASSETT, J.W. DOUGHERTY, G.R. FRITTER - "Sampling of Liquid Steel for
   Hydrogen" AIME Open Hearth Proceedings 39, 44-51 (1956).

3. S. KOBAYASHI, S. MAEKAWA, A. NAKAGAWA - "Study on the Method of Taking
   Sample for Determination of Hydrogen and Oxygen in Molten
   Steel During Steelmaking Process" - The Japan Steel Works
   Limited 1961.

4. B.M. SHIELDS, J. CHIPMAN, N.J. GRANT - "Thermalconductivity Method for
   Analysis of Hydrogen in Steel" - Trans. AIME 197, 180-184
   (1953).

5. B.B. BACH, J.V. DAWSON, L.W.L. SMITH - "Hydrogen in Cast Iron" -
   J. Research and Development, British Cast Iron Research
   Association 5, 490-501 (August 1953-June 1954).