Naval Surface Warfare Center
Carderock Division
West Bethesda, MD 20817-5700

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Platform Integrity Department
Technical Report

Challenges Associated with the Measurement of Diffusible Hydrogen in Steel Weld Metal Deposits Using the Hot Carrier Gas Extraction Method

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Daniel H. Bechetti, Jeffrey D. Farren, and Matthew F. Sinfield

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14. ABSTRACT:
The Naval Surface Warfare Center, Carderock Division (NSWCCD) Welding, Processing, and Nondestructive Evaluation Branch (Code 611) has undertaken a series of experiments aimed at elucidating the important details and potential challenges associated with the hot carrier gas extraction technique for measuring diffusible hydrogen in deposited weld metal. At the time of this report, the American Welding Society (AWS) was considering revising its specification for diffusible hydrogen testing (AWS A4.3) to include this relatively new method that is invoked by international standards (ISO 3690). However, exploratory work by NSWCCD and others raised questions concerning the technique's robustness, particularly with respect to proper specimen heating and complete hydrogen evolution. To characterize these concerns, two categories of trials were employed: (1) diffusible hydrogen measurements of weld deposits made with electrodes encompassing a wide range of hydrogen contents (3 to 50 mL/100 g) and (2) thermal-only tests using the hot carrier gas extraction apparatus.

The results of hydrogen analyses indicate that the time-temperature combinations for hot carrier gas extraction that are specified in the current version of ISO 3690 need to be evaluated for individual combinations of testing apparatus and weld metal hydrogen content to ensure complete hydrogen evolution and correct measurement. Additionally, significant changes to the measured amount of diffusible hydrogen can occur based on interpretation of the hydrogen evolution curve. Finally, the thermal conductivity detector of the Bruker G4 Phoenix was not susceptible to signal saturation during hot carrier gas extraction, even when weld metal deposits that contained extremely large amounts of diffusible hydrogen were analyzed.

The thermal-only tests indicate that potential causes of incomplete hydrogen evolution during hot carrier gas extraction for a given test apparatus include the lag in specimen heating relative to the presumed beginning of the test and undershoot of the hold temperature. For the apparatus used in this work, specimen orientation and the flow of the carrier gas across the specimen were also found to influence its thermal profile. The temperature of the apparatus immediately prior to the beginning of a test did not appear to influence specimen heating rate.

The results of both test categories are described in detail, and recommendations for overcoming the potential challenges identified for the hot carrier gas extraction method are provided.

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EXECUTIVE SUMMARY

The Naval Surface Warfare Center, Carderock Division (NSWCCD) Welding, Processing, and Nondestructive Evaluation Branch (Code 611) has undertaken a series of experiments aimed at elucidating the important details and potential challenges associated with the hot carrier gas extraction technique for measuring diffusible hydrogen in deposited weld metal. At the time of this report, the American Welding Society (AWS) was considering revising its specification for diffusible hydrogen testing (AWS A4.3) to include this relatively new method that is invoked by international standards (ISO 3690). However, exploratory work by NSWCCD and others raised questions concerning the technique's robustness, particularly with respect to proper specimen heating and complete hydrogen evolution. To characterize these concerns, two categories of trials were employed: (1) diffusible hydrogen measurements of weld deposits made with electrodes encompassing a wide range of hydrogen contents (3 to 50 mL/100 g) and (2) thermal-only tests using the hot carrier gas extraction apparatus.

The results of hydrogen analyses indicate that the time-temperature combinations for hot carrier gas extraction that are specified in the current version of ISO 3690 need to be evaluated for individual combinations of testing apparatus and weld metal hydrogen content to ensure complete hydrogen evolution and correct measurement. Additionally, significant changes to the measured amount of diffusible hydrogen can occur based on interpretation of the hydrogen evolution curve. Finally, the thermal conductivity detector of the Bruker G4 Phoenix was not susceptible to signal saturation during hot carrier gas extraction, even when weld metal deposits that contained extremely large amounts of diffusible hydrogen were analyzed.

The thermal-only tests indicate that potential causes of incomplete hydrogen evolution during hot carrier gas extraction for a given test apparatus include the lag in specimen heating relative to the presumed beginning of the test and undershoot of the hold temperature. For the apparatus used in this work, specimen orientation and the flow of the carrier gas across the specimen were also found to influence its thermal profile. The temperature of the apparatus immediately prior to the beginning of a test did not appear to influence specimen heating rate.

The results of both test categories are described in detail, and recommendations for overcoming the potential challenges identified for the hot carrier gas extraction method are provided.

INTRODUCTION

The presence of monatomic hydrogen in weld metals and/or heat affected zones (HAZs) is a well-known cause of weldment cracking and embrittlement in a variety of structural metals [1, 2]. In susceptible materials, this type of cracking may occur if proper control over weldment restraint, heat input, preheat and interpass temperatures, cleanliness, and filler metal selection and storage is not exercised. Hydrogen induced cracking (HIC, also referred to as hydrogen

assisted cracking or cold cracking since it occurs near room temperature) can be particularly insidious because it does not always occur immediately. Instead, cracks can develop after an incubation time that is often on the order of hours or days. Furthermore, hydrogen induced cracks can be difficult to detect via standard non-destructive testing (NDT) methods because they are often small, near subsurface, and tighter than many other welding-related discontinuities (*e.g.*, porosity, solidification cracking).

Steels are the structural metals most commonly associated with welding-related HIC. They are particularly susceptible to this method of degradation because of the phase transformations that occur during welding thermal cycles. Hydrogen solubility in the high temperature phases of iron-based materials (*e.g.*, face centered cubic austenite and the disordered liquid) is much larger than in the low temperature phases (*e.g.*, body centered cubic ferrite). Therefore, if hydrogen is present during welding (*e.g.*, because of moisture in filler metal fluxes or coatings, excessive atmospheric water vapor, or surface contaminants), it can readily dissolve into the molten weld pool and diffuse into the austenitic HAZ and/or solidified weld metal. As the material cools, it will transform into one or more body centered constituents, all of which have significantly lower solubility for hydrogen. However, hydrogen remains mobile in these constituents even at room temperature because of its small atomic size. As a result, hydrogen trapped in steel weld metals and HAZs can diffuse out of solution, aggregate, and induce cracking.

Despite a large body of work in the welding community dedicated to understanding the mechanism by which hydrogen actually induces cracking, no consensus has yet been reached. Mitigation of HIC in weldments has therefore been achieved primarily through cracking susceptibility tests, bulk quantification of diffusible hydrogen content, and fabrication controls designed to keep the amount of diffusible hydrogen in susceptible materials below the limit for HIC initiation. The term ‘diffusible hydrogen’ is used to distinguish mobile atoms that are free to diffuse and aggregate as described above from immobile hydrogen that is permanently or semi-permanently tied up as second phases (*e.g.*, hydrides) or at so-called hydrogen traps (*e.g.*, oxide inclusions). \

The commercial and military shipbuilding industries fabricate thousands of miles of welds annually under conditions that are well suited for the creation of hydrogen cracks. Welding in humid coastal environments, the use of high strength welding consumables and base materials, utilization of a wide variety of welding processes, and the possibility of very high restraint due to material thickness and structural fit up all increase the likelihood of HIC in these applications. To counter these factors, fabrication requirements aimed at minimizing the amount of hydrogen incorporated into high strength steel joints have been developed and implemented.

American Welding Society specification AWS A4.3:1993-ADD1 (hereafter referred to as “AWS A4.3”) provides the U.S.-standard test methods for measuring the diffusible hydrogen content of arc welded steel [1], while the international welding community leans more heavily on International Standards Organization specification ISO 3690:2012(E) (hereafter referred to as “ISO 3690”) [4]. One of the key differences between the two documents is the hot carrier gas extraction technique (“hot extraction”), which is currently allowed under ISO but not AWS.

In the U.S. testing for diffusible hydrogen has historically involved the use of slightly elevated temperatures (AWS A4.3 specifically recommends 45 or 150 °C [113 or 302 °F]) to

drive hydrogen out of a metallic specimen submerged in a liquid. The volume of liquid displaced is then converted into a volume of diffusible hydrogen evolved per 100 g of specimen mass. Typical liquids used for this analysis are glycerin, paraffin, and mercury, with mercury having been established in the 1980s as the preferred medium for accuracy and repeatability [3, 5, 6]. However, the significant health and environmental concerns associated with the use of mercury led to the consideration of gas chromatography (GC) as an alternate method. This technique involves driving the diffusible hydrogen out of a metallic specimen in a sealed container (also at 45 or 150 °C [113 or 302 °F]) and then evacuating the contents of the chamber into a gas chromatograph, where the thermal conductivity of the evolved gas is compared to that of a reference gas to calculate the amount of hydrogen present.

Studies comparing results of the mercury and GC methods were carried out in the 1990s and early 2000s, with satisfactory correspondence between the data gathered from the two methods [7, 8]. AWS A4.3 currently provides for the use of the GC technique and refers to American Society for the Testing of Materials standard ASTM E260 for specifics of the method [3, 9]. It has gained widespread acceptance across the welding consumable manufacturing industry for its ease, accuracy, and throughput. Required soak times are 72 hr. at 45 °C (113 °F) or 6 hr. at 150 °C (302 °F) because the temperatures are low, but a relatively constant throughput can be achieved with enough specimen containers.

As part of the continued evolution of diffusible hydrogen analysis techniques, ISO 3690 allows for accelerated GC via the hot carrier gas extraction method. In this technique, specimens are heated to the hydrogen evolution temperature of interest in a furnace that is attached to a gas chromatograph. The hydrogen is evolved and measured simultaneously as the sample heats and soaks for a prescribed minimum time. This method therefore eliminates the need to fabricate and maintain sealable canisters. Moreover, since ISO 3690 provides for soak temperatures up to a maximum of 400 °C (752 °F), the hot extraction technique purportedly offers the ability to complete a test in as little as 21 min., as opposed to the 6 or 72 hr. noted above. Finally, the apparatus used in this study provides a graphical output of detector signal to allow judgment of the completion of hydrogen evolution. A comparative round robin study of the hot extraction method with the static GC and mercury methods are given in [10, 11].

At the time of this report, the AWS subcommittee on Moisture and Diffusible Hydrogen (AWS A5W) was considering a revision to AWS A4.3 to include at least a partial adoption of ISO-3690. However, concerns about the accuracy and repeatability of the technique were raised in several reports published by the International Institute of Welding (IIW) [10, 11, 12]. Work by the Japanese Welding Engineering Society (JWES) used the hot carrier gas extraction method to analyze the diffusible hydrogen content of weld deposits made using H5, H10, and H15-grade electrodes [10]. The authors first concluded that the measured diffusible hydrogen content for weld deposits produced from a given electrode was dependent on test specimen size. They also determined that for 80 mm (3.15 in.) long specimens tested at an apparatus set temperature of 400 °C (752 °F), a 21 min. measurement duration was insufficient. They therefore recommended increasing the test durations required by ISO 3690 and basing them on specimen temperature rather than apparatus temperature.

The authors in [14] subsequently showed that decreasing specimen sizes lead to faster specimen heating and higher maximum temperatures during hot extraction, which likely explains the dependency of hydrogen content on specimen size observed in [12]. Given the Navy's vested

interest in ensuring the accurate characterization of diffusible hydrogen content by new and current techniques, the Naval Surface Warfare Center, Carderock Division's (NSWCCD) Welding, Processing, and Non-Destructive Evaluation Branch (Code 611) has undertaken a series of experiments with the objectives of investigating the concerns raised by the Japanese researchers and identifying potential challenges associated with the adoption of the hot extraction technique.

APPROACH

The diffusible hydrogen analyzer used in this work was a Bruker Model G4 Phoenix DH (purchased in 2008, see **Figure 1**) in combination with GA Client control software (version 1.5.0.2). The chamber for hot extraction is a 70 cm (27.6 in.) long, 3.2 cm (1-1/4 in.) diameter quartz tube, inside of which welded specimens are situated for analysis. A 20 cm (7.9 in.) long clamshell-type furnace containing two infrared heating elements encloses the middle of the tube. The apparatus is water cooled by a Haskris Model R100 recirculating chiller when in use. The G4 Phoenix is the same model as the hot carrier gas extraction apparatus used in [12].

Two categories of tests were performed to assess variables that may influence experimental results. Experimental methods for each are described in the following sections.

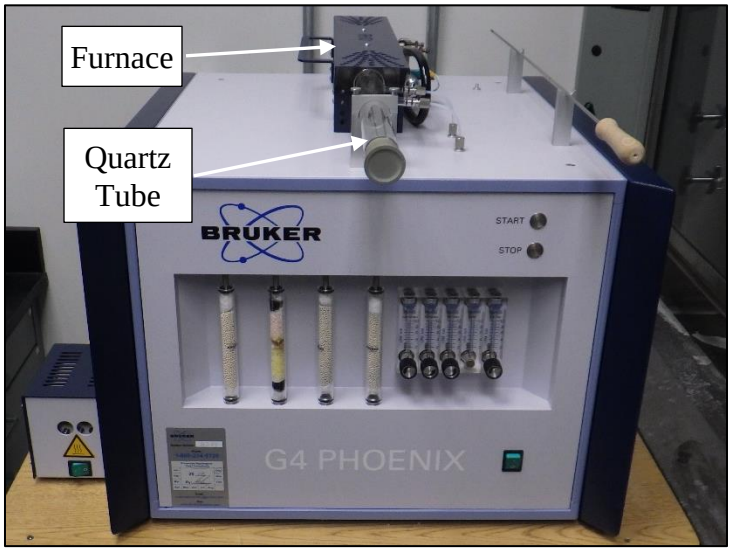

Figure 1. Bruker G4 Phoenix DH apparatus used in this work.

Diffusible Hydrogen Measurements

For tests involving actual measurement of diffusible hydrogen content, welded specimens were prepared in accordance with AWS A4.3. Data from low-, medium-, and high hydrogen content welding consumables were aggregated from several concurrent research programs. The low hydrogen consumables were shielded metal arc welding (SMAW) electrodes of types MIL-7018-M and MIL-10718-M. The medium hydrogen consumable was Lincoln Pipeliner NR-208-XP (AWS A5.29/A5.29M Type E81T8-G [13]) self-shielded flux cored arc welding (FCAW) wire electrode. The high hydrogen consumables were Murex Hardex N SMAW electrodes. Details about the electrodes and welding parameters are given in Table 1.

Tests were performed using the hot extraction method as described in ISO 3690 at a programmed furnace set temperature of 400 °C (752 °F). The carrier gas was high purity nitrogen flowing at 0.6 to 0.7 L/min (1.3 to 1.5 ft^3/hr). Hydrogen sensing in the machine was performed by a thermal conductivity detector (TCD). The minimum test length used was 60 min., which intentionally exceeded the ISO requirement of 21 min. for the purpose of this study. Prior to testing, the analyzer was calibrated using its internal calibration system via helium (He) dosing. This calibration involved dosing the carrier gas with ten different levels of He to confirm the response of the TCD across its low- and high sensitivity ranges. The dosing series for calibration was repeated at least three times to ensure stability of the calibration in accordance with the manufacturer's instructions. Consumables used within the gas chromatograph system were either conditioned at elevated temperature under flowing argon or replaced prior to testing. Diffusible hydrogen content was quantified by an algorithm in the control software that integrates the TCD signal curve between user-selectable beginning and end points.

Table 1. Details of the electrodes and welding processes used to fabricate the diffusible hydrogen test specimens analyzed in this work.

Welding Process	SMAW			FCAW
Electrode Manufacturer	ESAB	Lincoln Electric	Murex	Lincoln Electric
Product Name	Atom Arc	Excalibur	Hardex N	Pipeliner NR-208-XP
Lot Number	121979	1047R	Unknown	15243875
Classification	MIL-7018-M	MIL-10718-M	Unknown	E81T8-G
Diameter, mm (in.)	3.18 (1/8)	3.97 (5/32)	4.76 (3/16)	1.98 (5/64)
Typical Current, A	125-130	140-145	185-190	200-215
Typical Voltage, V	23-25	23-26	24-25	32-33
Typical Travel Speed, mm/s (in/min.)	1.9-2.3 (4.5-5.5)	2.1-2.8 (5.0-6.5)	1.9-2.3 (4.5-5.5)	3.4-4.2 (8.0-10.0)
Typical Heat Input, kJ/mm (kJ/in.)	1.4-1.5 (35-38)	1.2-1.6 (30-40)	2.0-2.4 (50-60)	1.7-1.8 (44-46)
Notes	Moisture exposed as part of a separate project	New canister	Uncontrolled environmental exposure, legacy electrode	

Thermal Tests

For tests used only to characterize the thermal behavior of the analyzer and specimens, an 80 mm (3.15 in.) long sample from a prior diffusible hydrogen test was instrumented with six Type-K thermocouples. The thermocouples were tack welded at the middle and ends of both the welded and unwelded faces as shown in **Figure 2**. Since the thickness of the weld metal deposits in this work was typically much smaller than the thickness of the base steel coupon, it was presumed that the near-surface temperature of the specimen was more relevant than the temperature at mid-thickness in the test specimen. To avoid disturbing the thermocouples connections, the specimen was fully inserted into the G4 Phoenix furnace tube prior to testing. This is a slight departure from the manufacturer's recommended procedure for hot extraction, wherein the specimen is inserted following an approximately 60 sec. delay for system initialization. For each test, the specimen was oriented as shown in the left photograph of **Figure**

2, that is, with thermocouples 1 and 4 facing the front (open) end of the furnace tube. Thermal data was recorded at 0.33 Hz using a Measurement Computing Model USB-2048 data acquisition device equipped with DAQAmi software, version 4.2.1.

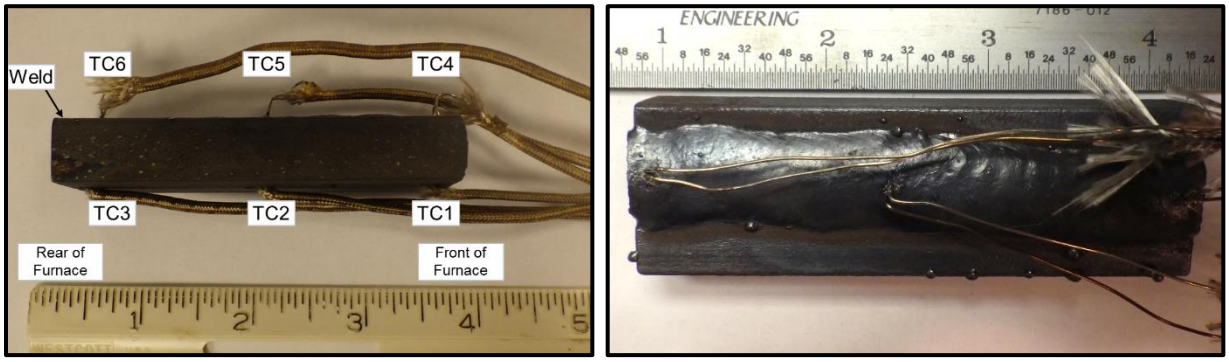

Figure 2. Photographs of the instrumented specimen used to characterize thermal behavior during hot extraction testing. (Left) side view showing all six thermocouples and (Right) top view showing the weld bead and the three thermocouples attached to it.

RESULTS AND DISCUSSION

Diffusible Hydrogen Testing

The first set of experiments in this work focused on diffusible hydrogen contents measured by the hot extraction technique. They were performed in order to quantify the effects of varying test parameters on the quality of the resultant data. The variables addressed were: test duration, curve integration point, and general level of specimen hydrogen content.

Test Duration and Resultant Hydrogen Content

Figure 3 shows the results of a 400 °C (752 °F) hot extraction test performed on a weld fabricated using Lincoln Pipeliner NR-208-XP, the medium-hydrogen content electrode investigated in this work. The dashed line connects the TCD signal at the start of the test (the "integration start" point) to the point at the ISO 3690-specified 21 min. mark (the "integration end" point). The resulting measured diffusible hydrogen content is 13.77 mL/100 g. However, the TCD signal has clearly not returned to the baseline level by that time, indicating that 21 min. minimum hot extraction was inadequate to evolve nominally all of the diffusible hydrogen from the sample. If the curve in **Figure 3** is integrated to the full test length of 60 min., a value of 21.58 mL/100 g is obtained (a 57 % increase).

Figure 4 illustrates the results from an eight-specimen test series for this welding consumable. As shown, at the 21 min. mark, all specimens reportedly contained less than 15 mL/100 g diffusible hydrogen. Upon increasing the test time to 60 min., an average measured increase of 48 % was observed. Finally, **Figure 5** demonstrates that this behavior was also observed in low-hydrogen MIL-7018-M welding consumables. As shown, even when specimens contained less than 4 mL/100 g of diffusible hydrogen, a 21 min. test length did not allow the TCD signal to completely return to baseline. This observation is consistent with those reported by [12, 13, 14] and indicates that the temperature of the specimen could also be substantially

lagging the apparent temperature of the furnace in this study. The testing described in the second part of this report investigates this concern more thoroughly.

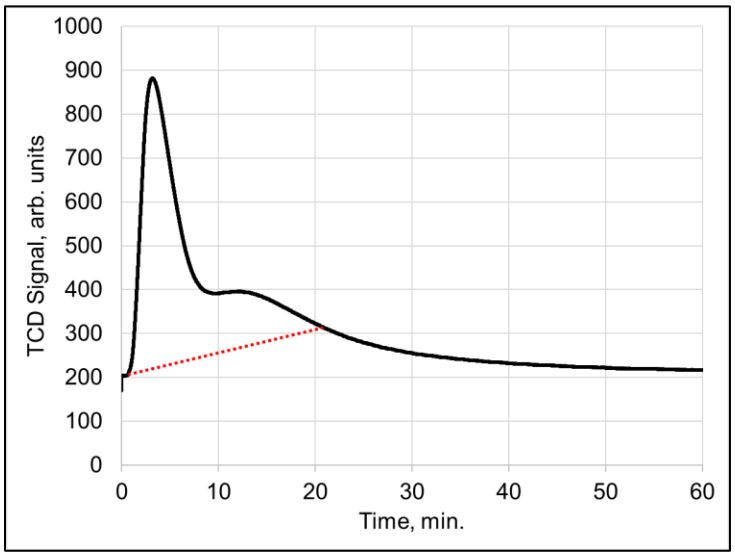

Figure 3. TCD signal curve (black) for hot extraction of diffusible hydrogen at a programmed temperature of 400 °C (752 °F) from a Lincoln Pipeliner NR-208-XP FCA weld prepared in accordance with AWS A4.3. The red line shows the portion of the curve integrated to calculate diffusible hydrogen content after 21 min.

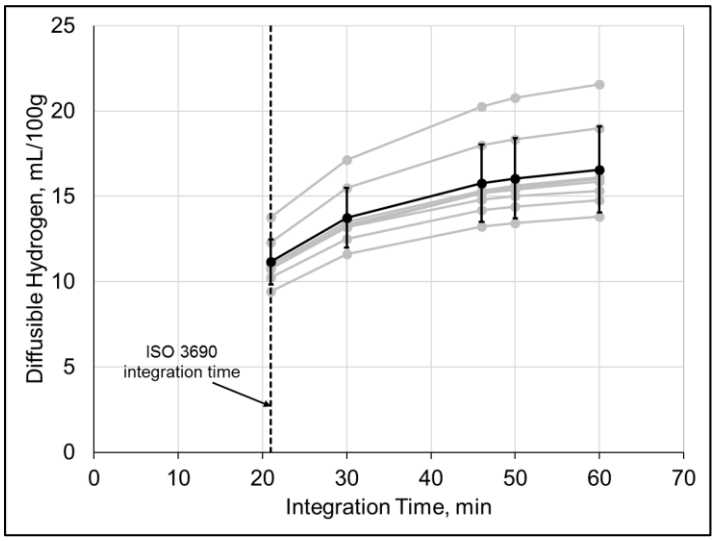

Figure 4. Measured diffusible hydrogen content as a function of hot extraction time from Lincoln Pipeliner NR-208-XP FCA welds prepared in accordance with AWS A4.3 and tested at a programmed temperature of 400 °C (752 °F) (gray). Black curve is the average of eight specimens. Error bars represent one standard deviation from the average.

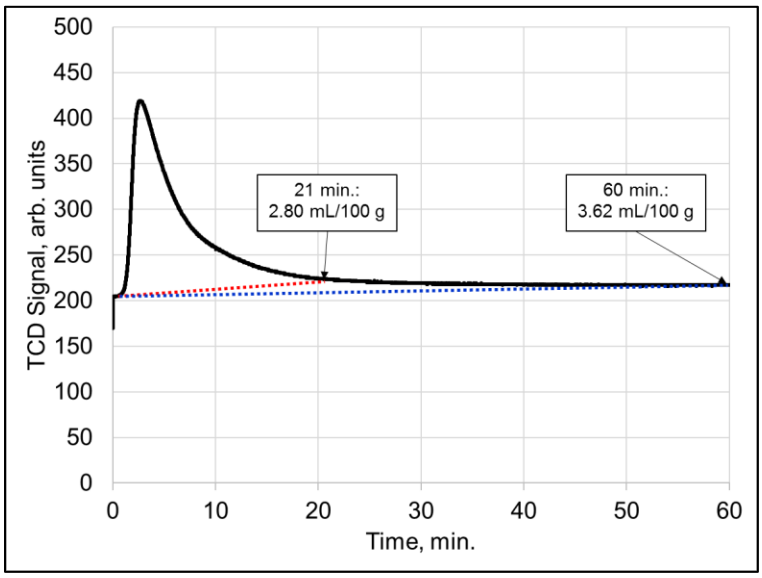

Figure 5. TCD signal curve (black) for hot extraction of diffusible hydrogen at a programmed temperature of 400 °C (752 °F) from a MIL-7018-M SMA weld prepared in accordance with AWS A4.3. The red line shows the portion of the curve that would be integrated to calculate diffusible hydrogen content after 21 min, and the blue line shows the effect of extending that integration time to a point where the signal has plateaued.

Effect of Curve Integration Point

In addition to the general observation presented above that the length of the hot extraction test significantly affects the resultant data, it was also noted that the specific choice of start and end points for integration can also have a large effect on the reported results. For example, **Figure 6** shows the TCD signal curve for a MIL-10718-M SMA weld deposit tested at a target temperature of 150 °C (302 °F). The ISO 3690-prescribed test duration for this temperature is 6 hr., and it is shown from **Figure 6** that this is a sufficient amount of time for the diffusible hydrogen to evolve from the specimen and allow the TCD signal to baseline. When a curve of this length is integrated, however, the effect of signal noise on the resulting measurement is substantial. The red and blue lines in **Figure 6** terminate at adjacent data points at the six hour mark but result in measured diffusible hydrogen values of 3.03 mL/100 g and 3.45 mL/100 g, respectively. This effect is illustrated at the terminal integration point but has an equally significant impact when varying the initial integration point.

The magnitude of this variation is not as large as those illustrated above for the shorter tests or the medium-hydrogen electrodes, but given the strict Navy diffusible hydrogen requirements (*e.g.*, a maximum allowable single-sample diffusible hydrogen content for MIL-10718-M electrodes of 4.3 mL/100 g), it is conceivable that such a variation could result in the incorrect acceptance or rejection of an electrode lot. Application of a filtering or smoothing algorithm to the TCD signal data could mitigate this problem, but care would need to be taken to

establish an appropriate procedure by which end-of-test signal noise is effectively removed without altering the peak size and shape near the beginning of the test.

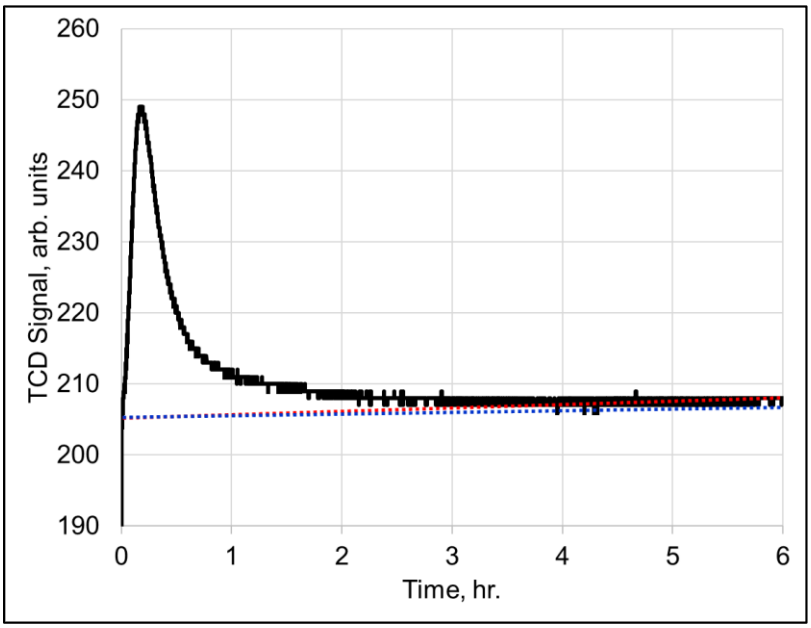

Figure 6. TCD signal curve (black) for hot extraction of diffusible hydrogen at a programmed temperature of 400 °C (752 °F) from a MIL-10718-M SMA weld prepared in accordance with AWS A4.3. The red and blue lines show the effect of changing the calculation stop point by one data point (0.2 sec.) after a 6 hr. test.

Potential Saturation of the Thermal Conductivity Detector

Unpublished prior investigations by NSWCCD into the measurement of diffusible hydrogen via the GC method revealed the potential for saturation of the thermal conductivity detector in the G4 Phoenix. This problem was encountered when diffusible hydrogen in weld deposits was evolved in a separate container and then fed into the apparatus in a single dose as described in ISO 3690, Section 4.3.2.4 [4]. The rapid influx of a high concentration of hydrogen across the TCD exceeded the detector's maximum measurable signal, truncating the peak of the signal curve and producing inaccurate measurements.

To determine whether this issue is a concern for the hot extraction method, welds made using Hardex N electrodes were fabricated and tested. The electrodes were provided by Puget Sound Naval Shipyard and Intermediate Maintenance Facility, and it was reported that they had been exposed to an uncontrolled atmospheric environment for a very long time (decades) because the material has limited applications and does not have hydrogen control requirements. It was therefore presumed that weld deposits made from these electrodes would contain a substantial amount of diffusible hydrogen and could potentially approach the upper signal limit of the TCD. **Figure 7** gives a typical 400 °C (752 °F) hot extraction curve for this material. Its hydrogen content was measured at 50.29 mL/100 g and, as such, the TCD signal peak was many times higher than those exhibited in Figures 3, 5, and 6. Still, no apparent saturation of the TCD was noted. It is therefore believed that the potential for TCD saturation during hot extraction is

not a significant concern, and that the gradual evolution of hydrogen for this method is advantageous for allowing analysis of specimens containing very large amounts of the gas.

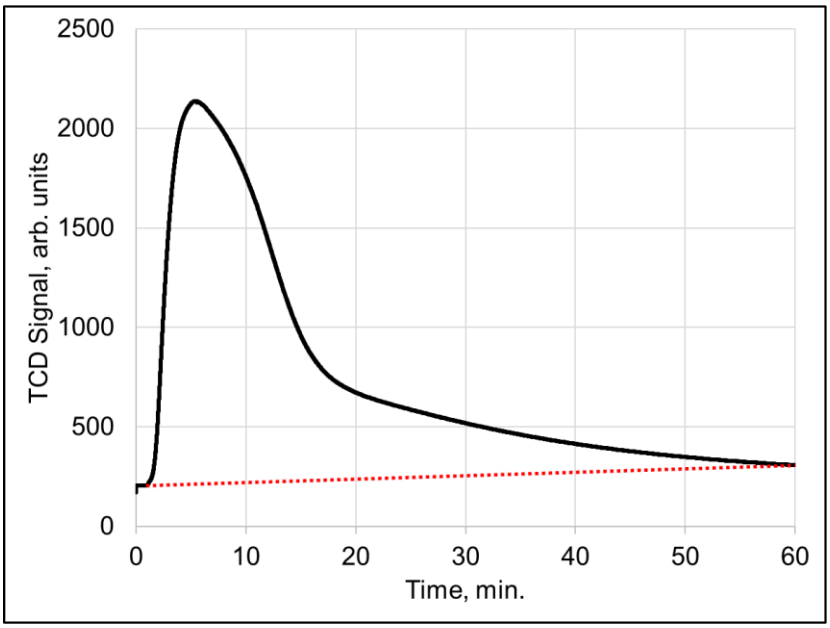

Figure 7. TCD signal curve (black) for hot extraction of diffusible hydrogen at a programmed temperature of 400 °C (752 °F) from a Hardex N weld prepared in accordance with AWS A4.3. The red line shows the portion of the curve that would be integrated to calculate diffusible hydrogen content after 60 min. Diffusible hydrogen content = 50.29 mL/100 g.

Thermal Behavior

The second set of experiments performed in this work derived from the observations of the preceding diffusible hydrogen tests and specifically focused on the relationships between test parameters and specimen temperature, because specimen temperature controls the rate at which hydrogen evolves. The investigated variables were: programmed furnace temperature, specimen ramp time, specimen orientation, longitudinal thermal gradients, and starting furnace condition.

Programmed Test Temperature vs. Measured Specimen Temperature

Figure 8 gives the temperature evolution in a diffusible hydrogen test specimen during hot extraction cycles with programmed peak temperatures of 150 and 400 °C (752 °F). As shown, when the programmed test temperature was set to 150 °C (302 °F), the specimen reaches a maximum temperature of 135 to 140 °C (275 to 284 °F). Similarly, when programmed to reach 400 °C (752 °F), the sample temperature equilibrated at 365 to 375 °C (689 to 707 °F). Such deviations in temperature may significantly reduce the amount of hydrogen evolved during the exposure period if its length is based solely on the programmed temperature. This potential is acknowledged by the variations in minimum holding time given in Table 4 of ISO 3690. At 360 °C (680 °F), a minimum time of 30 min. (as opposed to 21 min. for 400 °C [752 °F]) is required. At 140 °C (284 °F), the required hold time is 8 hr., as opposed to 6 hr. at 150 °C (302 °F).

A series of additional trials with increasing programmed temperatures were performed in order to determine the appropriate set point for 400 °C (752 °F) testing using the apparatus at NSWCCD. As shown in **Figure 9**, a furnace set point of between 430 and 435 °C (806 and 815 °F) was required for the midpoint of the welded samples to reach the 400 ± 3 °C (752 ± 5 °F) ISO 3690 requirement. It is therefore recommended that use of the hot extraction technique be accompanied by periodic verification of the relationship between the programmed and actual specimen temperatures to ensure proper hold time selection. As described in [12] and [14], such a relationship will be dependent on specimen size.

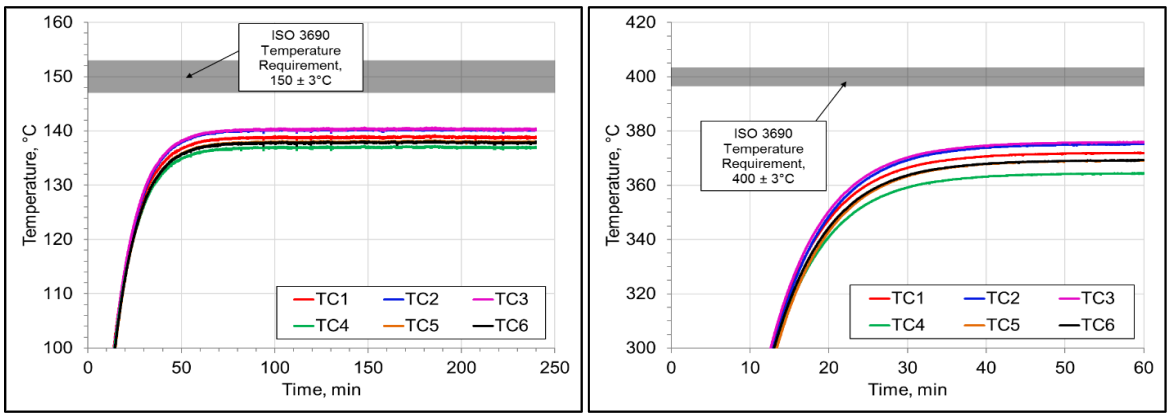

Figure 8. Heating behavior of an 80 mm (3.15 in.) long diffusible hydrogen specimen prepared in accordance with AWS A4.3 during hot extraction at a programmed furnace temperature of (left) 150 °C (302 °F) and (right) 400 °C (752 °F), showing that the specimen temperature undershot the intended test temperature.

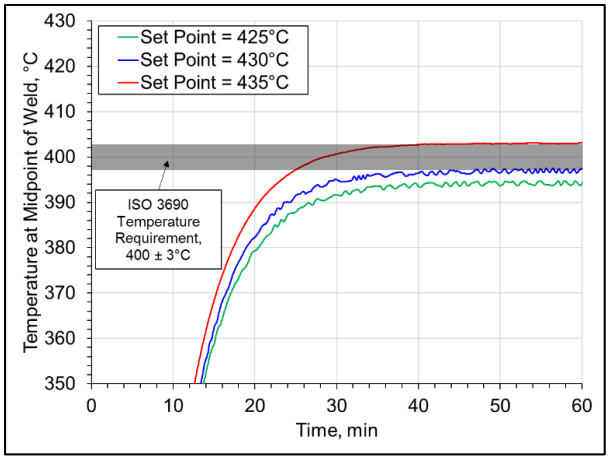

Figure 9. Specimen temperature as a function of time and programmed furnace temperature, showing that for 80 mm (3.15 in.) long specimens prepared in accordance with AWS A4.3, a programmed peak temperature greater than 430 °C (806 °F) was required to reach the specified peak temperature range for hot extraction of diffusible hydrogen at 400 °C (752 °F).

Specimen Thermal Ramp Time

In addition to the peak temperature concern, Figures 8 and 9 also indicate that there is a large delay between the start of the test and when the specimen actually reaches the required temperature window. This is caused by the kinetics of thermal diffusion in the specimen and is illustrated further in **Figure 10**, which shows the temperature at the weld midpoint as a function of time for a programmed peak temperature of 430 °C (806 °F). The four curves in this figure represent four slightly different test conditions which have been anonymized for ease of interpretation in **Figure 10** but will be discussed in the following section. It is not clear why the equilibrium temperature for these tests was slightly above the upper limit of the required range when prior tests at a programmed temperature of 430 °C (806 °F, see **Figure 9**) equilibrated several degrees cooler. It is possible that, for these tests, the arrangement of the thermocouple wires slowed or restricted the carrier gas flow that usually provides some convective cooling. In any case, the specimens required at least 24 min. of ramp time before reaching the 400 °C (752 °F) target. This delay exceeds the entire 21 min. minimum test length requirement given in ISO 3690 and therefore indicates a considerable potential for incomplete hydrogen evolution. That potential has been shown to routinely manifest in this work (Figures 3-5), and the temperature lag between the specimen and the furnace is therefore considered the primary driver of the diffusible hydrogen quantification problems identified above.

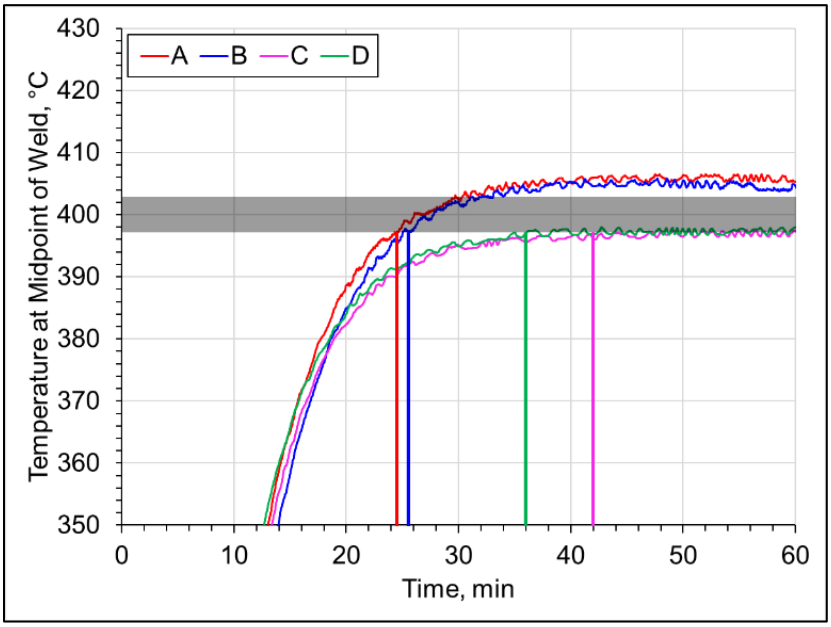

Figure 10. Specimen temperature as a function of time for 80 mm (3.15 in.) long specimens prepared in accordance with AWS A4.3 and heated to a programmed peak temperature of 430 °C (806 °F), illustrating the time delay between the start of the test and attainment of the required test temperature.

The furnace temperature reported by the control software could not be relied upon to accurately capture this effect. As shown in **Figure 11**, which presents the furnace temperature recorded by the apparatus's control thermocouple along with the measured thermal data from the accompanying specimen, the furnace appears to equilibrate at the programmed temperature just 3 min. after data begins recording. Note that the furnace temperature data does not start at room

temperature because there are several initialization steps that occur before the test data begins recording but after the furnace heating elements have turned on. For the test apparatus used at NSWCCD, this observation is likely due in part to the location of the control thermocouple. As shown in **Figure 12**, it is situated on the underside of the furnace tube in close proximity to the heating elements and therefore experiences a rapid temperature rise that is not attained within the specimens inside of the tube.

The test duration requirements given above (*e.g.*, 21 min. at 400 °C [752 °F]) originate from Table 4 of ISO 3690, which lists the minimum holding times "at a given temperature" and therefore implies that the clock for hydrogen evolution should start when the specimen, rather than the furnace, actually reaches the intended test temperature. As such, it is recommended that an allowance for specimen heating and thermal equilibration be included in the total test duration for hot extraction and direct specimen temperature measurement be used to determine an appropriate allowance.

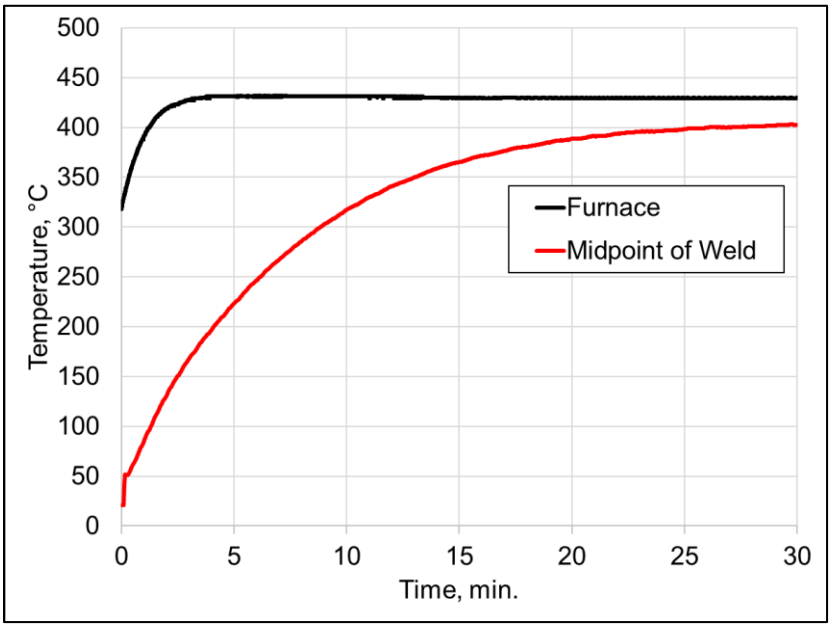

Figure 11. Temperature as a function of time for the furnace a specimen during a hot extraction thermal cycle to a programmed peak temperature of 430 °C (806 °F). Furnace appears to have equilibrated at the peak temperature in approximately 3 min.

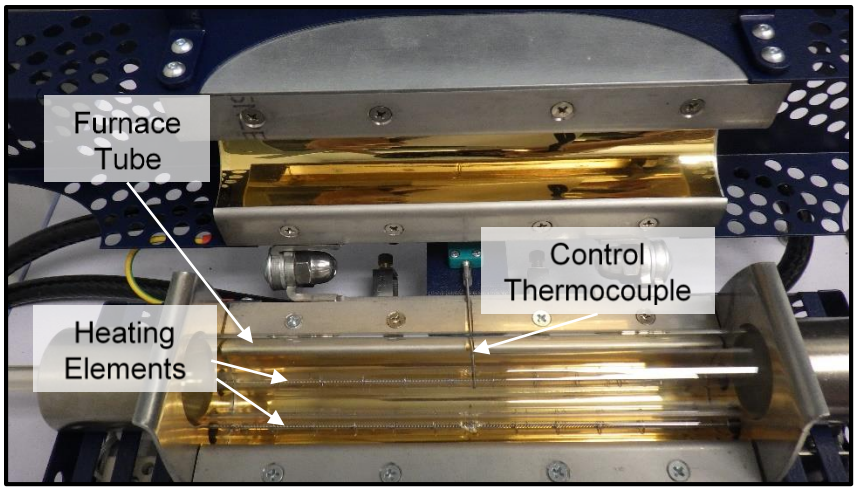

Figure 12. Heating chamber layout for the Bruker G4 Phoenix, showing location of the control thermocouple relative to the heating elements and furnace tube.

Effect of Specimen Orientation

Having noted the thermal behavior described above and the location of the heating elements in the G4 Phoenix relative to the furnace tube, the effect of a specimen's orientation on its temperature profile was investigated. Thermal measurements were taken in duplicate from two orientations: weld facing the top of the tube (the typical orientation) and weld facing the bottom of the tube. Assessing this variable by changing specimen orientation was favored over simply using the temperature data from the thermocouples on the non-welded side of the specimen because it was thought that differences in the surface area, distribution of mass, and geometry on the welded side could play a role in the thermal response.

The results of these trials are shown in **Figure 13**. **Figure 13** is identical to **Figure 10** but now includes the previously unreported information about specimen orientation. As shown, the equilibrium temperature at the midpoint of the weld is approximately 10 °C (18 °F) higher when the weld faces the bottom of the furnace (*i.e.*, facing the heating elements). Per Table 4 of ISO 3690, specimen temperature variations of as little as 10 °C (18 °F) can change the test duration requirement, so if a hot extraction test apparatus uses asymmetric heating, specimen orientation should be consistent across all specimens in a test series and consistent with the orientation used to assess heating profiles and select programmed peak temperatures.

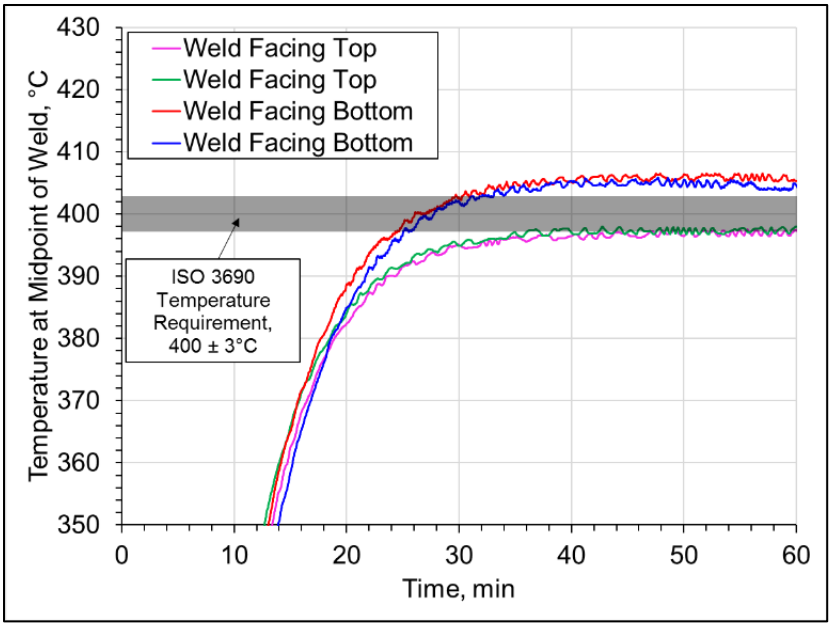

Figure 13. Specimen temperature as a function of time and orientation for 80 mm (3.15 in.) long specimens prepared in accordance with AWS A4.3 and heated to a programmed peak temperature of 430 °C (806 °F), showing the effect of specimen orientation on heating behavior.

Longitudinal Thermal Gradients

In order to assess whether the flow of room temperature carrier gas over the surface of diffusible hydrogen test specimens would significantly change its temperature, the data collected in the orientation experiments described above was reevaluated in terms of the thermocouple location along the length of the specimen. **Figure 14** shows the longitudinal temperature variation in the same four samples described by **Figure 13**. Two observations can be taken from this figure. First, when positioned with the weld facing the top of the furnace tube, specimen temperature decreases monotonically from the end of the specimen that faces the rear of the furnace tube toward the end of the specimen that faces the front. The front of the test apparatus at NSWCCD is the end from which carrier gas is injected into the tube, so cooler temperatures toward the front of the specimen are consistent with flow of incompletely heated gas across its surface. The magnitude of this temperature variation is about 5 °C (9 °F), so it is containable within the ± 3 °C (5 °F) temperature variation allowed by ISO 3690.

Second, the data in **Figure 14** indicate substantially more temperature variation along the specimen when oriented facing the bottom of the furnace. For both tests in that orientation, the middle of the specimen experienced the highest temperature and the front end experienced the coolest. The difference between the minimum and maximum temperatures in these specimens was 10 to 15 °C (18 to 27 °F), which would not be within the temperature bounds of ISO 3690. It is likely that the lowest temperature occurred at the front because of the carrier gas flow, but reason for the overall wider variation and the high temperature in the middle of the specimen is less clear.

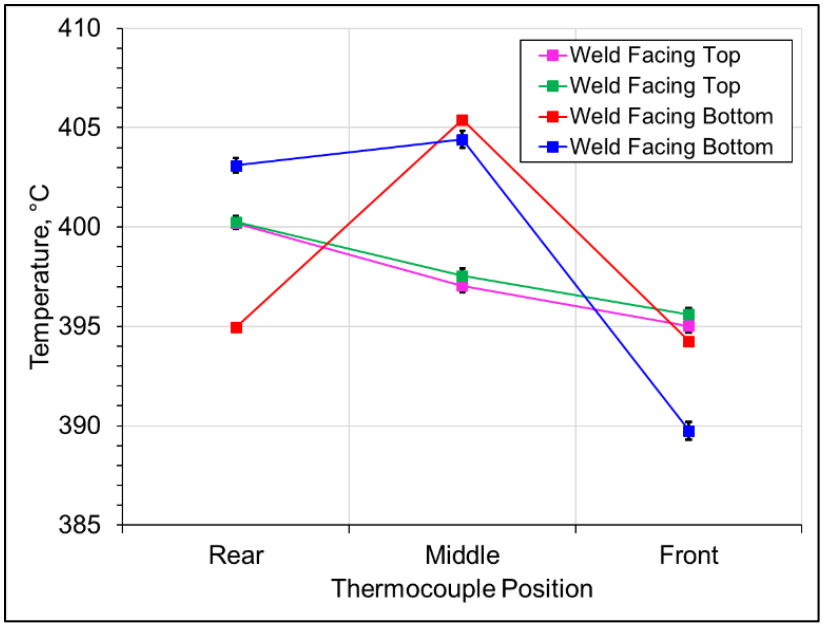

Figure 14. Specimen temperature as a function of position and orientation for 80 mm (3.15 in.) long specimens prepared in accordance with AWS A4.3 and heated to a programmed peak temperature of 430 °C (806 °F), showing the effect of position and orientation on equilibrium temperature. Temperature values are an average of 20 data points (40 sec.). Error bars are one standard deviation. Carrier gas inflow is from the front end of the furnace.

Starting Temperature of the Furnace

Finally, since the hot carrier gas extraction method allows rapid throughput of specimens, the effect of beginning a test with the furnace at room temperature (*e.g.*, as at the start of a workday) versus beginning it with the furnace at elevated temperature (*e.g.*, between specimens in a test series) was investigated. Rhode and coworkers noted that starting furnace temperature significantly increased specimen heating rate and therefore decreased hydrogen effusion time, especially when their apparatus's furnace tube was preheated to above the target test temperature [11]. However, they used a different apparatus than was employed in this work, and more importantly, they investigated specimens that were much smaller (3 mm [0.13 in.] diameter cylinders) than those investigated here.

Figure 15 shows the heating profile of 80 mm (3.15 in.) long 12.7 mm (0.50 in.) thick specimens tested using initial furnace temperatures of approximately 25 and 250 °C (77 and 482 °F). Because of the rapid cooling of the furnace at the completion of a test and the time required to get the next specimen in place, 250 °C (482 °F) was the maximum practical starting temperature that was achieved. As shown, there is very little difference in the heating behavior with initial furnace temperature. These results are ultimately unsurprising because of how rapidly the apparatus itself heated to the programmed temperature. As shown in **Figure 11**, only about 3 min. were required for the unit to consider itself fully heated, and the temperature at the start of data recording exceeded the 250 °C (482 °F) inter-specimen temperature investigated here. This, in combination with the logistical difficulty of decreasing the specimen exchange time to a point

where the furnace start temperature was much higher than 250 °C (482 °F), leads to the view that the effect of furnace starting temperature on diffusible hydrogen measurements via hot extraction is likely negligible.

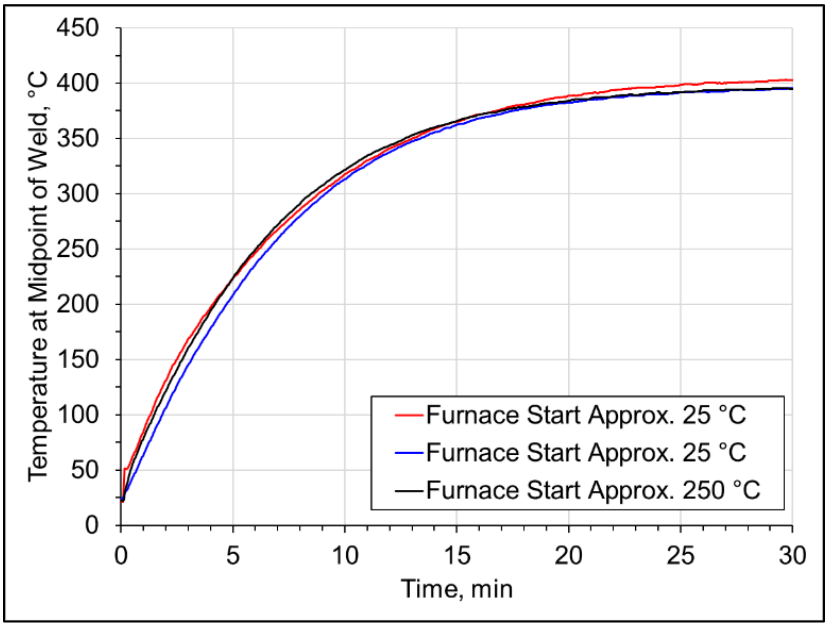

Figure 15. Specimen temperature as a function of time and starting furnace temperature for 80 mm (3.15 in.) long specimens prepared in accordance with AWS A4.3 and heated to a programmed peak temperature of 430 °C (806 °F), showing the minimal influence of initial furnace temperature on specimen heating behavior.

CONCLUSIONS

Based on the data presented here, the following conclusions are made:

1. The duration of testing required by ISO 3690 for diffusible hydrogen evolution via hot extraction at 400 °C (752 °F), if taken as beginning from the start of a test or the point at which the apparatus reports that it has reached the test temperature, is insufficient. Errors in diffusible hydrogen measurement because of this become larger as the hydrogen content of the tested material increases.

2. For longer test durations (*i.e.*, lower test temperatures), the times prescribed by ISO 3690 may be sufficient to evolve nominally all hydrogen from the specimens, but the effect of noise in the data on the measured hydrogen content can become significant.

3. Saturation of the Bruker G4 Phoenix TCD detector by materials containing very large amounts of diffusible hydrogen does not appear to be a concern for the hot extraction method because of the gradual evolution of hydrogen associated with the method.

4. The actual temperature reached by test specimens during hot extraction may not coincide with the programmed furnace set point for a given diffusible hydrogen analyzer.

5. A primary cause of the problem identified in Conclusion 1 is the lag in specimen heating with respect to the furnace chamber.

6. Asymmetry of the heat source in a hot extraction apparatus may cause significant temperature differences between different surfaces of the test specimen.

7. The flow of carrier gas across the welded surface of hot extraction specimens may induce a longitudinal temperature gradient in the specimen that affects conformance of specimen temperature to ISO 3690 requirements.

8. Increasing the furnace temperature at the beginning of a hot extraction test from 25 to 250 °C (77 to 482 °F) does not appear to have a significant impact on the heating behavior of specimens.

RECOMMENDATIONS

Based on this work, the following recommendations are made for use of the hot carrier gas extraction method for the measurement of diffusible hydrogen in steel weld deposits:

1. Periodic evaluation of the heating behavior of the standard diffusible hydrogen specimen (*e.g.*, via a specimen instrumented with thermocouples) should be considered to ensure that correct combinations of temperature and soak time for a selected programmed furnace temperature are developed and followed.

2. For a given apparatus, specimen size, and material, the lag between the apparent furnace temperature and the specimen temperature should be characterized so that an allowance can be added to the test duration to help ensure that nominally all diffusible hydrogen evolves from a test specimen during hot extraction.

3. A 90 min. soak duration at a specimen temperature 400°C (752 °F) is likely sufficiently long to evolve nominally all of the diffusible hydrogen from weld deposits containing 3 to 50 mL/100 g of diffusible hydrogen.

4. Smoothing or other mathematical treatment of data curves may be necessary to mitigate significant effects of data noise on measured diffusible hydrogen values during longer term (greater than 1 hr.) tests.

5. It is recommended that specimen orientation be held constant throughout a hot extraction test series and coincide with the orientation used to establish specimen heating behavior.

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