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A Critical Evaluation of the Glycerin Test

Constituents other than hydrogen are present in gas collected during testing, and variations in glassware shape and size dramatically affect gas volumes actually collected

BY M. A. QUINTANA

ABSTRACT. In recent years there has developed a rising interest in the measurement of the diffusible hydrogen content of weldments. As a result, the glycerin test has been adopted as a standard test method for diffusible hydrogen measurement throughout the welding industry. However, recent work has revealed that test results are of questionable validity. Analyses of the gas collected utilizing this technique indicate that constituents other than hydrogen are present in significant proportions and that those proportions exhibit significant variation. In addition, variations in hardware shape and size can dramatically affect the gas volume actually collected.

This paper discusses these problems in detail and identifies the probable causes. Among the items discussed are the solubility properties and purity of the glycerin bath, the effect of environmental factors on the bath, the effect of sample preparation and handling on test results, and the size and shape of glassware.

Introduction

For years it has been recognized that hydrogen present as an interstitial impurity has an adverse effect on the mechanical properties of steels. Frequently, hydrogen uptake, resulting in a degradation of properties, occurs during processing. For welded structures, hydrogen uptake occurs as a result of dissociation of hydrogen gas and hydrogen-containing compounds during welding which produces atomic hydrogen in the arc atmosphere. Some common sources of hydrogen are moisture contained in SMA (shielded metal-arc) electrode coatings, lubricants on solid and cored wires, and moisture and other contaminants present in shielding gases.

Because of the detrimental effects of hydrogen uptake during welding, considerable effort has been devoted to the control of the hydrogen potential of welding consumables and processes. This has been achieved, in part, through the careful selection of lubricants for drawing operations and an increased emphasis on cleanliness and control of contaminants. Perhaps the greatest effort has been expended for SMA electrodes where the control of weld metal hydrogen levels has been achieved through minimization of coating moisture levels (Refs. 1-3).

This approach is reasonable for covered electrodes, since the coating moisture does contribute to the hydrogen content of the resulting deposit (Refs. 3, 4). However, there are limitations. Since the relationship between coating moisture and hydrogen content can vary significantly with electrode type (Ref. 3), a given coating moisture level can result in a wide range of weld metal hydrogen contents depending upon the coating system. It, therefore, becomes necessary to evaluate the actual hydrogen content of the deposit. When considering a process such as FCAW (flux cored arc welding) or GMAW (gas metal arc welding), indirect tests have limited meaning (Ref. 5), and the hydrogen content of the deposit must be measured directly.

Diffusible Hydrogen Measurement Tests

Several tests have been developed for the direct measurement of weld metal diffusible hydrogen content. The diffusible hydrogen content is that portion of the total hydrogen content which is evolved rapidly from a sample at or near room temperature. Two widely accepted methods for measurement are very similar in that they involve the use of a collecting fluid (Refs. 6, 7). Welded specimens are allowed to degas in some form of eudiometer tube filled with fluid. Evolved gases are collected in the upper portion of the tube over the fluid and the volume is measured. Results are reported as the volume of gas collected per unit mass of weld deposit.

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M. A. QUINTANA is a Welding Metallurgist, Electric Boat Division, General Dynamics, Groton, Connecticut.

Individual test procedures differ in the size and preparation of welded samples and in the collecting fluid used; however, the principle of operation is the same. In one case, mercury is used as the collecting fluid (Ref. 6), and the specimen is allowed to degas at room temperature. In the other case, glycerin is used as the collecting fluid (Refs. 7, 8). This test involves placing a welded specimen in a glycerin filled eudiometer tube immersed in a glycerin bath maintained at 45 ± 3°C (113 ± 5.4°F). As the specimen degases, bubbles pass up through the glycerin and collect in the upper, calibrated portion of the eudiometer. The volume of gas collected is measured and normalized by the mass of the weld deposit.

Glycerin Test Problems

Due to the health hazards associated with the use of mercury, the glycerin test has been widely used in the United States. As a result, the glycerin test has become an accepted standard by which welding consumables are evaluated (Ref. 8). However, rather serious problems with the glycerin test have been reported (Refs. 9-16). It has been demonstrated that diffusible hydrogen levels determined by the glycerin method are consistently lower (~50%) than comparable mercury test values (Refs. 9, 10, 13, 16). The obvious implication is that the glycerin test does not recover all of the evolved hydrogen. In addition, glycerin test results have been shown to exhibit far more scatter than comparable mercury test results (Ref. 9).

Recent investigations have also pointed out other problems associated with the glycerin test. Analysis of the gas collected over glycerin conducted during this investigation indicates that gases other than hydrogen are present in the gas sample in significant proportions, making the validity of the glycerin test questionable. Other researchers have reported similar results (Refs. 14, 15).

Procedural variations are likely responsible for some of the observed problems with the glycerin test. Two procedural variables of concern are the heating of base material prior to welding and the time elapsed between completion of welding and quenching. Prior heating of the base material is thought to liberate any hydrogen present in solution which might contribute to the weld metal diffusible hydrogen content (Ref. 9). The expected result is a reduction in the amount of hydrogen evolved by the specimen.

The time elapsed between completion of welding and quenching is believed to be important from the standpoint of diffusion (Refs. 9, 17). Since diffusion rates are higher at elevated temperatures, appreciable amounts of hydrogen can be lost to the atmosphere if sufficient time is available prior to quenching. Therefore, one would expect a greater amount of hydrogen evolved from the welded specimen while immersed in the glycerin if the time elapsed to quenching is kept to a minimum.

Other variables of concern are related to the condition of the glycerin bath itself. Glycerin, upon exposure to the atmosphere, readily absorbs a variety of gases including water vapor, oxygen, and nitrogen. Even though a glycerin test assembly is initially assembled with relatively pure glycerin, it does not necessarily remain in that condition indefinitely. Further, it is possible that contaminants absorbed by the glycerin bath are responsible for contamination of the hydrogen collected over glycerin during testing (Refs. 14, 15). To further complicate the situation, the solubility of hydrogen in glycerin (Refs. 18, 19) can result in the loss of hydrogen evolved from the test specimen to the bath through dissolution. The extent to which dissolution occurs is affected by the water content of the glycerin (Refs. 18, 19), which can be appreciable after extended periods of time.

Investigation Objectives

As a result of the problems described above, the results obtained using the glycerin test are not reproducible between laboratories (Ref. 20) and are of questionable validity. The fact that such results are used as acceptance criteria for welding consumables is of tremendous concern. Because of this, a thorough evaluation of the glycerin test is in order. It is the intent of the investigation described in this paper to characterize some of the problems which are inherent in the glycerin test and to identify their probable causes.

Experimental

Specimens fabricated under identical conditions should, within reason, result in the same amount of diffusible hydrogen per unit mass of weld deposit. With the hydrogen content maintained relatively constant for a series of tests, other conditions can be selectively varied in order to determine what impact they have on the volume and composition of the collected gas. To demonstrate this, several tests were conducted. Initially, using the flux cored arc welding (FCAW) process, the effect of glassware size and shape was demonstrated. Subsequent testing using the spray gas metal arc welding (GMAW) process demonstrated the effects of base material pretreatment, elapsed time to quench, and water content of the glycerin bath. In addition, a series of tests was conducted simultaneously with the GMAW tests to illustrate other factors which affect the composition of gas samples.

The chemical compositions of base materials and filler materials used during this investigation are presented in Table 1. The glycerin used was 99% pure,

Table 1—Summary of Chemical Analyses of Base Materials and Filler Metals, Wt-%

	C	S	P	Si	Mn	Cr	Ni	Cu	Mo	V	Zr	Specification
Base material for FCAW and first of GMAW tests	.22	.013	.012	.12	.79	.04	.04	.03	.02	.002	<.001	QQ-S-741 SIM. to ASTM A36
Base material GMAW tests at 11.2% water content	.21	.017	.004	.11	.80	.04	.06	.09	.01	.01	<.001	QQ-S-741 SIM. to ASTM A36
Base material GMAW tests at 18.3% water content	.21	.015	.003	.11	.76	.04	.05	.04	.01	.006	<.001	QQ-S-741 SIM. to ASTM A36
Base material GMAW tests at 23.5% water content	.21	.015	.003	.11	.79	.04	.06	.04	<.01	.006	<.001	QQ-S-741 SIM. to ASTM A36
FCAW deposit from buildup pad	.07	.011	.007	.25	.74	.03	2.57	.02	.01	.016	–	SIM. to MIL-E 24403/1B, type MIL-81T1-Ni2
GMAW deposit from buildup pad	.06	.003	.006	.43	1.10	.07	2.03	–	.43	.004	<.001	MIL-E-23765/2, type MIL-100S-1

commercial grade purchased from Brand-Nu Laboratories, Meriden, Connecticut, and was contained in a large fiberglass tub, 508 × 508 × 254 mm (20 × 20 × 10 in.). The bath temperature of 45°C (113°F) was maintained, utilizing a quartz immersion heater, mixer, and thermostat. In addition, a thermometer was mounted in the bath adjacent to the eudiometer tubes to verify proper operation of the thermostat. The procedure for conducting all glycerin tests was extracted with some modification from MIL-S-24403A (Ref. 8) and is outlined in Appendix A.

FCAW Tests

Each glycerin test consisted of 4 individual specimens, each placed in separate eudiometer tubes. The first set of tests utilized handmade glassware, fabricated by fusing ~5.5 mm (0.22 in.) ID, 127.0 mm (5.0 in.) long burrettes to the tops of 59.2 mm (2.3 in.) ID, 254.0 mm (10.0 in.) high bell jars. The second set of tests utilized factory made glassware having a 46.5 mm (1.8 in.) ID, 210 mm (8.3 in.) high bell portion and a 10.8 mm (0.43 in.) ID, 127.0 mm (5.0 in.) high calibrated portion. (See illustrations in Appendix B.)

Using the factory made glassware, 40 additional specimens were tested in sets of 4 over a period of 10 weeks in order to determine the reproducibility of the test. All specimens for this portion of the investigation were fabricated using the same welding conditions, *i.e.*, 24.5-25.0 arc volts (V), 150-160 amperes (A), 1.9 mm/s (4.4 ipm) travel speed, 75% Ar and 25% CO_2 by volume shielding gas at 18.9 L/min (40.0 cfh) gas flow rate.

GMAW Tests

Due to the high degree of scatter experienced with the FCAW tests, it was decided that 4 specimens tested at once did not represent an adequate statistical sample. Therefore, 12 individual specimens were welded for each subsequent test.

Since GMAW is an inherently low hydrogen process, the hydrogen potential of the process was elevated and maintained by introducing hydrogen in the shielding gas. The resulting gas composition was 1% H_2, 4.6% CO_2, 94.4% Ar by volume. This approach was taken in order to maintain the hydrogen potential at a relatively constant level for all tests. Starting with new, uncontaminated glycerin, three sets of specimens were tested over a three-week period in order to provide a broad data base for comparison with the FCAW tests and other GMAW tests.

A fourth set of specimens was fabricated using pretreated base material. The pretreatment involved heating at 700°C (1292°F) for 1 hour (h). The fifth set of specimens tested represented a shorter elapsed time between completion of welding and water quench. Specimens in this set were quenched within 5 seconds(s) of extinguishing the welding arc. In all other cases, 25-30 s were allowed to elapse between completion of welding and water quench. All specimens for the GMAW tests were welded using the same conditions (26-26.5 arc volts, 320-340 A, 5.1 mm/s (12 ipm) travel speed, 21.2 L/min (45 cfh) gas flow rate).

In order to determine the effects of glycerin water content, an additional set of 12 specimens was tested at each of 5 levels: 4.2%, 8.9%, 11.2%, 18.3%, and 23.5% water by volume. All specimens were welded under the conditions previously stated. Water content of the bath was determined by gas chromatography, using a Hewlett Packard 5750 Gas Chromatograph equipped with a thermal conductivity detector. It contained dual 6 ft (1.83 m) stainless steel columns packed with 80/100 mesh Poropak Q (Supelco; Bellefonte, Pa.); the OD of each column measured ⅛ in. (3.2 mm) while the ID was 2 mm (0.08 in.).

Gas Analyses

At the completion of each GMAW test, gas samples were recovered from the eudiometer tubes for analyses. In order to obtain enough gas to perform an analysis, the gas collected over several individual specimens was combined as a single sample.

In all, 2 or 3 samples were retrieved for each set of 12 specimens. Gas was transferred from the eudiometer tubes to vials capped with septums that had been immersed in the glycerin bath. These samples were then analyzed using gas chromatography.

The unit used for all gas analyses was Carle Instruments Co. GC-8700, Basic Gas Chromatograph equipped with a thermal conductivity detector. It contained dual 6 ft (1.83 m) stainless steel columns (⅛ in. or 3.2 mm OD, 2 mm or 0.08 in. ID) packed with molecular sieve 5A. These columns were supplied with the instrument when purchased. Argon carrier gas was used for all analyses.

"Hydrogen Injections"

In order to demonstrate, qualitatively, the effect of time on the composition of the gas collected over glycerin, tests were performed whereby pure hydrogen was bubbled through the glycerin contained within an eudiometer tube. This was accomplished by the injection of hydrogen from a gas tight syringe. Gas collected at the top of each of two eudiometer tubes was recorded and analyzed as previously discussed.

In one case, the gas was transferred to a vial and analyzed immediately after collection in the top of the tube. In the second case, gas was allowed to remain in contact with the glycerin in the eudiometer tube for the entire 48 h test period before recovery and analysis.

All "hydrogen injection" testing was performed in conjunction with three of the GMAW test series by placing two additional eudiometer tubes in the glycerin bath for injections.

Table 2—Summary of FCAW Glycerin Test Results

Test no.	Gas Collected Per 100 g Deposit (average of four), mL	Range, mL
FCAW 1	4.7[a]	3.6-6.5
FCAW 2	6.6	5.6-7.3
FCAW 3	10.3	5.8-13.8
FCAW 4	4.4	3.2-5.0
FCAW 5	4.0	3.4-4.6
FCAW 6[b]	3.8	3.4-4.0
FCAW 7	4.7	4.3-5.6
FCAW 8	5.5	4.5-6.2
FCAW 9[b]	5.0	4.3-5.7
FCAW 10[b]	5.3	3.8-6.8
FCAW 11[b]	4.6	3.5-6.8
FCAW 12	3.1	1.9-3.8

[a]The handmade glassware was used for this test. Machine made glassware was used for all other tests.
[b]Gas collected after completion of these tests was analyzed and found to contain the following: FCAW 6 – 65.5% H_2, 4.5% O_2, 30.0% N_2 by volume; FCAW 9 – 55.6% H_2, 6.4% O_2, 37.2% N_2 by volume; FCAW 10 – 61.8% H_2, 7.7% O_2, 26.9% N_2, 3.6% CO_2 by volume; FCAW 11 (2 gas samples) – 66.8% H_2, 7.4% O_2, 25.8% N_2 and 57.6% H_2, 8.8% O_2, 33.6% N_2 by volume.

Results and Discussion

The FCAW tests were performed to illustrate qualitatively some of the inherent difficulties with the glycerin test and to establish a data base large enough to evaluate the dispersion of test results. Glassware size and shape were the first items of concern.

Table 2 lists all results of this phase of the investigation. FCAW 1 represents handmade glassware having a small neck and a wide bell. FCAW 2 represents machine made glassware having a slightly wider neck and narrower bell. The volume of gas collected using handmade glassware is ~30% lower than that

obtained using the machine made glassware.

At the end of the 48 hour period, the volume of gas collected was read and recorded. However, this did not include the volume in the gas bubbles which adhered to the steel specimen or attached to the glass surface or were entrained in the glycerin. This can account for a significant volume of gas, the magnitude of which depends on the size and shape of the glassware employed. Passage of bubbles up through the glycerin is slow (Ref. 13) because of the relatively high viscosity of glycerin. Consequently, currents set up by the flow of bubbles can easily deflect the rising bubbles and direct them away from the upper portion of the tube.

In the case of FCAW 1, the neck region was relatively small, making passage of bubbles difficult. It was observed during testing that this was an area of severe congestion. Bubbles accumulated there and would break free to rise only after extended periods of time (several hours). This "bottle-necking" interrupted the movement of following bubbles which would then impinge and adhere either to the bottom of the pileup or to the adjacent glass surface.

Bubbles adhering to the glass surface were predominantly located in the shoulder area of the bell jar where they appeared to remain for the duration of the test. Also, in the case of FCAW 1, the shoulder area was slightly larger than in the case of FCAW 2, allowing the collection of more bubbles in this region and making it more difficult for those bubbles to move any further. The wider necked glassware employed for FCAW 2 completely eliminated the congestion previously observed, and the narrower and more tapered shoulder visibly reduced the accumulation in this area. This resulted in more of the evolved gas reaching the calibrated portions of the tubes for FCAW 2.

It should be noted that more scatter was experienced with FCAW 1 results than with FCAW 2 results. This is believed to be caused by the inconsistent glassware shape for FCAW 1. Pronounced irregularity existed in the shoulder areas with no two pieces of glassware being exactly the same. Those having more tapered shoulders would trap less gas in this area while flatter shoulders would trap more. This may account for the higher degree of scatter within the FCAW 1 results. Note that comparison is made only between FCAW 1 and FCAW 2 results because these tests were performed consecutively. Since several weeks elapsed between FCAW 1 and FCAW 3, comparison between the first two tests and any others would be questionable because of possible changes in glycerin purity.

Tests FCAW 3 through FCAW 12, welded using the same conditions as the previous two tests resulted in significant variation in test results. The averages ranged from 3.1 to 10.3 mL/100g for the same package of welding electrode. For the 40 specimens, this produced an average value of 5.3 mL/100g with a standard deviation of 2.2 mL/100g (±42%).

Although some variation can be expected for a flux cored electrode, it is unlikely that variation of the magnitude experienced would result from inconsistencies within a single package. Analyses of the collected gas for FCAW 6, 9, 10, and 11 indicated that the gas collected over glycerin was not entirely hydrogen and that extraneous gases were present in significant quantities. Oxygen and nitrogen were found in all cases in varying concentrations. A small amount of CO_2 was detected for FCAW 10. Considering that the glycerin test apparatus is exposed to the atmosphere for extended periods of time and that oxygen and nitrogen are soluble in glycerin (Refs. 18, 19), the most likely source of these components in the gas samples was the glycerin itself.

In general, the FCAW tests raised many questions. The importance of using standardized and properly sized glassware was established. However, the wide scatter of test results and the presence of gases other than hydrogen established a need to further investigate the suitability of the glycerin test, itself.

Since the hydrogen potential of the flux cored wire used could have changed significantly during storage between tests, the wide scatter in test results was likely due to a combination of changing hydrogen content and changing test conditions. In order to accurately monitor the effects of changing test conditions, the hydrogen potential of the welding process would have to be more carefully controlled. To accomplish this, the GMAW process was selected for subsequent testing. Hydrogen potential could be held relatively constant by controlled addition of hydrogen to the shielding gas during welding. Any changes in measurements could then be attributed primarily to the specific variables being evaluated.

Table 3 summarizes the data obtained from the first GMAW tests. GMAW 4 and 5 illustrate the effect of base material pretreatment and elapsed time to quench on test results. For no pretreatment and a 25-30 s time to quench, the average value is 6.8 mL/100g with a standard deviation of 1.8 mL/100g. The result of base material pretreatment is to shift the entire range of values to a lower level. Pretreated specimens produced an average of 5.1 mL/100g with a standard deviation of 1.7 mL/100g. It is clear from these results that the base material can contribute to the amount of collected gas and that this contribution can be reduced by heating of base material prior to welding.

As shown in Table 3, no significant change in the volume of gas collected results from the reduction in elapsed time to quench. During the first three tests, 25-30 s were allowed to pass before welded specimens were water-quenched. Initially, it was thought that allowing this period of time to pass would have resulted in some loss of hydrogen from the specimen due to diffusion at an elevated temperature. If less time were allowed to elapse, less hydrogen would

Table 3—Summary of GMAW Test Results—Base Data, Effect of Pretreatment, Effect of Time to Quench

Test no.	Gas Collected per 100 g deposit (average of 12 unless otherwise noted ±std. dev.), mL/100 g	Range, mL/100 g	Gas analysis vol-% mL/100 g	Composition H_2	O_2	N_2	Time to Quench, seconds	Base material Pretreatment	Age of bath, weeks
GMAW 1	7.4 ± 1.3	5.4	7.4	64.4	7.2	28.4	25-30	None	1
(avg. of 4)		−8.8	7.4	63.8	7.6	28.6			
GMAW 2	7.7 ± 1.8	4.4	7.7	68.3	5.3	26.4	25-30	None	2
		−9.7	7.7	69.0	6.2	24.8			
GMAW 3	5.7 ± 1.4	3.3	5.8	64.1	5.5	30.4	25-30	None	4
		−7.8	5.8	66.3	4.8	28.9			
GMAW 4	5.1 ± 1.7	1.6	4.6	49.2	8.5	42.3	25-30	700°C	5
		−7.8	5.5	51.7	7.6	40.8		For 1 hour	
GMAW 5	5.6 ± 0.4	5.0	6.1	58.1	5.4	36.5	≤5	None	6
		−7.6	5.6	55.7	5.7	38.6			

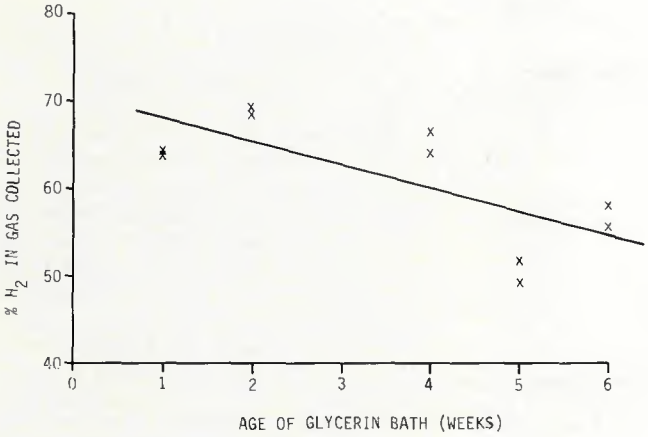

Fig. 1 — Hydrogen content of gas collected vs. age of bath

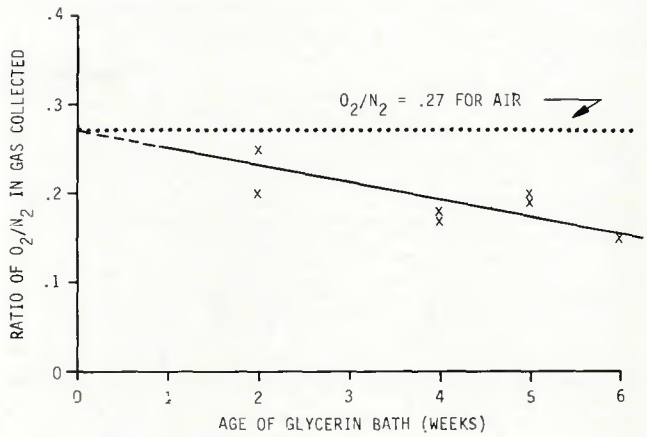

Fig. 2 — Oxygen/nitrogen ratio vs. age of bath

be lost and a higher test result would be expected.

Results from GMAW 5 indicate that, if this effect occurs at all, it is not significant for time elapsed less than 30 s. The average for ≤5 s time-to-quench is 5.6 mL/100g with a standard deviation of 0.4 mL/100g. Although this is 1.2 mL/100g lower than for the 25-30 s case, the difference in average values must be considered insignificant because the range of values for the ≤5 s test falls entirely within the range for the 25-30 s tests. It should be noted that the dispersion of values is far less for the ≤5 s tests than for the 25-30 s tests. It is not reasonable to expect that this should have occurred simply as a result of time to quench. Variation in scatter is believed to be caused by other variables in the system.

Results of gas analyses for GMAW 1 through GMAW 5 are presented in Table 3 and Figs. 1 and 2. The hydrogen content of the collected gas samples varies between 50% and 70% by volume, the balance of each being composed of oxygen and nitrogen in varying proportions. The trend established in Fig. 1 indicates that the hydrogen content of the gas collected is highest when the bath is relatively new and decreases as the bath ages. As with the hydrogen content, Fig. 2 demonstrates that the relative proportion of oxygen to nitrogen given by the $\%O_2/\%N_2$ ratio steadily decreases as the bath ages.

A plausible explanation for the presence of oxygen and nitrogen in the gas collected over glycerin is based on the well established solubility of these gases in glycerin (Refs. 18, 19). If glycerin is exposed to atmosphere, as in the case of this test, dissolution of gases will continue until some steady state is reached. The composition of any volume of gas held over the glycerin should reflect the presence of these dissolved gases and would be expected to change in response to changes in glycerin composition caused by dissolution at the glycerin/atmosphere interface.

Based upon the fact that the gas evolved from the welded specimens is hydrogen (Refs. 21, 22), the bubbles formed at the specimen surface can be assumed to be composed solely of hydrogen. Since glycerin will contain oxygen and nitrogen due to dissolution at the glycerin/atmosphere interface and since hydrogen is also soluble in glycerin (Refs. 18, 19), it is reasonable to expect that some transfer of gases across the hydrogen bubble/glycerin interface will occur. The driving force for this transfer is the difference in chemical potentials between the gas and liquid phases.

Thermodynamics requires that, for equilibrium, the chemical potential of a component in the liquid phase must equal the chemical potential of that component in the gas phase in contact with the liquid (Ref. 23). Initially, it is assumed that gas bubbles formed contain no oxygen or nitrogen; therefore, their corresponding chemical potentials in the gas phase are zero. The corresponding chemical potentials in the liquid phase have some finite values based on the composition of the glycerin. This indicates that a transfer of oxygen and nitrogen from the liquid to the gas would be expected. Similarly, the chemical potential of hydrogen in the gas phase is initially higher than it is in the liquid phase (if the liquid is not saturated), and one would expect a transfer of hydrogen from the gas to the liquid. The net result is that the bubbles evolved from the welded specimens will lose hydrogen and become contaminated with oxygen and nitrogen.

It is essential to note that the ratio of oxygen to nitrogen in the gas collected is not constant and behaves predictably. Initial dissolution of atmospheric gases in glycerin should reflect the relative proportions of oxygen and nitrogen in the atmosphere. As dissolution continues with time, this ratio of oxygen to nitrogen may change owing to preferential dissolution of one component relative to another. These changes should be reflected in the composition of the gas collected over the glycerin inside the tube. This effect is demonstrated in Fig. 2. The ratio of oxygen to nitrogen steadily decreases with time. When the line is extrapolated back to zero time, the ratio is 0.27, precisely the ratio for air.

The extent to which the transfer of gases occurs will depend upon the time available for the process and the surface to volume ratio of the gas phase. The effect of time is obvious: gas transfer across the interface will continue with time until equilibrium is achieved. The effect of surface to volume ratio is more subtle. Consider for example, that 4 mL of hydrogen are evolved from a specimen. If the bubbles produced are ~1 mm (0.04 in.) in diameter, the surface to volume ratio is ~60 cm^{-1}. If the bubbles produced are ~.5 mm (0.02 in.) in diameter, the surface to volume ratio is ~120 cm^{-1}. In the latter case, there is more surface available for the transfer of gas. Consequently, more gas transfer will occur if bubbles are very small and the time spent in contact with the liquid is long.

In the glycerin test, conditions exist which impede the movement of bubbles and increase the time that they spend moving through the glycerin. The relatively high viscosity of glycerin results in slow movement of bubbles. Some bubbles collide with and adhere to the glassware, while others become caught in convection currents. All of these factors tend to increase the time gas spends in contact with the liquid as finely dispersed bubbles. This is important, because the gas phase dispersed as small bubbles has a much higher surface to volume ratio than it does after it collects in the calibrated portion of the tube.

The results presented in Table 4 and

Table 4—Summary of Data—"Hydrogen Injection" Series

Test no.	Type of sample	Gas composition, vol-% H_2	O_2	N_2
GMAW 3	Collected over welded specimen[a]	64.1/66.3	5.5/4.8	30.4/28.9
	Injected and removed after 48 h	97.7	Trace	2.3
	Injected and removed immediately	100.0	0	0
GMAW 4	Collected over welded specimen[a]	49.2/51.7	8.5/7.6	42.3/40.7
	Injected and removed after 48 h	94.0	Trace	6.0
	Injected and removed immediately	100.0	0	0
GMAW 5	Collected over welded specimen[a]	58.1/55.7	5.4/5.7	36.5/38.6
	Injected and removed after 48 h	98.8	Trace	1.2
	Injected and removed immediately	100.0	0	0

[a]Two gas samples were analyzed.

Fig. 3 further illustrate the influence of the above mentioned factors on the kinetics of gas transfer. A comparison of gas composition between samples collected over welded specimens and injected samples removed after 48 h illustrates the effect of surface to volume ratio. Welded specimens produce finely dispersed gas bubbles (large surface to volume ratio), whereas injection from a syringe produces a few extremely large bubbles which collect almost immediately in the top of the eudiometer tube (small surface to volume ratio). For each test, high surface to volume samples contain less hydrogen and more oxygen and nitrogen than the low surface to volume samples.

The influence of time is illustrated by a comparison of injected samples removed immediately and injected samples removed after 48 h. In each case, the samples remaining for 48 h contained less hydrogen and more nitrogen than the samples removed immediately. The data qualitatively support the preceding explanation for gas transfer across the gas/liquid interface. These results also indicate that most of the gas transfer occurs at the bubble surfaces rather than at the meniscus formed inside the calibrated portion of the eudiometers. Comparison of the two injected samples for each test confirmed that no significant transfer had occurred while the injected gas rose to the top of the tubes. Comparison of the welded samples with the injected samples for the same test time show that very little transfer occurred at the meniscus for the injected samples after 48 h.

Another factor, which influences glycerin test results, is the water content of the glycerin bath. It is established that glycerin readily absorbs water vapor from the atmosphere (Ref. 18). Since glycerin and water are infinitely soluble in one another (Ref. 24), the amount of water that the glycerin will absorb depends primarily on the relative humidity of the air over the glycerin (Ref. 18). At the end of the FCAW tests, analysis for water content of the glycerin showed an increase from a negligible level to 10% by volume. During the winter months, the relative humidity in the laboratory was typically in the vicinity of 30%, which should result in a water content of ~ 10% by volume (Ref. 18). Since the relative humidity during the summer months ranges from 50 to 60%, a water content of ~25% by volume is expected (Ref. 18).

Because of the variation in glycerin water content with humidity and its possible effect on results, tests were conducted at 5 water contents between 0 and 25% by volume. Results are reported in Table 5 and illustrated in Figures 4 and 5. As the water content was increased to 11.2% by volume, the volume of gas collected increased to a maximum at 10.4mL/100g, accompanied by a corresponding increase in the hydrogen content of the gas samples as shown in Fig. 5. As water content was increased further, there was a decrease both in the volume of gas collected and in the amount of hydrogen present.

Two consequences of the dissolution of water in glycerin are a dramatic reduction in viscosity and an increase in solubility limits for oxygen, nitrogen and hydrogen (Refs. 18, 19). The reduction in viscosity results in a more rapid movement of bubbles through the glycerin, since Stokes law states that velocity is inversely proportional to viscosity. Therefore, the time required for bubbles to reach the top of the eudiometer is directly proportional to viscosity and should be reduced as viscosity is reduced.

Between 4.2% water and 11.2% water, the viscosity drops from ~ 110 centipoise to ~45 centipoise (Ref. 18), reducing the time for bubbles to reach the top by 60%. It would be expected, based on the preceding discussion, that less gas transfer occurs. Therefore, less hydrogen is lost through dissolution resulting in potentially higher gas volume collected and higher hydrogen content of the collected gas samples.

Between 11.2% water and 18.3% water, the change in viscosity is only ~23 centipoise (Ref. 18), reducing the time only by an additional 20%. Although further increases in volume and hydrogen content would be expected, the changes would not be as pronounced as they are in the 4.2–11.2% range and might even be masked by other factors such as gas solubility.

When the water content of the glycerin increases, any steady state or equilibrium which may have developed previously is disrupted and the dissolution process previously outlined proceeds, producing the expected reductions in gas volume collected and hydrogen content. It is believed that when the effect of reduced viscosity begins to level off in the region of 11.2% water, the effects of solubility become dominant producing the drop in volume and hydrogen content evident in Fig. 6.

It is interesting to note that the gas volume and its composition tend to

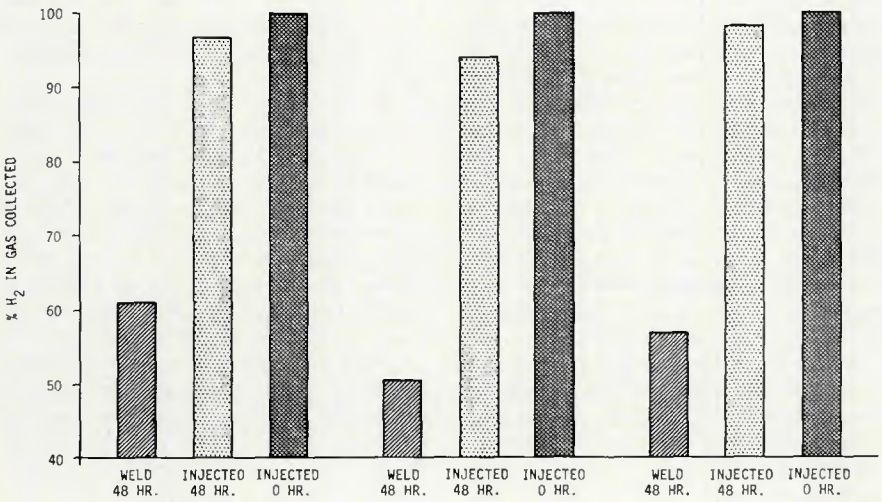

Fig. 3—Illustration of kinetic effects

Table 5—Summary of Data—Effect of Water Content

Test no.	Gas Collected per 100 g Deposit (average of 12 ± std. dev.), mL/100 g	Range, mL/100 g	Gas analysis, vol-% mL/100 g	Composition H_2	O_2	N_2	H_2O in Glycerin, vol-%
GMAW 6	5.8 ± .6	4.7	5.5	56.3	10.0	33.7	4.2
		−6.7	6.2	62.2	8.3	29.5	
GMAW 7	8.3 ± .6	6.8	7.9	59.2	8.8	32.0	8.9
		−9.0	8.3	62.8	7.6	29.6	
GMAW 8	10.4 ± 1.0	8.6	10.7	72.9	6.3	20.8	11.2
		−11.9	10.4	75.4	5.2	19.4	
			10.2	73.4	5.7	20.9	
GMAW 9	7.3 ± 1.4	3.2	7.6	58.1	7.6	34.3	18.3
		−8.8	8.1	60.1	7.0	32.9	
			8.1	62.1	6.2	31.7	
GMAW 10	6.6 ± 1.3	4.7	5.7	59.5	7.4	33.1	23.5
		−8.3	6.7	55.1	6.8	38.1	
			7.4	57.4	6.4	36.2	

increase or decrease simultaneously. Figure 6 illustrates this interdependence for GMAW 6 through 10. As the hydrogen content of the gas samples increases, the volume also increases. As gas transfer is suppressed, less of the hydrogen evolved by the welded specimen is lost through dissolution, producing gas samples of greater volume and higher hydrogen content. Since the data presented in Fig. 6 represent welded specimens which should have had the same actual hydrogen content, it follows that Fig. 6 represents the locus of points representing a single diffusible hydrogen content.

Depending upon the specific conditions of the glycerin test assembly (glycerin water content, glycerin gas content, etc.), the test can produce results ranging from 4.7 to 11.9mL/100g for only one unique diffusible hydrogen content. Because of this wide range produced by normally uncontrolled variables, it is difficult if not impossible to detect changes in actual diffusible hydrogen content using the glycerin test. More important is the fact that it is not possible to determine what the actual weld metal diffusible hydrogen content is without using some other method as a standard (Refs. 6, 21).

It is important to note that other collecting fluids have similar problems and that a simple substitution of an alternate collecting fluid may not correct the problems encountered with glycerin. Other researchers have analyzed the gas collected over various liquids with the following results: glycerin, 79.1–87.8% H_2; distilled water, 58.1–72.4% H_2; ethyl alcohol, 23.1–38.6% H_2; paraffin, 9.5–18.5% H_2; ethylene glycol, 18.1–32.3% H_2; carbon tetrachloride, 9.5–19.6% H_2 (Refs. 14, 15). All concentrations were reported in volume-percent. Very limited work performed in this laboratory with silicone oil resulted in only 5.0–31.5% H_2 by volume in the collected gas.

Conclusion

Some of the problems inherent in the glycerin test have been identified. FCAW test results established the importance of using properly sized and standardized glassware to reduce scatter. The effects of base material pretreatment and time to quench were investigated. Only base material pretreatment was found to have a measurable effect on test results. Any effect of time to quench may have gone undetected due to the overriding influence of transient glycerin conditions such as gas solubility.

Although much of the discussion concerning gas solubility is presumed, the data presented do support the explanations provided. Water content and gas solubility in glycerin are identified as probable causes for many of the problems experienced with the glycerin test as a result of their influence on gas transfer across the gas bubble/glycerin interfaces.

It is important to note that there may be other causes, which did not become apparent during this investigation. These problems cannot be controlled without

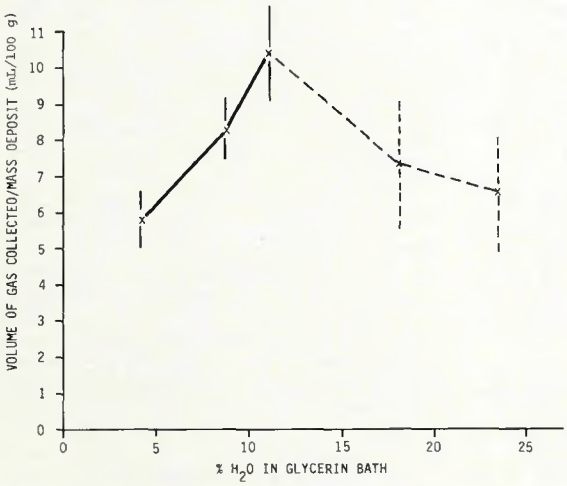

Fig. 4—Effect of bath water content on volume of gas collected

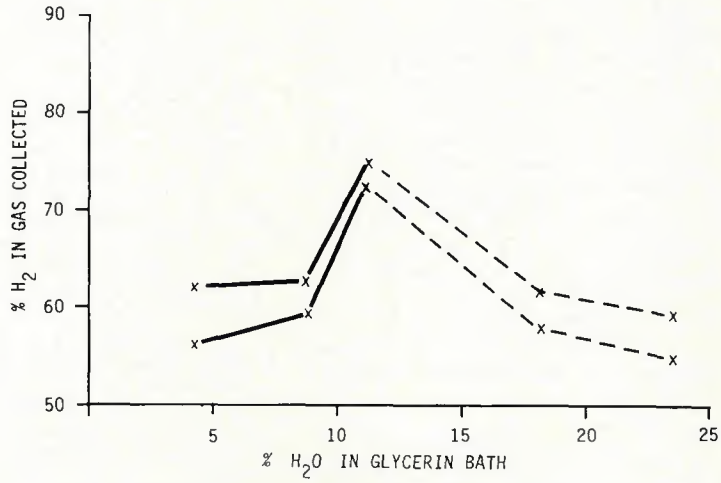

Fig. 5—Effect of bath water content on %H_2 in gas collected

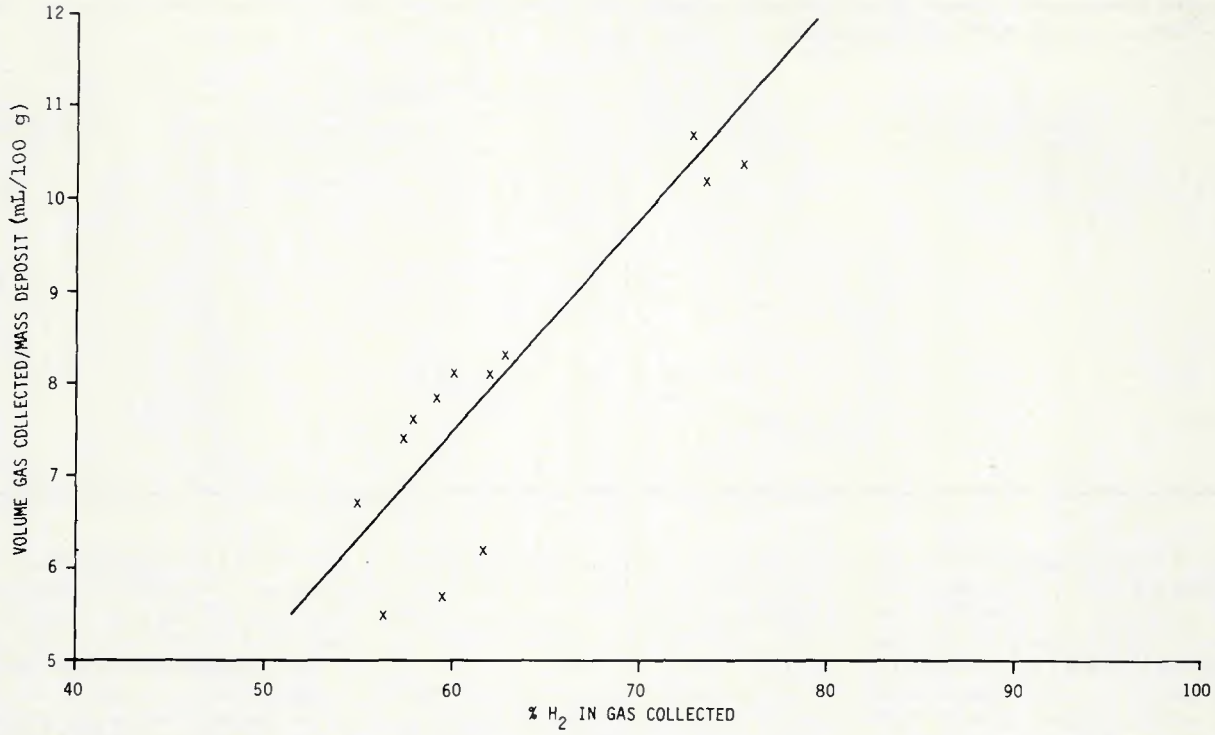

Fig. 6 — Relationship between gas exchange and volume of gas collected

isolation of the test assembly from the atmosphere and complete saturation of the glycerin with hydrogen. The former would prevent contamination of gas samples with oxygen and nitrogen, while the latter would prevent loss of hydrogen through dissolution. Another alternative is the use of a collecting fluid in which atmospheric gases and hydrogen have negligible solubility, such as mercury (Ref. 6), or the elimination of a collecting fluid altogether, as in the recently developed gas chromatographic method (Ref. 21).

In summary, it is concluded that the glycerin test is not a reliable method for measuring weld metal diffusible hydrogen content. Results are dependent upon variables which are not normally controlled as test conditions, and the relationship between actual diffusible hydrogen content and the volume measured over glycerin is unclear. Alternative test methods have been developed which demonstrate far more reliability than the glycerin test. The standard mercury test has been used successfully by many researchers, although some problems relating to the consistency of sample preparation have been reported (Ref. 25). A relatively new method based on gas chromatography (Refs. 21, 22) promises to alleviate many of the difficulties encountered with the use of collecting liquids.

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APPENDIX

A. Procedure For Conducting Glycerin Test

1. Specimens were cut from 1.0 × 0.5 in. (25.4 × 12.7 mm) flat bar to a length of 5.0 in. (127 mm).

2. Paint and scale was removed by surface grinding and finishing with a 120 grit buffing wheel.

3. All specimens were die stamped for identification.

4. Any grease and loose dirt was removed by scrubbing with a soft bristle brush and washing in alcohol.

5. Individual specimens were weighed to the nearest 0.1 gram (0.004 oz.) and placed in a dessicator for storage until ready for welding.

6. When ready for welding, the required number of specimens were removed from the dessicator (four for FCAW tests, twelve for GMAW tests).

7. A single stringer bead approximately 4 in. (101.6 mm) long was deposited on one of the 1 × 5 in. (25.4 × 127 mm) faces of each specimen. Specimens were held stationary during welding by clamping in a heavy copper fixture.

8. Within 30 s of the completion of welding, each specimen was cleaned and quenched in water at approximately 20°C (68°F) for ~15 s. Cleaning of all FCAW specimens was performed by hand brushing and burring. Cleaning of all GMAW specimens was accomplished by power brushing.

9. After quenching, each specimen was placed in an insulated bucket containing liquid nitrogen for FCAW specimens and an acetone/dry ice slurry for GMAW specimens. After completing a set of specimens, all specimens were transported to the glycerin test apparatus.

10. Specimens were removed one at a time from the bucket, rinsed in acetone until all evidence of frost had dissipated, dried and placed under individual eudiometer tubes in the glycerin bath maintained at 45 ± 3°C (113 ± 5.4°F). Specimens were stored at reduced temperature for no more than 1.5 hours.

11. The welded specimens were kept immersed in glycerin for a period of 48 h, at which time the volume of gas collected in the top of the eudiometer was read and recorded.

12. Specimens were removed from the glycerin bath, rinsed in water, dried and weighed to the nearest 0.1 gram (0.004 oz). The weight of the deposit was determined by the difference between initial and final weights.

13. For each sample, the ml of gas collected per 100 g of deposited weld metal was calculated.

B. Glassware

A representative sample of handmade glassware is shown in Fig. 7 and factory-made glassware in Fig. 8. The dimensions of each are as follows:

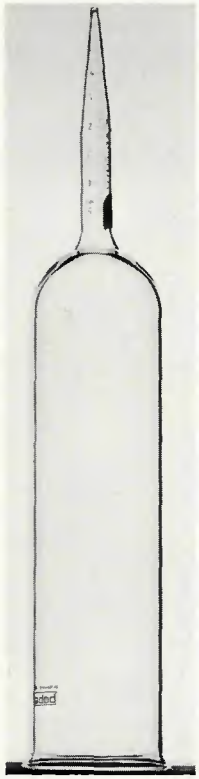

Fig. 7 (right) — Sample of handmade glassware

Fig. 8 (left) — Sample of factory-made glassware

1. Handmade glassware wherein dimensions are approximate. Calibrated portion — 5.5 mm (0.22 in.) ID, 127.0 mm (5 in.) height; lower bell portion — 59.2 mm (2.33 in) ID, 254 mm (10 in.) height.

2. Factory-made glassware. Calibrated portion — 10.8 mm (0.43 in.) ID, 127.9 mm (5.04 in.) height; lower bell portion — 46.5 mm (1.83 in.) ID, 210 mm (8.27 in.) height.

WRC Call For Papers

The High-Strength Steel Subcommittee of the WRC Weldability Committee is soliciting papers for a planned session at the 1985 AWS Annual Show in Las Vegas.

The title of the session is Permissible Levels of Weld Metal Hydrogen for Joining High-Strength Steels. Steel strength levels of 80 ksi yield and greater are of interest.

A very important area of concern for the welding industry, this critical question must be answered to complement most of the recent papers which address only measurement techniques.

Please submit 200-word abstracts to the Chairman of the High-Strength Steel Subcommittee, Gerald Uttrachi, Manager, Market Development, Welding & Cutting Systems, Linde Div., Union Carbide Corp., Old Ridgebury Rd., Danbury, CT 06817. The committee will review and make recommendations for a session to present this work in Las Vegas in April, 1985.

Papers may also be considered separately for acceptance by the AWS Papers Committee if abstracts meet the 500-word minimum requirement.