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Validation of oxygen purge techniques for stress corrosion cracking tests

J HESKETH, P COOLING and G HINDS

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VALIDATION OF OXYGEN PURGE TECHNIQUES FOR STRESS CORROSION CRACKING TESTS

J. Hesketh, P. Cooling and G. Hinds
Materials Division

SUMMARY

The effectiveness of standard laboratory oxygen purge techniques used to prepare deaerated solutions for stress corrosion cracking tests has been assessed under a range of purging conditions. The rate of decrease of dissolved oxygen concentration in deionised water was observed to depend more strongly on the depth of the sparging outlet below the waterline than on the volume of the void space or the area of the solution/gas phase interface. This is ascribed to faster gas exchange at the bubble/solution interface than at the waterline/gas phase interface. Furthermore, in concentrated NaCl solution the deaeration rate was found to be retarded by around 20% compared to that in deionised water. The standard NPL pre-test procedure for overnight deaeration of 10 L and 20 L test solutions was demonstrated to be fully effective in reducing dissolved oxygen levels to below 10 ppb, the value specified by EFC 17 for the testing of corrosion resistant alloys in the presence of hydrogen sulphide. In contrast, the widely accepted procedure of sparging a solution with nitrogen at 0.1 L/min for 1 hour per litre of solution was shown to be inadequate (i) in concentrated NaCl solutions and (ii) in vessels with relatively low solution height, including standard culture vessels of up to 5 L in volume and vessels that are only partially filled. Validation of individual deaeration procedures via measurement of dissolved oxygen concentration is recommended to ensure best practice.

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National Physical Laboratory
Hampton Road, Teddington, Middlesex, TW11 0LW

Approved on behalf of NPLML by Dr M Gee
Knowledge Leader, Materials Division.

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1. INTRODUCTION

When performing laboratory based corrosion tests, adequate control of the test environment is vital in creating an experiment that is both reliable and repeatable. For oil and gas applications a common requirement is the exclusion of oxygen from the test environment to replicate the conditions in service. Most common standards for stress corrosion cracking (SCC) testing of corrosion resistant alloys specify the use of oxygen-free test solutions. There is often a lack of definition in such standards of what is meant by 'oxygen-free'. However, the most widely accepted criterion is that found in the EFC 17 guideline document [1], which specifies a dissolved oxygen concentration of below 10 ppb. Practically it is not feasible to measure the oxygen concentration during every test; hence it is necessary that a robust procedure is in place to ensure that solutions meet the requirements for testing.

A widely adopted method for purging solutions of oxygen is that recommended in NACE TM0177 'Laboratory Testing of Metals for Resistance to Sulfide Stress Cracking and Stress Corrosion Cracking in H_2S Environments' [2]. This states that to achieve an oxygen-free solution, the solution needs to be sparged with nitrogen at a rate of 0.1 L/min for 1 hour per litre of test solution. At NPL, it is standard practice for solutions to be deaerated overnight (> 16 hrs), which is considered to be sufficient for most applications since solution volumes rarely exceed 15 L. For experiments performed within an autoclave, the nitrogen flow is used to simultaneously deaerate the vessel, via sweep-through purging, as it is assumed that the presence of the autoclave has little effect on the time taken to reach the desired oxygen concentration. However, as NACE TM0177 [2] makes no reference to experimental data regarding the removal of oxygen from solution, it was deemed prudent to test the reliability of the method in relation to typical laboratory procedures conducted at NPL.

In this work, the effects of nitrogen flow rate, salt concentration and solution volume on the rate of decrease of dissolved oxygen concentration in the test solution were investigated in a typical autoclave configuration used for SCC testing. Tests were carried out using both flexible welded stainless steel hosing and PTFE tubing. The effect of purging only the vapour phase above the solution rather than the solution itself was also examined.

2. EXPERIMENTAL

2.1 Test Configuration

Four different experimental configurations were used in this investigation, as shown in Figure 1. Unless otherwise stated, the nitrogen used was oxygen-free grade (> 99.99% purity).

- Setup A comprised sparging either deionised (DI) water or 20% NaCl (w/w) solution with nitrogen via PTFE tubing (length 2 m, outer diameter ¼″) in a sealed culture vessel. The exhaust nitrogen was passed through a Dreschel bottle containing 100 mL of deionised water.

- Setup B was identical to Setup A except that the PTFE tubing was replaced with flexible welded 316 stainless steel (SS) hosing (length 2m, outer diameter 12 mm).

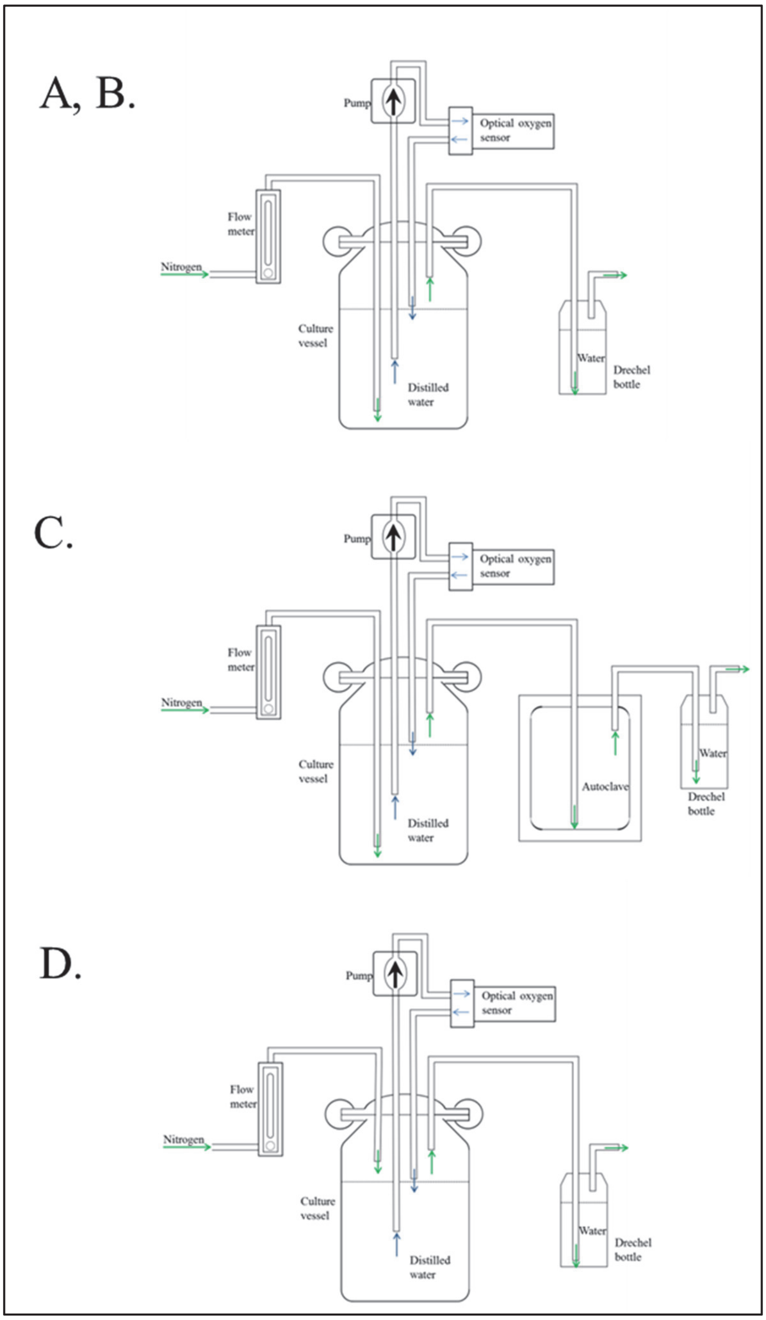

Figure 1: Configuration of Setup A and Setup B (top), Setup C (middle) and Setup D (bottom).

- Setup C comprised sparging of DI water with nitrogen via PTFE tubing (length 2 m, outer diameter ¼″) in a sealed culture vessel. The exhaust nitrogen was fed into the inlet of a sealed 20 L autoclave. The outlet of the autoclave fed to a Dreschel bottle containing 100 mL of DI water.

- Setup D was identical to Setup A, except that the inlet of the PTFE tubing was located above the water line. Hence, no bubbles were formed in the test solution and gas exchange only took place across the waterline/gas interface.

2.2 Dissolved oxygen measurement

The dissolved oxygen concentration in the test solution was measured using an Orbisphere 410 optical oxygen sensor (optode) with a detection range of 2 ppm > $[O_2]$ > 0.5 ppb, which was calibrated with oxygen-free grade nitrogen in house. The principle behind the operation of this device takes advantage of the dependence of luminescence lifetime of a platinum-based luminophor on dissolved oxygen concentration. This type of sensor was selected as it does not consume oxygen during operation, making it a more suitable choice than more conventional electrochemical sensors. The setup was configured so that solution was pumped from the centre of the culture vessel through the oxygen sensor and back to the culture vessel as shown in Figure 1. In order to minimise oxygen ingress through the tubing during the measurement, ¼″ stainless steel tubing was used to transport the solution to and from the pump/sensor.

2.3 Test Procedure

Using Setup A, four different volumes (1 L, 5 L, 10 L and 20 L) of DI water were sparged with oxygen-free nitrogen at a rate of 0.1 L/min. In each case the smallest vessel possible was used (1.25 L, 5.65 L, 11.45 L and 23.0 L, respectively). To mitigate the risk of undetected oxygen ingress, the vessels and connections were completely disassembled between tests. Using the same setup, two further solutions (5 L and 10 L) were deaerated, but in this instance the vessels used were oversized (11.45 L and 23.0 L, respectively), leaving a large void space above the solution. The same setup was used to deaerate 20 L of solution using nitrogen supplied from a generator (~ 99.9% purity) at a significantly higher flow rate (> 4 L/min). This was then repeated but the culture vessel was not sealed – oxygen ingress was allowed. Finally, the experiment was repeated using 10 L volumes of 20% NaCl solution in an 11.45 L vessel, in order to investigate any potential effect of high salt concentration on the deaeration rate.

Using Setup B, 1 L of solution was sparged at 0.1 L/min; this was repeated once following complete disassembly.

Using Setup C, 10 L solutions were sparged at 0.1 L/min and 0.25 L/min.

Using Setup D, 1 L, 5 L, 10 L and 20 L solutions were sparged at 0.1 L/min.

Dimensions of the culture vessels are presented in Table 1.

Table 1: Dimensions of vessel/solution combinations used.

Vessel volume (L)	1.25	5.65	11.45	11.45	23.0	23.0
Solution volume (L)	1	5	5	10	10	20
Solution depth (cm)	12	21.5	13.5	27	16.5	33
Water surface area (cm^2)	87.4	178	365	332	633	616

2.4 Analysis

The time taken to achieve a dissolved oxygen concentration of 10 ppb in the test solution, t_d, was expressed in terms of deaeration efficiency with respect to the widely accepted NACE standard procedure [2] of sparging for 1 hour per litre of solution, using the following equation:

$$Deaeration\ efficiency = \frac{V\,(L)}{t_d\,(h)} .100\ \% \tag{1}$$

where:

V = solution volume

Using this criterion, sparging procedures with a deaeration efficiency of less than 100% can be identified as not fit for purpose.

3. RESULTS

The variation of dissolved oxygen concentration with time in 1 L, 5 L, 10 L and 20 L DI water solutions sparged with nitrogen at 0.1 L/min using Setup A is shown in Figure 2. The time required for the dissolved oxygen concentration to fall to 10 ppb and the deaeration efficiency (as defined in Equation 1) are summarised in Table 2. As expected, t_d increased with solution volume; however this relationship was non-linear and the deaeration efficiency was significantly lower for smaller volumes of solution. For solution volumes of 5 L and below, the deaeration efficiency was less than 100%, indicating that the widely accepted guideline of 1 hour per litre of solution is not fit for purpose in these cases. The deaeration efficiency also decreased significantly when the solutions (5 L and 10 L) were deaerated within larger vessels (11.45 L and 23.0 L respectively), as shown in Figure 3.

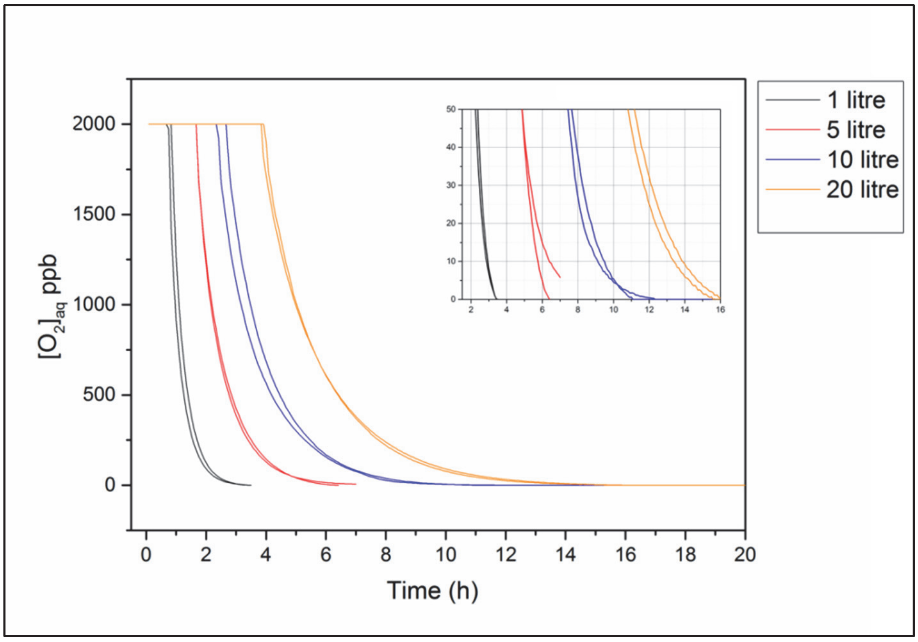

Figure 2: Variation of dissolved oxygen concentration with time during sparging of 1 L, 5 L, 10 L and 20 L of DI water at a nitrogen flow rate of 0.1 L/min.

Table 2: Summary of test results using Setup A.

Solution volume (L)	**Vessel volume (L)**	**Nitrogen flow rate (L/min)**	**t_d (h)**	**Deaeration efficiency (%)**
1	1.25	0.1	2.9	34
			3.0	33
5	5.65	0.1	5.8	86
			6.4	78
	11.45		7.9	63
10	11.45	0.1	9.2	109
			9.6	104
	23.0		13.0	77
20	23.0	0.1	13.4	149
20	23.0	0.1	13.9	144
		> 4	8.5 (sealed)	235
		> 4	10.8 (unsealed)	185

The effect of high flow rate (using a nitrogen generator) on the deaeration of 20 L solutions is shown in Figure 4. The deaeration efficiency increased from around 150% (0.1 L/min) to 235% (> 4 L/min). Such was the effectiveness of deaerating using the generator that it was possible to deaerate 20 L of solution to below 10 ppb dissolved oxygen in under 11 h without even sealing the vessel lid. In this instance, one of the threaded ports (~ 20 mm diameter) was not sealed with a silicone gasket, which allowed some oxygen ingress. Since the effect of nitrogen flow was not investigated systematically for a range of solution volumes, any attempt to use a nitrogen generator to expedite deaeration times should be validated prior to use.

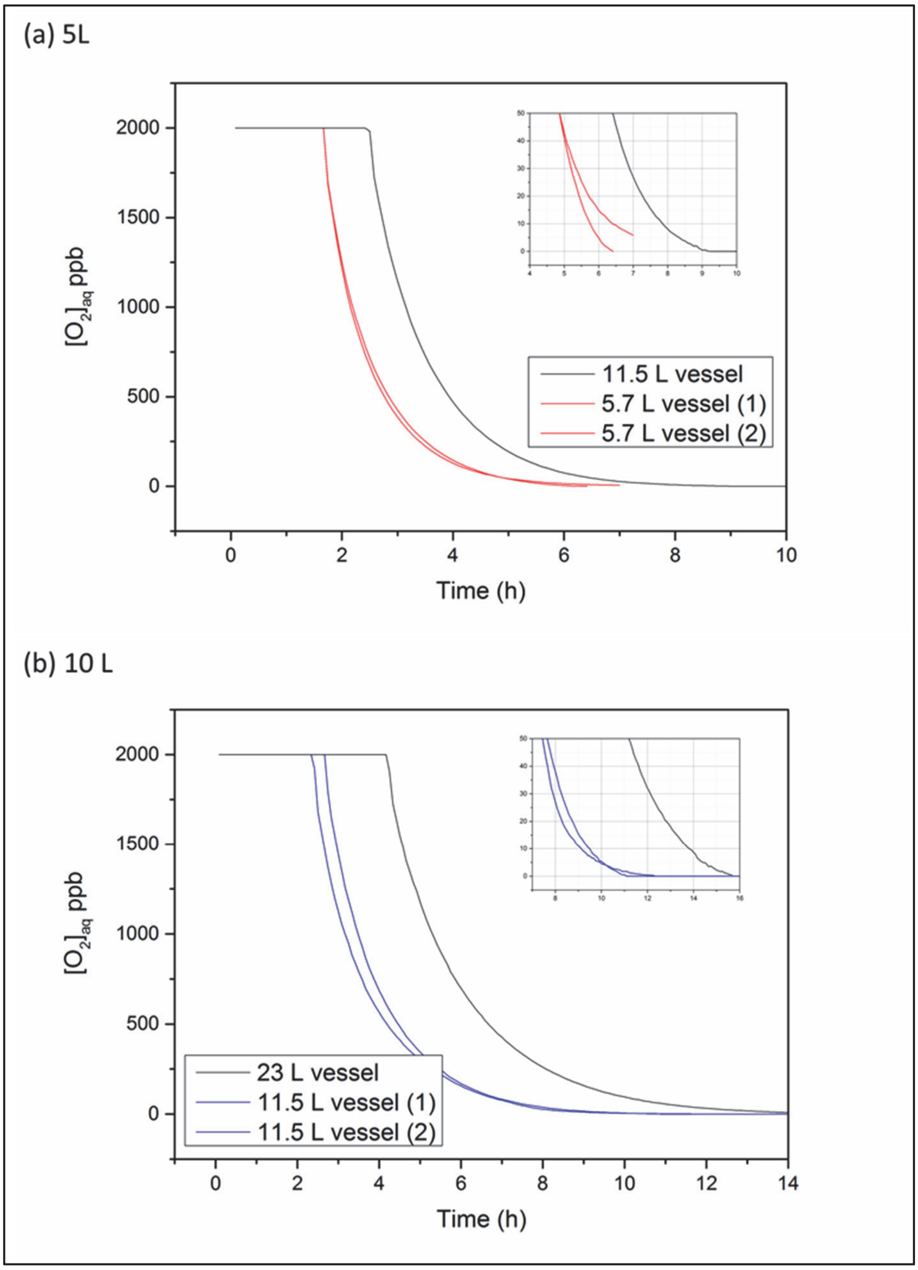

Figure 3: Variation of dissolved oxygen concentration with time as a function of vessel size during sparging of (a) 5 L and (b) 10 L of DI water at a nitrogen flow rate of 0.1 L/min.

Due to the low deaeration efficiencies recorded for 1 L of DI water obtained using Setup A, it was proposed that replacing the PTFE tubing with flexible 316 SS welded hosing might produce more satisfactory results, owing to the lower oxygen permeability in the latter. However, replacing the PTFE tubing with 316 SS hosing resulted in only a slightly reduced deaeration time, as shown in Figure 5. A deaeration efficiency of 40 % was observed with the 316 SS tubing, compared to 34% for the PTFE tubing.

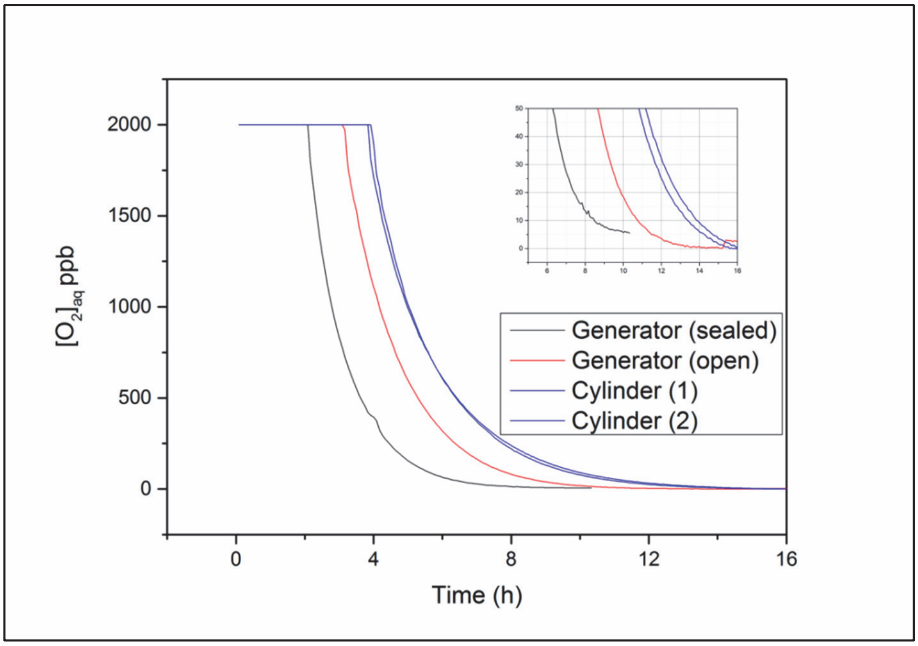

Figure 4: Variation of dissolved oxygen concentration with time during sparging of 20 L of DI water from a high flowrate generator (> 4 L/min) and a gas cylinder (0.1 L/min).

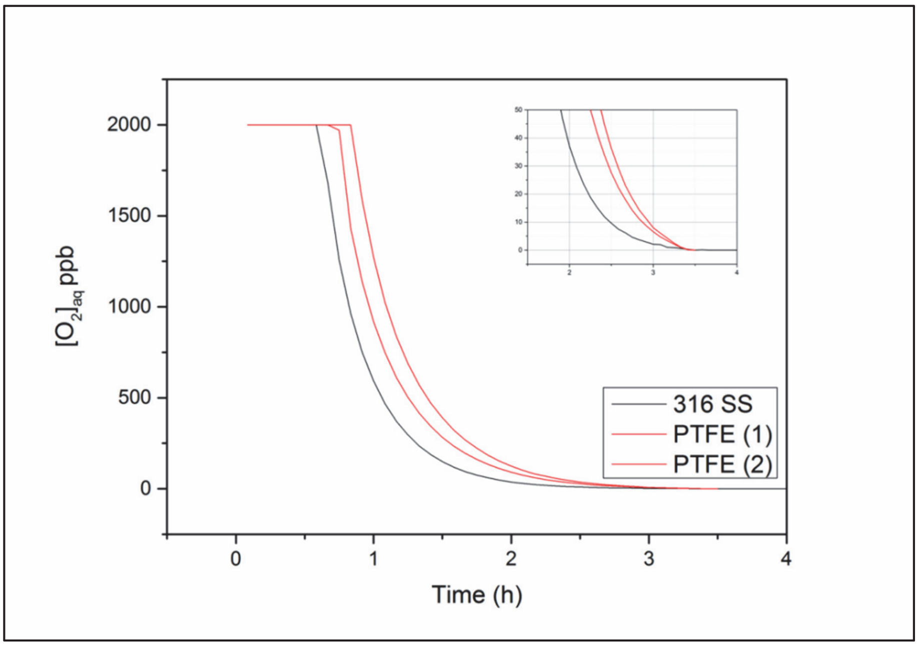

Figure 5: Variation of dissolved oxygen concentration with time during sparging of 1 L of DI water at a nitrogen flow rate of 0.1 L/min through flexible 316 SS tubing. The corresponding plots using PTFE tubing are included for comparison.

The effect on deaeration efficiency of using the exhaust nitrogen to deaerate a 20 L autoclave is shown in Figure 6. The time taken for the dissolved oxygen concentration to reach 10 ppb was 8.8 h, compared to an average of 9.4 h when the exhaust gas was fed directly to a Dreschel bottle. This variation in deaeration time is within experimental error; in any case, no significant negative effect of the presence of the autoclave was observed. When the nitrogen flow rate was increased from 0.1 L/min to 0.25 L/min, the deaeration time was reduced from 8.8 h to 7.3 h. Increasing the nitrogen flow rate by 150% only reduced the deaeration time by 17%, demonstrating that this is not an efficient way of speeding up the process.

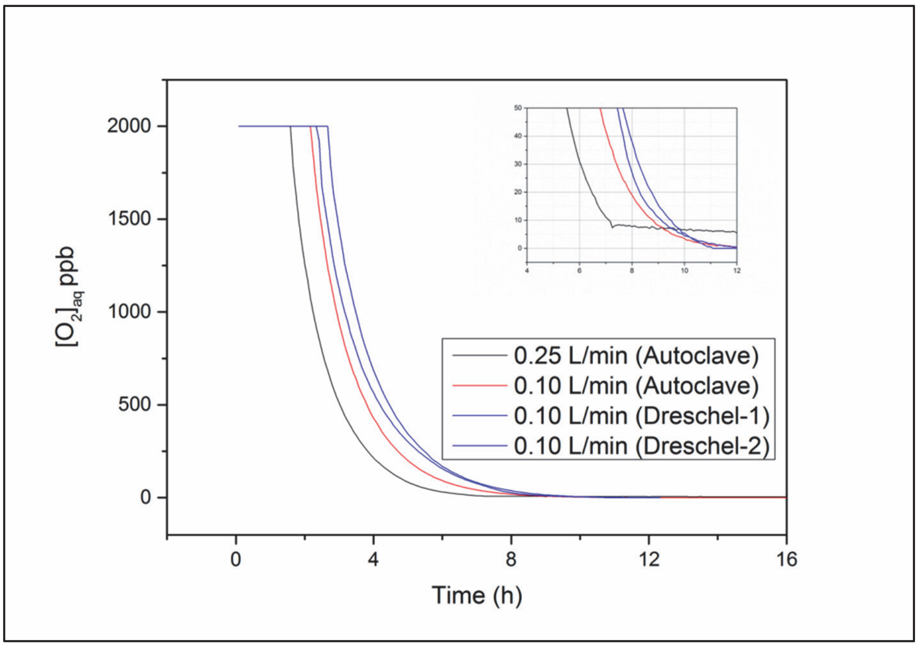

Figure 6: Variation of dissolved oxygen concentration with time during sparging of 10 L of DI water at nitrogen flow rates of 0.1 L/min and 0.25 L/min with the gas outlet connected to a 20 L autoclave. The corresponding plot with the gas outlet connected to a Dreschel bottle is included for comparison.

The effect of placing the PTFE tube above the waterline is shown in Figure 7. Due to a datalogging error, the results for the 20 L solution are not available. However, the final time taken to reach the target oxygen concentration was manually recorded to the nearest hour. In each case, the efficiency of the deaeration process was greatly diminished, taking about an order of magnitude longer for the dissolved oxygen concentration to reach 10 ppb. These results are summarised in Table 3 and demonstrate the relatively high rate of gas exchange between the bubble/solution interface compared with that at the waterline/gas phase interface.

Table 3: Summary of test results using Setup D (sparging outlet above waterline).

Solution volume (L)	**1**	**5**	**10**	**20**
t_d (h)	22.8	51.7	102	151
Deaeration efficiency (%)	13	12	9	9

Finally, the effect of high NaCl concentration on the deaeration efficiency for 10L solutions is shown in Figure 8 and summarised in Table 4. The figure shows an abrupt drop in oxygen concentration for the salt solutions at approximately 3 hours, which is caused by the reduced upper limit sensitivity of the sensor under these conditions. Although it appears that the initial rate of deaeration is higher in the presence of 20% NaCl, this rate slows down with time and the deaeration efficiency is decreased by around 20% in the salt solution. Applying this correction to the DI water values in Table 2 further highlights the limitations of the NACE standard procedures when applied to concentrated brines [2].

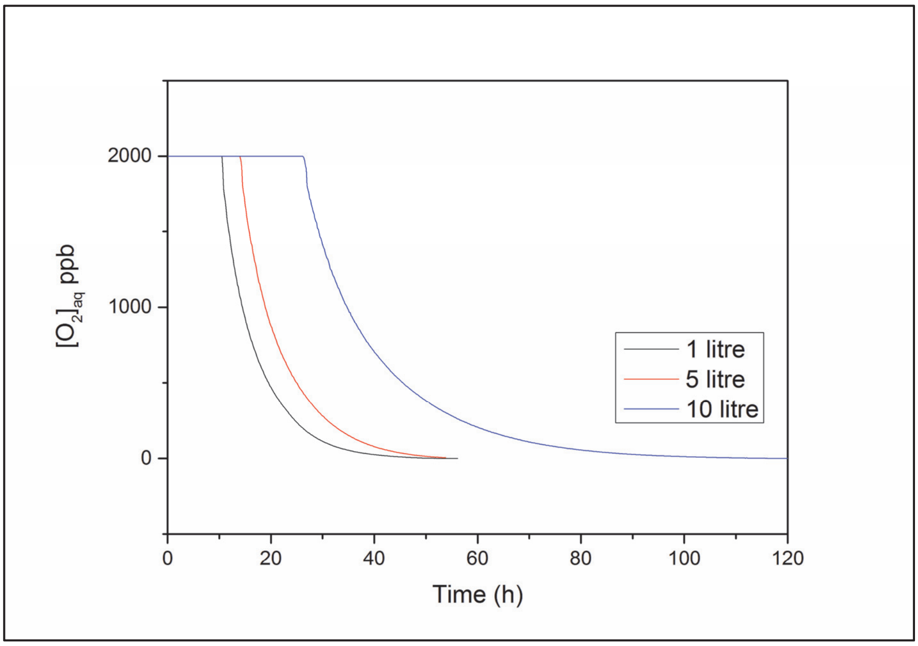

Figure 7: Variation of dissolved oxygen concentration with time during sparging of 1 L, 5 L and 10 L of DI water at a nitrogen flow rate of 0.1 L/min with the sparging outlet above the waterline.

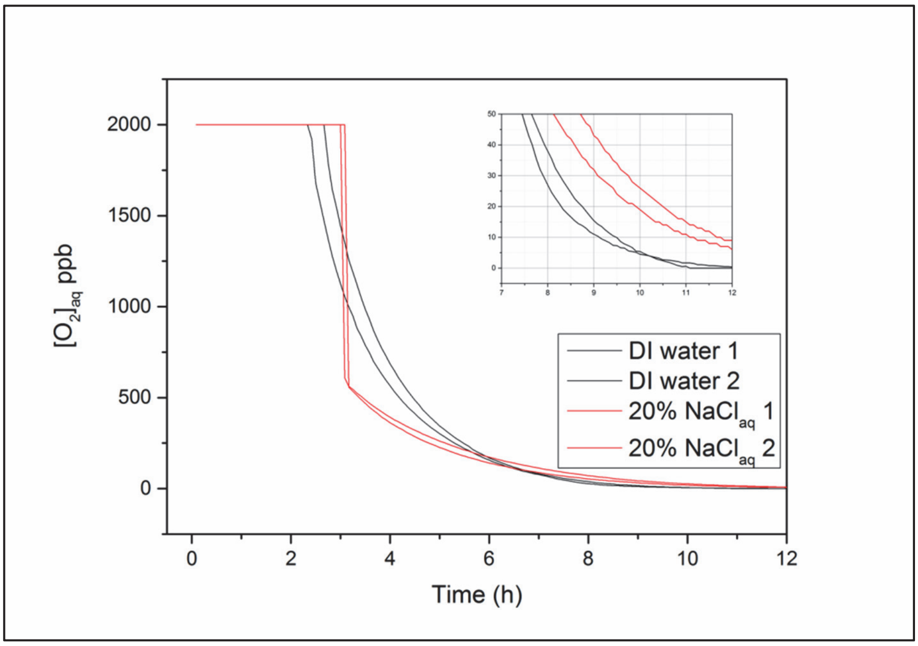

Figure 8: Variation of dissolved oxygen concentration with time during sparging of 10 L of DI water and 10L of 20% w/w NaCl solution at nitrogen flow rates of 0.1 L/min.

Table 4: Effect of high salt concentration on deaeration efficiency.

Solution	**Vessel volume (L)**	**Nitrogen flow rate (L/min)**	**t_d (h)**	**Deaeration efficiency (%)**
DI water (10 L)	11.45	0.1	9.2	109
			9.6	104
20% NaCl (10 L)	11.45	0.1	11.1	90
			11.7	86

4. DISCUSSION

The primary conclusions from this work are that the deaeration efficiency depends critically on the height of the solution in the deaeration vessel and on the presence of dissolved salts. These factors can both render inadequate the widely accepted procedure of deaerating at 0.1 L/min for 1 hour per litre of solution.

The hampering effect of salinity on the time taken to reach 10 ppb of dissolved oxygen is a concerning observation given that stress corrosion cracking tests routinely require the use of concentrated brines. The NPL pre-test procedure of deaerating solutions overnight (> 16 hrs) is adequate for solutions of 20% NaCl in volumes up to 10L and should be adequate for 20 L solutions based on the data for DI water. However, experimental validation is required for larger or more concentrated solutions.

Another key observation from the results obtained with the sparging outlet above the waterline is that the rate of gas exchange is faster across the bubble/solution interface than at the waterline/gas phase interface. In order to determine whether this could be due to a surface area effect, the total bubble surface area at any given time during sparging may be calculated as follows. When the outlet of the PTFE tubing is submerged, as in Setup A, there are approximately 9 bubbles per 27 cm of solution depth (the height of the waterline in a 11.45 L vessel containing 10 L of solution). Each bubble takes approximately 1 second to complete the 27 cm ascent to the waterline. Making the assumption that each bubble is a sphere of equal size and reaches terminal velocity over a relatively short distance, an estimation of the total surface area of the bubbles can be made using:

$$A_T = (\pi n)^{\frac{1}{3}}\left(6t\dot{V}\right)^{\frac{2}{3}} \tag{2}$$

where:

A_T = Total surface area of the bubbles at a given time
n = Number of bubbles in solution at a given time
t = Time taken for a bubble to reach the waterline
$\dot{V}$ = Nitrogen flow rate

Taking n = 9, t = 1 s and $\dot{V}$ = 1.67 cm^3/s gives a total surface area of the bubble/solution interface of ~ 14 cm^2 (in a 11.45 L vessel containing 10 L of solution). This is significantly lower than the surface area of the waterline/gas phase interface (332 cm^2), which demonstrates that the comparatively fast rate of gas exchange through the bubbles is not a surface area effect. Instead, it can be inferred that gas exchange at the bubble surface is enhanced by shear mixing associated with the upward movement of the bubbles.

Hence, the apparent deaeration inefficiency for smaller volumes of solution is most likely associated with the shorter residence time of bubbles in the solution as they travel from the sparging outlet to the waterline. The deaeration efficiency is mostly influenced by the shape of the vessels; larger vessels are typically taller (the waterline is approximately 2.5 times higher in a full 11.45 L vessel than a full 1.25 L one), which increases the total area of the bubble/solution interface since at a given time there are more bubbles in the solution. This may also serve to explain why using oversized vessels was largely inefficient. Placing solution in a larger vessel reduces the water level, and therefore the total area of the bubble/solution interface. It also increases the volume of gas above the solution, although this is less important due to the relatively slow exchange rate of gas across the waterline/gas interface. The correlation between deaeration efficiency and the distance from the sparging outlet to the waterline is shown in Figure 9, which gives a linear fit with an R^2 value of 0.95.

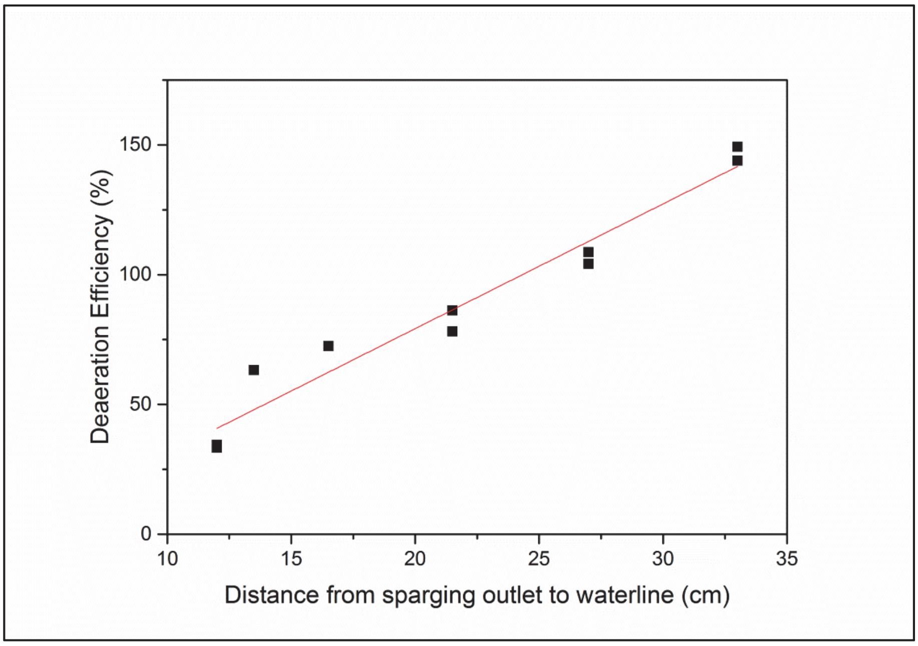

Figure 9: Plot of deaeration efficiency against distance between sparging outlet and waterline when purged with nitrogen at 0.1 L/min through PTFE tubing.

Although the bubble/solution interface dominates the deaeration process, there is some contribution from the waterline/gas interface, which when considered allows for a slightly more accurate prediction of deaeration time. From Table 3 it can be seen that on average, deaeration by diffusion across the waterline/gas interface alone is about 11% as efficient as deaeration from combined diffusion across the bubble/solution and waterline/gas interfaces. The contribution from both interfaces can be taken into consideration by plotting [(0.89 x solution depth) + k_1(0.11 x Waterline interface area)] against deaeration efficiency, where

$k_1 = 0.081$ cm^{-1}. This is shown in Figure 10 and gives an R^2 value of 0.98. This provides a framework for prediction of deaeration time with the test setups described herein, however, slight variations such as different tube diameters will alter the value of k_1. As a result, measurement of dissolved oxygen levels is always preferable and predicted values should be used as a guideline only.

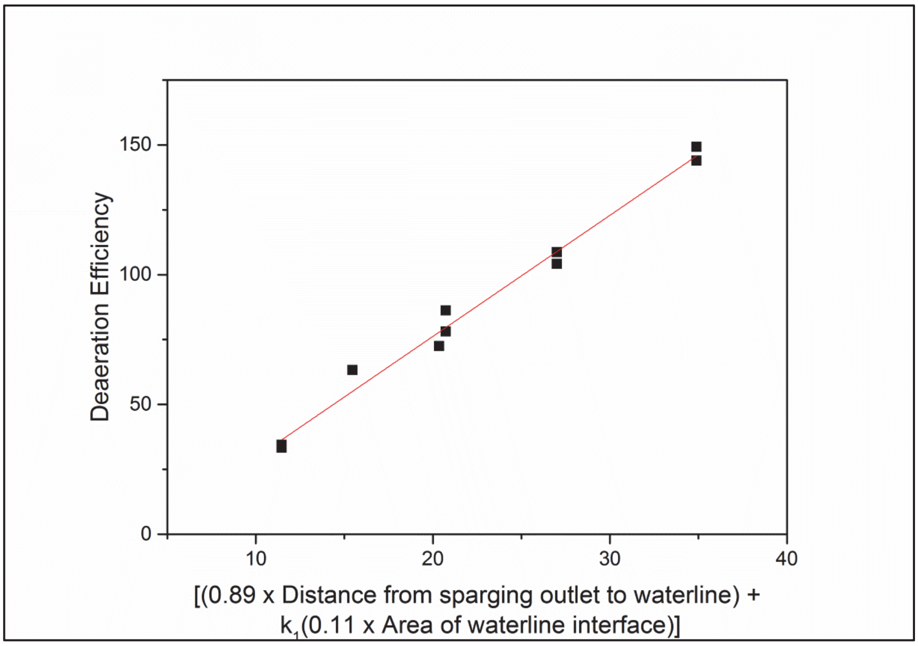

Figure 10: Plot of deaeration efficiency against [(0.89 distance from sparging outlet to waterline) + k_1(0.11 Area of waterline)] when purged with nitrogen at 0.1 L/min through PTFE tubing.

Based on these observations, the deaeration efficiency could be increased by any process that increases the residence time of the bubbles in the solution. Since the deaeration efficiency is strongly dependent on the bubble/solution interface, the total area of which is inversely proportional to the radii of the bubbles, it is also reasonable to assume that the use of a sparger or any other mechanism of reducing the size of each bubble would increase the deaeration efficiency. It should be noted however that the use of spargers in the concentrated brines commonly used in SCC testing is not recommended due to the potential for blockage via salt deposition. Agitation of the solution, e.g. by stirring, would also increase the efficiency as this increases the volume of solution in direct contact with the bubbles and enhances mixing.

5. CONCLUSIONS

- The standard NPL pre-test procedure for overnight deaeration of 10 L and 20 L test solutions has been shown to be fully effective in reducing dissolved oxygen levels to below 10 ppb, the value specified in EFC 17 for the testing of corrosion resistant alloys in the presence of hydrogen sulphide.

- However, the widely accepted procedure of sparging a solution with nitrogen at 0.1 L/min for 1 hour per litre of solution was shown to be inadequate for in vessels with relatively low solution height, including standard culture vessels of up to 5 L in volume and vessels that are only partially filled.

- This procedure was also shown to be unsuitable for concentrated brines in standard culture vessels of up to 10 L in volume.

- Given the high sensitivity of deaeration efficiency to vessel depth and salt concentration, a conservative approach to deaeration time is recommended, particularly when deaerating shallow solutions or those containing elevated quantities of solute.

- To achieve the most efficient deaeration for a fixed volume of solution, the solution depth should be maximised by using a vessel with the smallest diameter available.

- To ensure best practice, it is recommended that validation of individual deaeration procedures be carried out via measurement of dissolved oxygen concentration.

6. REFERENCES

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