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THE EVALUATION OF SECONDARY SYSTEM OXYGEN-SCAVENGING CHEMICALS USING A WATER-CIRCULATING RIG

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1. Background

The control of oxygen levels within boiler systems is of vital importance in the minimisation of structural material corrosion rates, particularly where ferrous alloys are used. To this end, a variety of oxygen scavengers are used and the chemical(s) chosen vary between different water systems. A number of factors can be considered, including the following:

- Efficiency of oxygen scavenging

Although the numerical values obtained by these experiments cannot directly be read across to actual full-scale systems, they are useful for comparative purposes.

- By-products and intermediaries produced

The formation of corrosive, (chemically-) hazardous by-products will render a chemical unsuitable for use as a PWR dosing agent. Additionally, where the system is contained within a confined space, e.g. as a submarine power plant, considerations such as toxicity and volatility of secondary dosing chemicals and their by-products are important, since these could lead to health effects, particularly cumulative effects, for operational personnel. Under these further constraints, standard oxygen scavengers such as hydrazine become incompatible, as do chemicals which break down to produce hydrazine as the active component, e.g. carbohydrazide ((NHNH)₂C=O). The use of organic chemicals is, in general, questionable under these conditions, due to the possibility of alternative reaction pathways at different temperatures and/or pressures.

- Radioactivation effects

Where the chemical is to be used as a primary system oxygen scavenger, activation by neutron flux is an important criterion. Whilst it is virtually impossible to remove **all** activatable species, particularly for more complex oxygen scavengers, isotope selection is often used to reduce activation effects, e.g. the use of ⁷LiOH.

- pH considerations

The generation of acidic or basic by-products can have a marked effect on system pH and therefore on the overall corrosion rate, although an optimum pH of pH_{25°C} ~ 11 is the target for steel-based systems.

- Dissolved solids

The use or production of high concentrations of dissolved solids gives rise to corrosion problems within the PWR secondary system, where the boiling of water leads to the formation of corrosive coatings on internal system surfaces.

- Compatibility with other components

Dosing chemicals have to be compatible with system materials, a variety of which will be present at different points within the reactor systems, as well other dosing chemicals. They also have to be suitable for use with other system components, e.g. ion exchange resins, which will be assessed in future tests.

- Method of Analysis

There must be a readily available, convenient and accurate method for the measurement of the oxygen scavenging chemical(s). Thus, chemical selection is affected by access to safety facilities (extraction, disposal, containment), availability of analysis equipment and chemicals (stability, shelf-life, supply frequency, cost) and

suitability of the method in terms of other dosing chemicals and their possible interference with the species being determined.

A number of oxygen scavengers are used in PWR applications, in both primary and secondary systems and a continuing program of evaluating alternatives is important, particularly where the currently used chemicals have hazardous properties, e.g. hydrazine (Ref. 1).

2. Experimental Rig

To assess the efficiency, mode of action and possible by-products of chemical dosing agents, e.g. oxygen scavengers, a circulating water rig was constructed within the Nuclear Department. The rig uses a demineralised water supply as a source of make-up water to fill a recirculating loop of approximately 10 litres volume. The rig pipework is made of polythene, with standard 'off the shelf' pipe fittings and connectors. The use of plastic was preferred to metals, e.g. stainless or mild steels, since, although these would allow the use of higher temperatures, they could significantly alter reaction rates, e.g. by catalytic action. Although this might be closer to actual in-service conditions, the intention is to compare different oxygen scavengers under constant, standard conditions. The following parameters can be measured within the rig:

1. pH measured by in-line monitor.
2. Conductivity measured by in-line monitor (ABB 4600 probe).
3. Dissolved oxygen level measured by Orbisphere 26060 meter using an in-line flow cell.
4. Temperature, via a sensor in the dissolved oxygen meter probe.

In addition, the injection point can also be used as a sampling point, since a small sample of solution can be removed by syringe, for further analysis, usually ion chromatography (Dionex 120 or Metrohm 761 Compact IC) or FT-IR. A further facility within the rig is the inclusion of two ion exchange columns, which can be valved in or out of the system, as required. One of the columns is a R-H/R-OH column (Amberlite MB604, 500g), used to clean up the water before a run is commenced and to remove reaction products after a run has been completed. The resin is regenerated after use and the extent of water polishing assessed using the in-circuit conductivity meter. The second ion exchange column can be used either as a catalyst support, or as an oxygen scavenger producer, e.g. in the sulphite form.

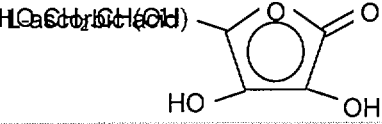
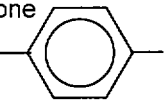
Chemical evaluation can be carried out at room temperature (the pH meter gives a direct readout of temperature), or at elevated temperatures, using a small heater, built into the system. The maximum water temperature is governed by the tubing and fitting materials, as well as pressure considerations, e.g. from the generation of gaseous reaction products, but temperatures up to 70°C can safely be used.

A circuit diagram of the rig is shown at Figure One, followed by a photograph of the actual system as constructed at Figure Two. There were initial problems with leaking fittings and use of the water reservoir, but these have now been solved.

The system has already been used for some preliminary testing and this showed that range switching of instruments was not linear and could cause unexpected spikes in the recorded reading. These have been solved by the use of a continuously recording PC-based data logger. The system has also proved useful as a teaching tool, to demonstrate the action of ion exchange and chemical treatment, e.g. to show water purification rates.

3. Oxygen Scavengers

The following oxygen scavengers were available for the initial tests:

Chemical	Formula & RMM	Synonyms	Reference
Ascorbic acid 	RMM 176.13	Vitamin C	(1)
N,N-diethylhydroxylamine	$(C_2H_5)_2NOH$ RMM 89.14	DEHA	1, 3
Hydroquinone 	HO OH	1,4-benzenediol	1, 2
Hydrazine hydrate	$NH_2NH_2 \cdot H_2O$ RMM 110.11 RMM 50.06		1, 2, 3
Sodium sulphite (anhydrous)	Na_2SO_3 RMM 126.04		

These reflect a mix of simple inorganic and more complex organic oxygen scavengers, with sodium sulphite being used as the benchmark chemical and hydrazine, although inapplicable for use within a confined space included again for comparison.

The reactions involved in oxygen scavenging are often very complex, pursuing different reaction pathways at different temperatures (Ref. 2) and there are complications even with the use of sodium sulphite, which produces hydrogen sulphide, sulphur dioxide (which can itself recondense to form sulphurous acid) and sulphate ions, which are themselves corrosive in this environment.

4. Experimental Results

Initial testing using this rig is aimed at confirming the viability of using the rig for assessment of the selected chemicals, rather than establishing reaction paths. These tests assumed an oxygen content of around 10ppm and sufficient oxygen scavenger was added to remove a total of 100mg O_2 (0.0031moles).

An example of the full data acquired using the system is given at Figures 3 & 4. Preliminary oxygen scavenging results are shown at figures 5-9; the data is normalised to give a common starting oxygen concentration for different temperatures and results are presented in the form of the reduction in oxygen concentration from the initial value. These figures show that the water-circulating rig can be used to assess the efficiency of oxygen scavengers and indicate that the chemicals tested can be generally graded in terms of oxygen removal efficiency thus:

Sodium sulphite > DEHA > L-Ascorbic acid > Hydrazine > Hydroquinone

.... where, for sodium sulphite, there would appear to be a threshold temperature between 32°C and 41°C, at which oxygen-scavenging efficiency increases significantly.

5. Conclusions & Further Work

Further work at elevated temperatures and higher concentration ranges will be carried out over subsequent months and it is also envisaged to use the rig to assess the efficiency of other deoxygenation methods, e.g. sulphite-bearing resins and catalysis, using a resin as an inert support. It is also proposed to assess other dosing chemicals, e.g. pH raisers and to use the sampling facility to obtain further information regarding the characterisation of breakdown products.

6. Acknowledgements

I would like to acknowledge the help and assistance provided by my colleagues Sean Jarman, Terry McCarthy and Chris Felstead in the design and construction of the water rig, its operation and mopping up after the many unexpected pipe leaks.

7. References

1. Selection criteria for the best secondary water chemistry – Nordmann, F.; Fiquet, J.-M., Chemistry in Water Reactors (SFEN) vol. 2, 1994, p515-526.
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4. Study of hydrazine alternatives under AGR plant operating conditions – Rudge, A.; Woolsey, I. S.; Lewis, G. G.; Tyldesley, J. D., Water Chemistry of Nuclear Reactor Systems 7 (BNES), 1996, p399-406.

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Figure One – Schematic Diagram of Water Circulating Rig

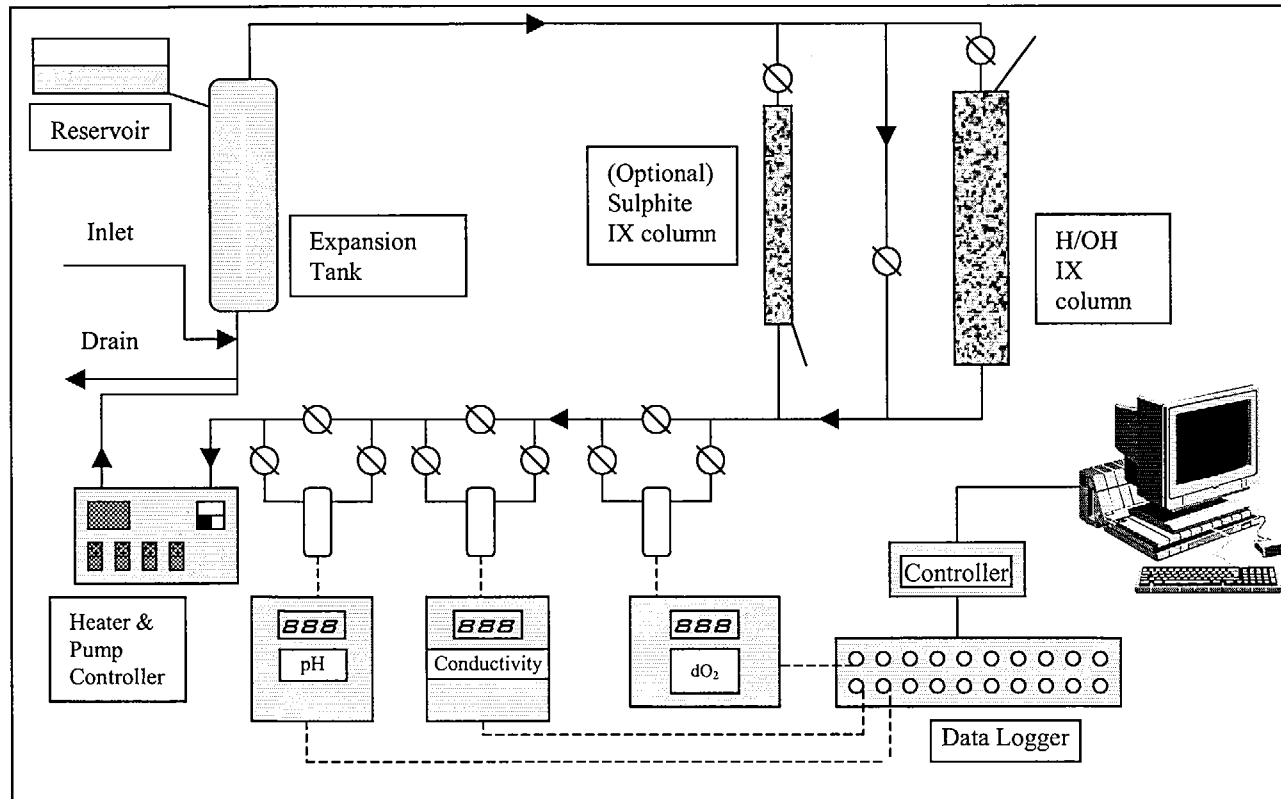


Figure Two – Photograph of Water Circulating Rig

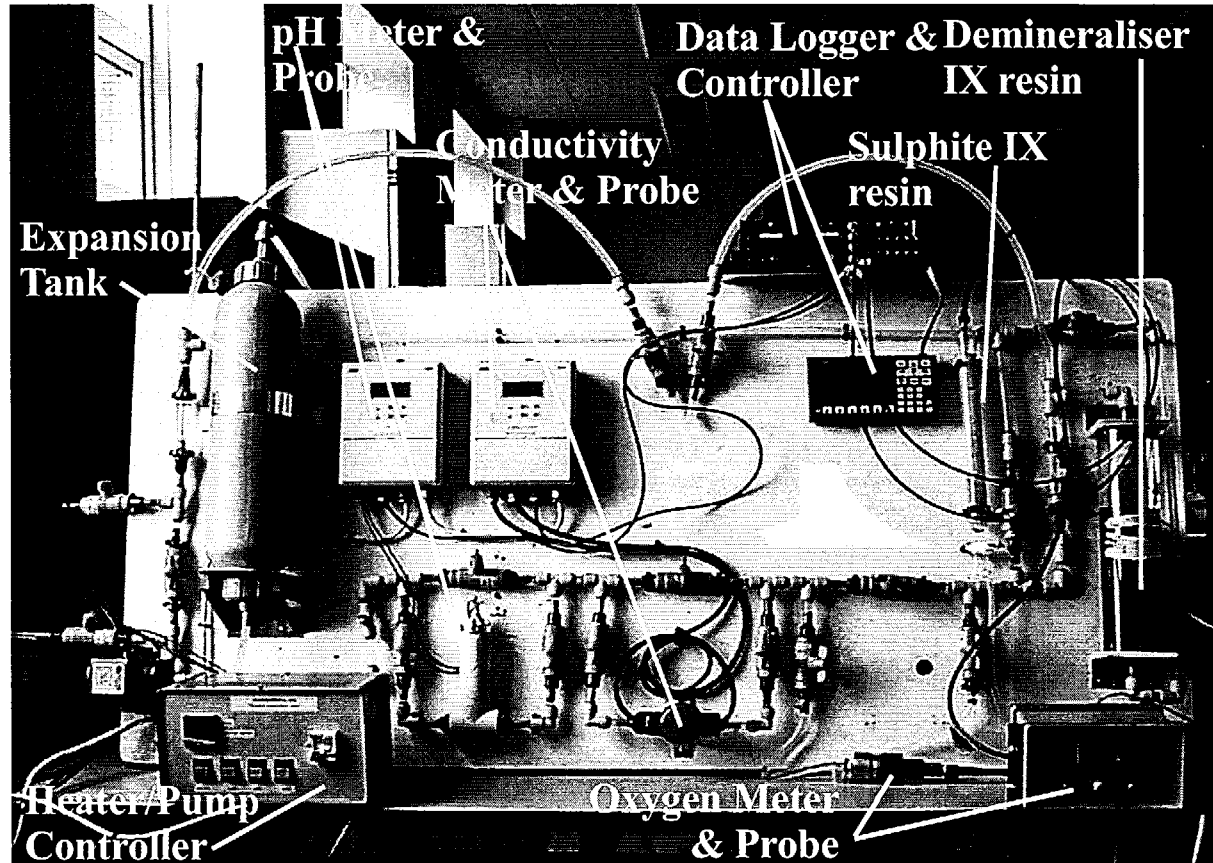


Figure Three – Sodium Sulphite – Variation in Conductivity and Temperature with Time

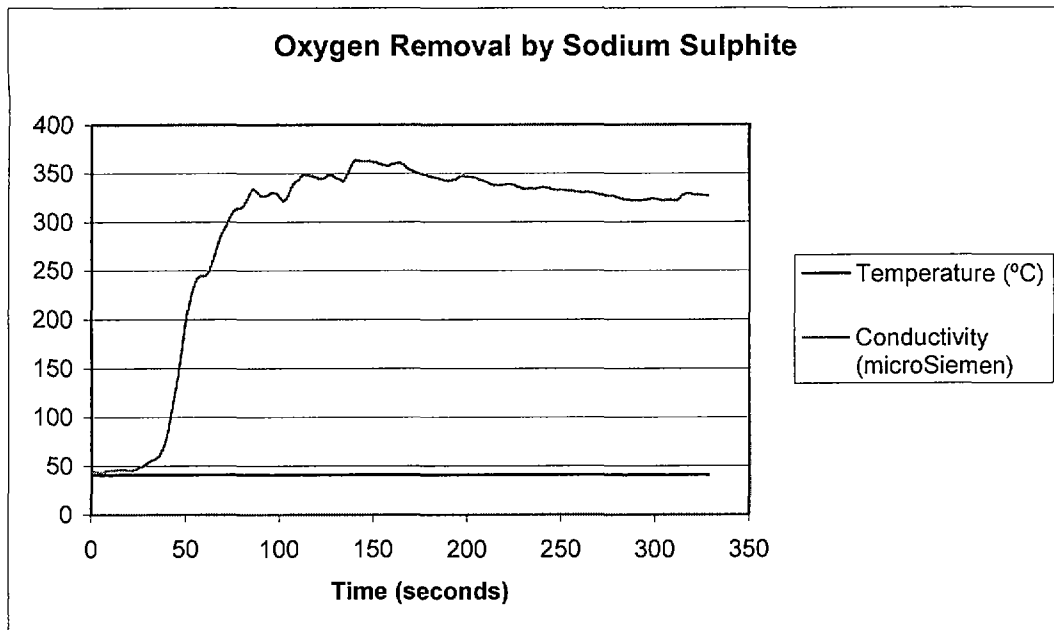


Figure Four – Sodium Sulphite – Variation in pH and Dissolved Oxygen with Time

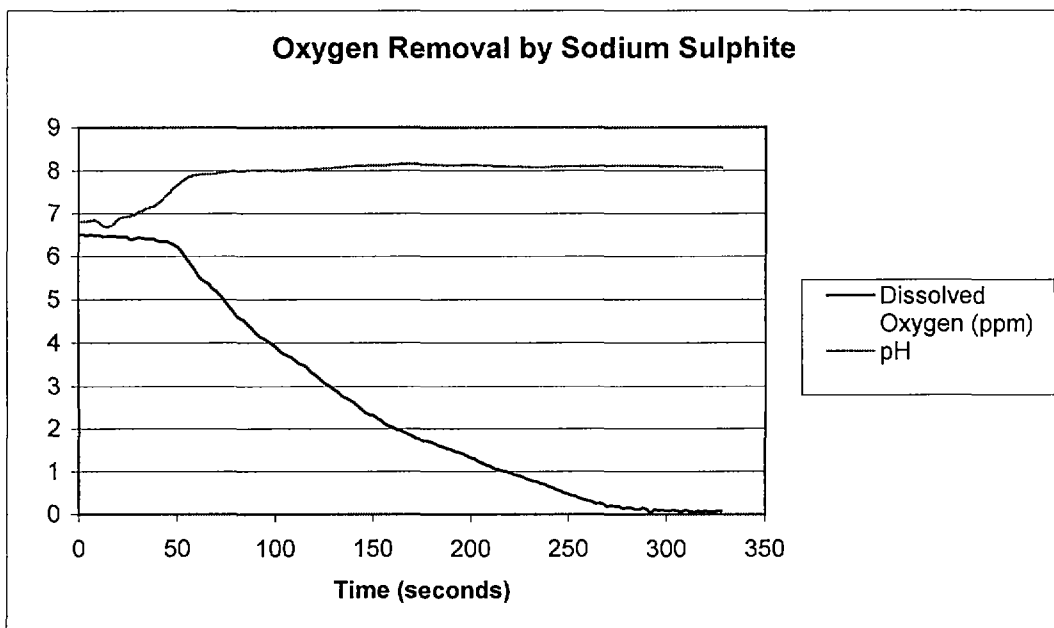


Figure Five – Sodium Sulphite

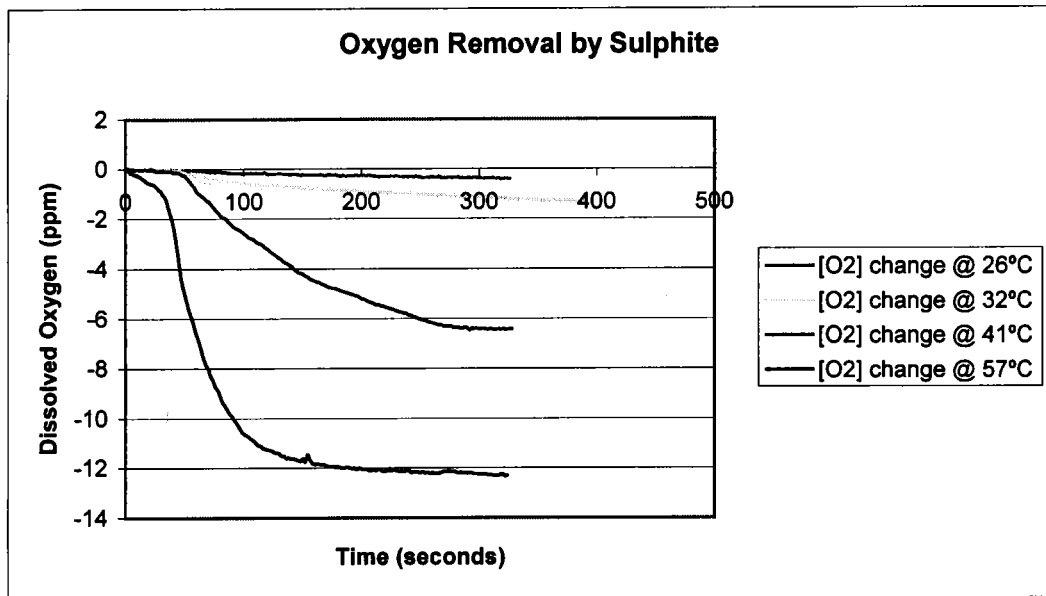


Figure Six - DEHA

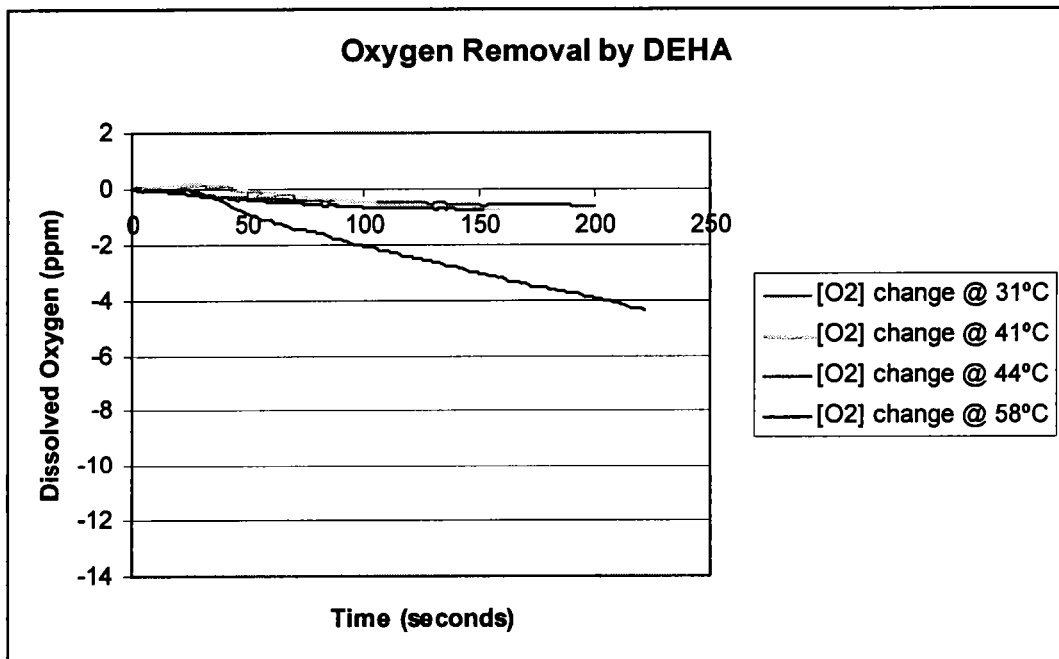


Figure Seven – L-Ascorbic Acid

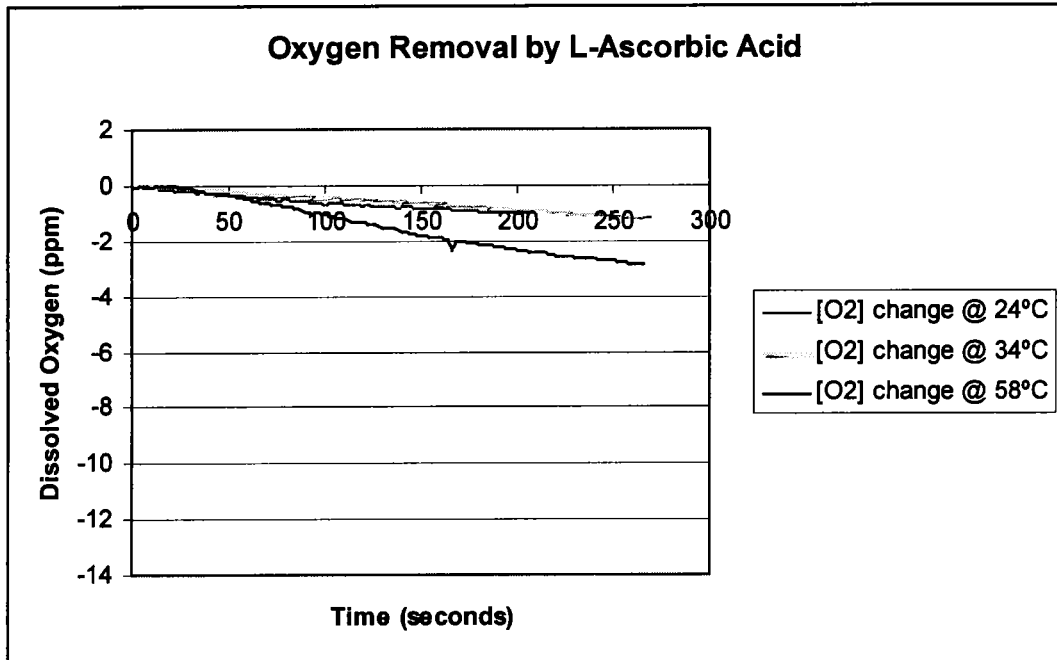


Figure Eight – Hydroquinone

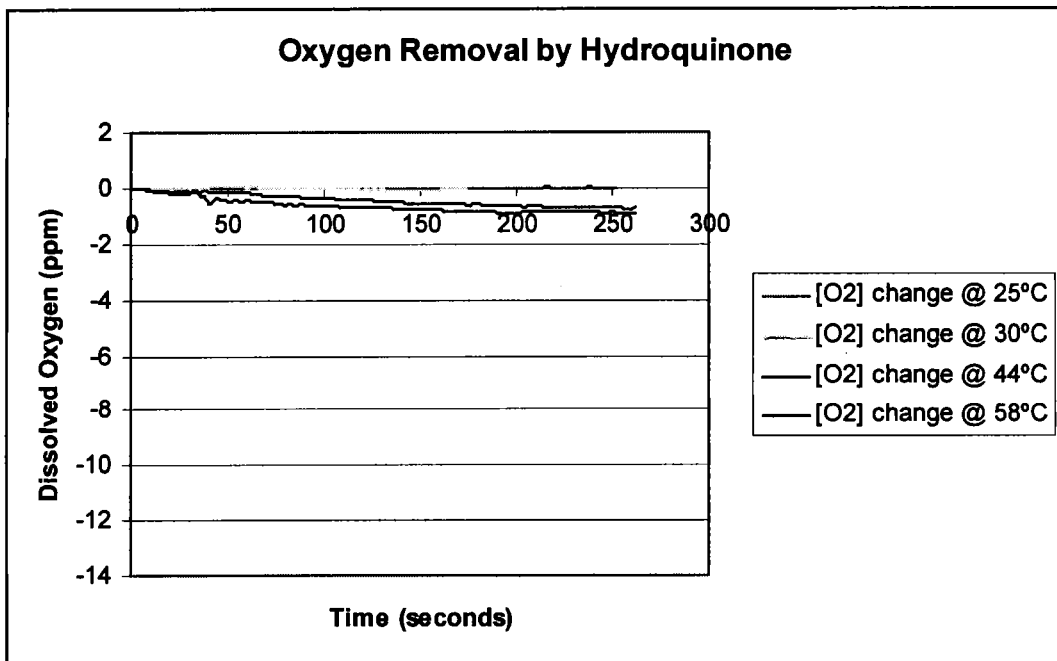


Figure Nine - Hydrazine

