

Radiation Chemistry in the Nuclear Power Reactor Environment: From Laboratory Study to Practical Application

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Introduction

The CANDU (CANada Deuterium Uranium) Pressurised Heavy Water Reactor is a well-established design, with over 30 units in operation or under construction around the world. With more than 350 cumulative years of operation, the CANDU power plant is a safe and reliable electricity production system which combines the use of natural uranium, heavy water, and on-power refuelling. AECL supports its CANDU business with comprehensive research and product development programs that range from underlying research, to applied research, to design, and through to the product itself.

At the Chalk River Laboratories (CRL), underlying and applied radiation chemical research is performed to optimise the processes occurring in the four aqueous systems in and around the core. Key system parameters are given in Table 1 for the Heat Transport System, Moderator, Liquid Zone Controls and End Shields. Further details of the CANDU layout are given in ref. (1). A reliable understanding of radiolysis processes is crucial to controlling reactor chemistry. Knowledge of water radiolysis helps to minimise explosive hazards due to the production of hydrogen/deuterium, minimise the corrosion of materials, and reduce plant emissions.

TABLE 1

Typical Parameters for Aqueous Systems Subject to Radiolysis (CANDU 6: 700 MW)

System	D ₂ O/H ₂ O	Operating temperature (°C)	System volume (m ³)	pH _a [*]	Oxygen (µg/kg)
Heat Transport System	D ₂ O	266-310	175	10.2-10.4	<10
Moderator	D ₂ O	60-70	240	5.0-6.5	~2000
Liquid Zone Control	H ₂ O	38-93	4.5	5.5-8.5	~1000
End Shields/Shield Tank	H ₂ O	60-66	570	10.0-10.5	<10

*pH_a represents the measured pH of a sample at 25°C using an electrode calibrated for H₂O.

Supporting Laboratory Studies at CRL

To understand radiation chemistry in the reactor environment, data sets to model the radiolysis of H₂O and D₂O at temperatures up to 310°C are being assembled. References (2) and (3) summarise the data on kinetics and yield that are available for light and heavy water, respectively. Additional data on kinetics for D₂O are currently being measured at CRL, and Table 2 summarises the reactions studied since the publication of reference (3).

Validation of the Kinetic Models

Most of the reactions involved in the radiolysis of light water have been investigated at elevated temperatures (2), but there are uncertainties associated with the rate constants which could be significant when combined. At CRL, validation of the light-water database has been started by performing γ radiolysis benchmarking experiments at room temperature. In these tests, the time profile of the hydrogen peroxide yield to a steady-state value is measured in H₂O containing different

concentration ratios of H₂ and O₂. The subsequent modelling of the time-dependent yield of H₂O₂ has allowed error bounds to be narrowed. Table 3 summarises the rate constants that have been optimised, together with literature values and the results of recent confirmatory pulse radiolysis investigations at CRL which were performed as a result of the benchmarking program.

TABLE 2
Summary of Recent Kinetic Measurements in D₂O—Work in Progress

Reaction	Temperature (°C)	k ₂₀ (dm ³ mol ⁻¹ s ⁻¹)	E _{act} (kJ mol ⁻¹)	Comments
e _{aq} ⁻ + 'OD	20–150	3.1 × 10 ¹⁰	7.4) unable to separate due to similarity of pK _a 's for xOD and D ₂ O ₂ .
'OD + D ₂ O ₂	20–100	9.0 × 10 ⁶	11.5	
'OD + DO ₂ ⁻	20–100	2.9 × 10 ⁹	12.2	
'O ⁻ + D ₂ O ₂	20–100	2.9 × 10 ⁹	12.2	
'O ⁻ + DO ₂ ⁻	20–100	5.0 × 10 ⁸	10.4) Currently under investigation.
DO ₂ + DO ₂ ⁻	20–300	~1 × 10 ⁵	~24	
DO ₂ ⁻ + O ₂ ⁻	20–300	~1 × 10 ⁷	?) Includes pK _a (DO ₂ x) at elevated temperatures.
O ₂ ⁻ + O ₂ ⁻	20–300	<5 × 10 ⁻¹	^a	

^ak(O₂⁻ + O₂⁻) at 300°C ~1 × 10⁷ dm³ mol⁻¹ s⁻¹.

TABLE 3
Summary of Reaction Rate Constants at 20°C Revised through Benchmarking

Reaction	Reference (4) k (dm ³ mol ⁻¹ s ⁻¹)	Reference (2) k (dm ³ mol ⁻¹ s ⁻¹)	γ radiolysis k (dm ³ mol ⁻¹ s ⁻¹)	Pulse radiolysis k (dm ³ mol ⁻¹ s ⁻¹)
e _{aq} ⁻ + O ₂	(1.7–2.2) × 10 ¹⁰	1.62 × 10 ¹⁰	1.74 × 10 ¹⁰	1.89 × 10 ¹⁰
e _{aq} ⁻ + H ₂ O ₂	(0.95–1.2) × 10 ¹⁰	1.27 × 10 ¹⁰	1.23 × 10 ¹⁰	1.23 × 10 ¹⁰
OH + H ₂	(3.4–6.0) × 10 ⁷	3.68 × 10 ⁷	3.28 × 10 ⁷	3.28 × 10 ⁷
OH + H ₂ O ₂	(2.0–3.8) × 10 ⁷	2.59 × 10 ⁷	2.87 × 10 ⁷	2.70 × 10 ⁷
OH + O ₂ ⁻	(0.7–1.1) × 10 ¹⁰	1.02 × 10 ¹⁰	1.07 × 10 ¹⁰	—

Case Study of the Application of Laboratory Data to Reactor Operation

The ability to reliably predict the radiation chemistry within the reactor core enables the chemistry to be optimised. For example, the inclusion of radiolytic reactions involving solutes allows the effects of potential changes to plant chemistries to be assessed.

As an example, in CANDU reactors that produce ⁶⁰Co commercially, there is a regulatory limit as part of the safety case (1) that the moderator-dissolved deuterium concentration cannot exceed 4.5 ml kg⁻¹ for extended periods. This limit is operationally restrictive at reactor startup where excess deuterium production is attributed to the addition of the nitrate salt of gadolinium to compensate for the ¹³⁹Xe transient in the fuel (Figure 1).

The enhanced production of deuterium is caused by the nitrate ions, which interfere with the radiolytic reactions that would recombine dissolved D₂ with O₂ and D₂O₂. Radiation-chemical experience indicated that the substitution of a more radiolytically inert counter-ion would minimise the production of deuterium. This suggested the use of the sulphate salt of gadolinium to compensate for the xenon transient. However, it is important to assess any potential drawbacks to the chemistry change in addition to the radiation-chemical benefits prior to reactor application.

In this case, the radiolytic production of reduced sulphur compounds from the sulphate ions could potentially have a deleterious effect on the stainless steel calandria. Laboratory radiolysis tests were performed using stainless steel coupons

sealed in pyrex ampoules containing gadolinium sulphate solution. X-ray photoelectron spectroscopy of the irradiated coupon surfaces showed no evidence of the presence of reduced sulphur species.

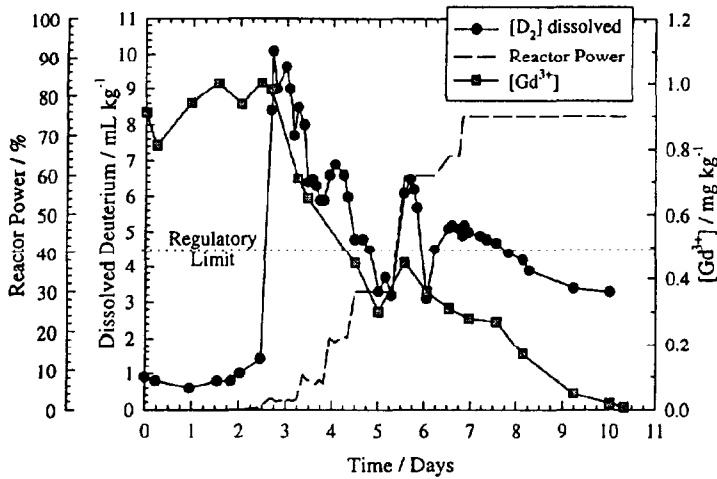


Figure 1. Reactor startup using gadolinium nitrate reactivity shim.

Laboratory γ radiolysis of H_2O solutions containing gadolinium nitrate or gadolinium sulphate (Figure 2) demonstrated, at the 10 mg kg^{-1} gadolinium level, that the substitution of the nitrate with sulphate would significantly reduce the production of deuterium. Modelling of the system (Figure 2) with the light-

water radiolysis (2) database which included a simplified nitrate reaction set concurred with the experimental results. Partitioning of gaseous species between liquid and gas phases according to Henry's law was incorporated into the model.

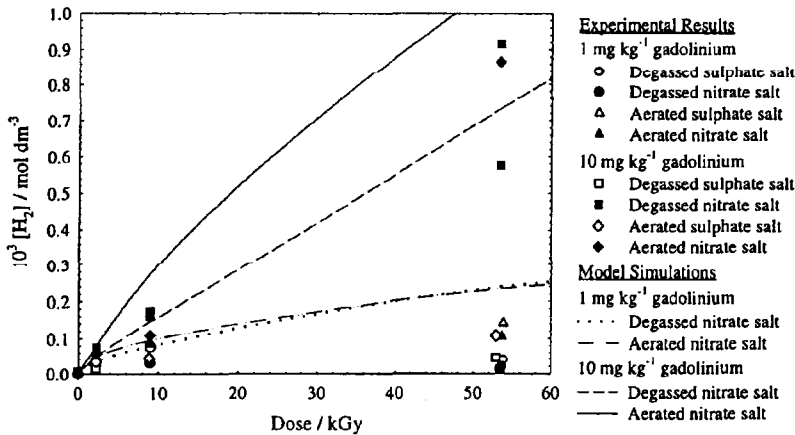


Figure 2. Hydrogen production from γ radiolysis of gadolinium solutions.

Reactor start-ups using gadolinium sulphate to compensate for the xenon transient resulted in lower dissolved deuterium levels (Figure 3).

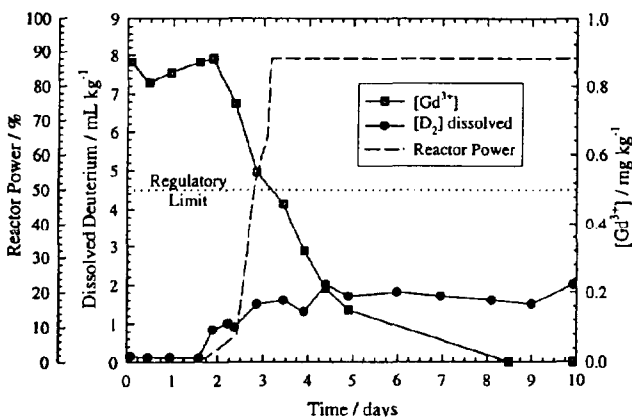


Figure 3. Reactor startup using gadolinium sulphate reactivity shim.

Conclusions

Overall, the laboratory and reactor studies have resulted in an improvement in safe plant operation. The chemistry control in the moderator has now been improved, and the operational constraints imposed by the excess deuterium production have been removed.

This is one example which demonstrates that the use of γ -radiolysis studies combined with kinetic modelling can be applied to operating power reactor systems to result in improved chemistry control and optimised operating conditions.

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