

# SCWR MATERIALS AND CHEMISTRY

## STATUS OF ONGOING RESEARCH

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### I. INTRODUCTION

The idea of using a supercritical water (SCW) coolant in a water-cooled reactor dates back to the 1960s, [1, 2] although no such reactor was ever built. More recently, two types of supercritical water-cooled reactor (SCWR) concept have evolved from existing light water reactor (LWR) and pressurized heavy water reactor (PHWR) designs: (a) a number of designs [3, 4, 5] consisting of a large reactor pressure vessel containing the reactor core (fueled) heat source, analogous to conventional Pressurized Water Reactor (PWR) and Boiling Water Reactor (BWR) designs, and (b) designs with distributed pressure tubes or channels containing fuel bundles, analogous to conventional CANDU<sup>1</sup> and Reactor Bolshoy Moschnosty Kanalny (RBMK) nuclear reactors. [6] Designs in both concepts are typically direct cycle, with out-of-core portions similar to existing fossil-fired generators. Aside from the design concept itself, the most important technical issue is likely to be the identification of a) materials for in-core and out-of-core components and b) an appropriate coolant chemistry. The reference design for the SCWR [7, 8] calls for an operating pressure of 25 MPa, a core inlet temperature of about 280°C and a core outlet temperature up to 620°C. Peak fuel cladding temperatures could be as high as 850°C in some designs. [9]

The SCW coolant in both the pressure vessel and pressure tube concepts lies in both the liquid and supercritical fluid areas of the T-P phase diagram (Figure 1). The coolant will pass through the critical point at some location in the reactor core. The corrosivity of SCW varies widely depending upon the values of properties such as the density, ion product and dielectric constant, as well as on the nature of any solutes present (impurities, dissolved oxygen) and their concentrations. [10] At the low density ( $\sim 0.1 \text{ g/cm}^3$ ) expected at the core outlet of an SCWR, SCW is a non-polar solvent able to dissolve gases like oxygen to complete miscibility. While the solubility of ionic species is expected to be extremely low under these conditions, the formation of neutral complexes increases with temperature, and can become important under near-critical and super-critical conditions. It has been suggested that the most important temperature range is from 275 to 450°C, over which the properties of water change dramatically, and solvent compressibility effects exert a huge influence on solvation. With the exception of a few recent studies, [11] the thermochemistry of neutral hydrolysed metal species is poorly understood, even at temperatures well below the critical point.

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<sup>1</sup>CANDU<sup>®</sup> CANada Deuterium Uranium, is a registered trademark of Atomic Energy of Canada Limited (AECL).

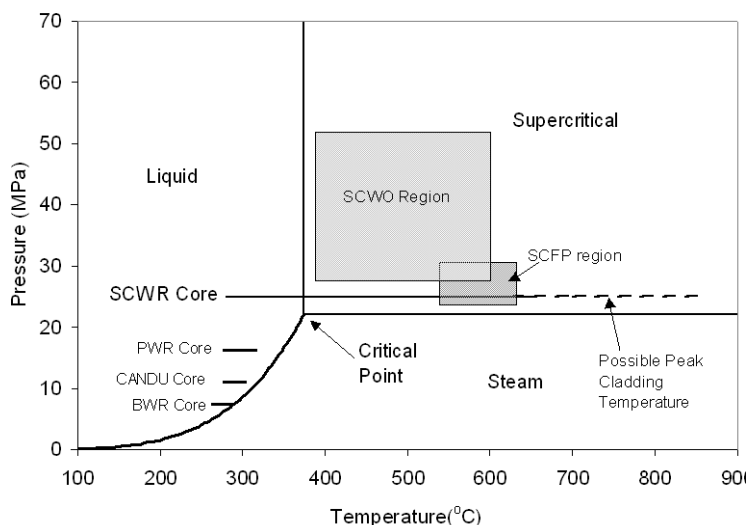


Figure 1: Temperature-pressure phase diagram of water. The operating regions of present BWR, PWR and CANDU plants and of proposed SCWR designs are indicated. Also shown are the operating regions for supercritical fossil-fired boilers (SCFP) and supercritical water oxidation (SCWO) processes. Adapted from [12].

The GIF SCWR materials and chemistry provisional project management board (PPMB) has identified two major challenges that must be overcome to ensure the safe and reliable performance of an SCWR:

1. Insufficient data are available for any single alloy to unequivocally ensure its performance in an SCWR, especially for alloys to be used for in-core components.
2. Current understanding of SCW chemistry is inadequate to specify a chemistry control strategy, as the result of the large changes in physical and chemical properties of water through the critical point, coupled with the as yet poorly understood effects of water radiolysis.

To address these challenges, two Work Packages, one on SCWR Materials and the other on Radiolysis and Water Chemistry, have been developed for the GIF SCWR Materials and Chemistry draft Project Plan. This paper broadly outlines these work packages, describes some of the key challenges, and presents some of the progress being made to overcome these challenges.

## II. MATERIALS

Although they have different requirements for most core components (*e.g.*, reactor pressure vessel internals, nozzles, supports in a pressure vessel design; ceramic insulator, metallic liner in a pressure tube design), the pressure vessel and pressure tube designs share common issues with respect to materials for out-of-core components and fuel cladding. There are therefore strong synergies between the materials R&D needs of the two designs.

Initial alloy selection for testing for the SCWR was guided by existing data from supercritical and ultra-supercritical fossil-fired power plants and supercritical water oxidation (SCWO) systems. While extensive testing was carried out in support of the development of SCWO processes, the chemistry conditions were typically not of direct relevance to an SCWR, being very acidic with high concentrations of aggressive species such as chloride ion. Therefore, although knowledge gained from current reactor designs, modern boiler technologies and research in support of SCWO has provided valuable insights that have aided in the identification of key parameters, the PPMB has concluded that there are still significant gaps

in our knowledge about the properties of the materials under proposed SCWR operating conditions.

To address these gaps the draft Project Plan divides the work package on materials into two main tasks:

1. Study of Un-irradiated Materials
2. Study of Irradiated Materials

Each main task has been further subdivided into the following sub-tasks:

1. Development of Materials Databases in SCW
2. Material Testing and Performance Evaluation
3. R&D on Coatings and Surface Modification

A four tier testing strategy has been developed (Figure 2), reflecting the fact that fundamental data on relevant materials properties can be measured with great precision and a high

degree of control in test loops and autoclaves (Figure 2, Levels 1-3). Tests using irradiated materials or simulated radiolysis conditions significantly increase the experimental challenges. Complete control of all test parameters will be difficult in an in-reactor test loop (Figure 2, Level 4). For example, direct measurement of the electrochemical corrosion potential (ECP) of a test specimen in an in-core loop is not possible with existing technologies.

Sub-task 2 in the Project Plan (Material Testing and Performance Evaluation) focuses on acquiring data on, and developing a mechanistic understanding of, the following key material properties:

1. Corrosion and Stress Corrosion Cracking (SCC)
2. Dimensional and microstructural stability
3. Strength, embrittlement and creep resistance.

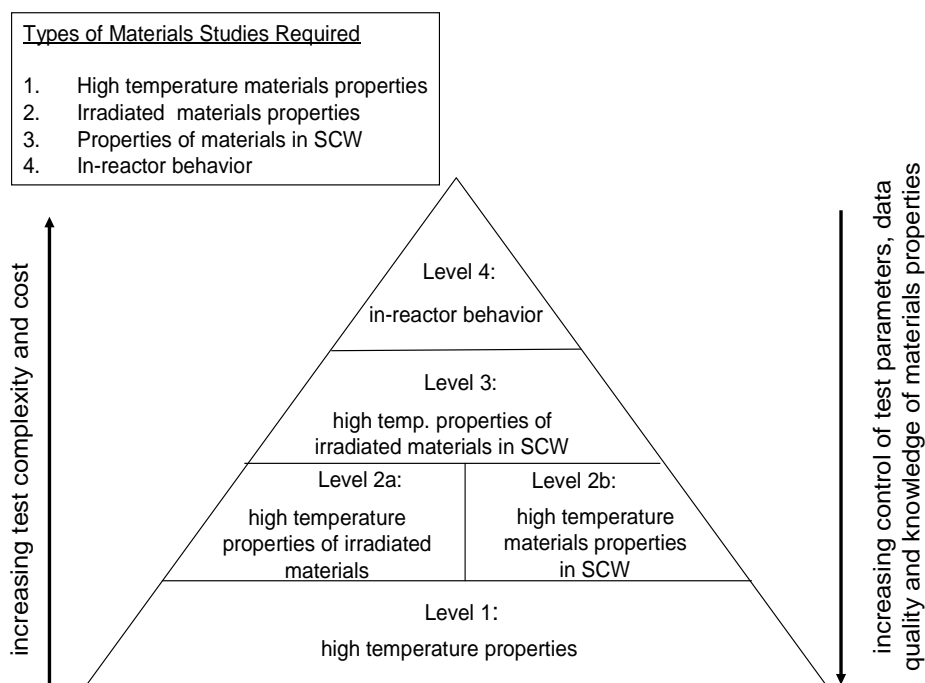


Figure 2: Schematic of the four-tier test program for the GIF SCWR Materials Work Package.

Alloy class	Temperature (°C)	Water chemistry	Exposure time (h)
Austenitic SS	290-650	DO <sup>a</sup> from deaerated <sup>b</sup> to 8 ppm	24-3000
Ni-base	290-600	DO from deaerated to 8 ppm, Conductivity <0.1 mS/cm	24-3000
Ferritic-Martensitic	290-650	DO from deaerated to 8 ppm, Conductivity <0.1 mS/cm	100-3000
Oxide Dispersion Strengthened steels	360-600	25 ppb	200–3000
Zr-base	400-500	Deaerated DO, Conductivity <0.1 mS/cm	<2880
Ti-base	290– 550	8 ppm DO, Conductivity 0.1 mS/cm	500

a – dissolved oxygen

b – typically <10 ppb

TABLE I: Summary of Materials Corrosion Testing Under SCWR Conditions (adapted from [14])

Table I summarizes the alloy classes and test conditions examined to date. The alloy classes tested include ferritic-martensitic (F/M) and austenitic steels, Ni-base alloys, Oxide Dispersion Strengthened (ODS) steels, Zr-base alloys, and Ti-base alloys; most of the focus has been on the first four classes. Several alloys have been the subject of numerous studies (*e.g.*, Alloy 625), but some data under relevant conditions are currently available for approximately 90 alloys. The available corrosion data under SCWR conditions show that the oxidation rate of steels, especially F/M steels, is rather high, increasing rapidly above 500°C. In addition to general corrosion, SCC (intergranular and transgranular) is expected to be a critical degradation mode in an SCWR [13, 14]. The mechanism of SCC in SCW is currently being studied using techniques such as slow strain rate testing and U-bend specimens; more sophisticated loading methods are also being developed (*e.g.*, [13]). SCC requires both a mechanical and a chemical component (*e.g.*, T, P, water chemistry, loading mode, material processing), so that a large

number of parameters must be studied. The existing data show that austenitic stainless steels and Ni-base alloys exhibit greater susceptibility for SCC than F/M alloys.

The key experimental variables affecting corrosion identified to date are temperature, water density (pressure), dissolved oxygen concentration, water conductivity and surface finish. Tests have been performed at temperatures ranging from below the critical temperature up to 650°C. The water chemistry has typically been low conductivity “pure” water with dissolved oxygen concentrations ranging from <10 ppb to 8 ppm. Test durations have ranged from 24 to 3 000 hours. After exposure to SCW, test specimens have been characterized using techniques ranging from weight change to surface analytical methods such as Scanning Electron Microscopy, Transmission Electron Microscopy and Scanning Auger Microscopy. Tests have been performed in static autoclaves, capsules, and loops; each type of test facility has advantages and disadvantages. To facilitate comparison of data from different laboratories and tests facilities, a series of round robin tests are planned, commencing in 2009, using a standard set of test conditions (Table II) and coupon preparation procedures.

To assist in interpretation of the large amounts of data now becoming available for some alloys, a key project task (Sub-task 1) is the development of a database of corrosion and materials data. Data for the database will be taken from the existing literature in addition to data from experiments underway as part of the project.

Parameter	Value
Temperature (°C)	550
Pressure (MPa)	25
Dissolved Oxygen Concentration (ppb)	50 and 8000
pH <sub>25°C</sub>	~7 at room temperature and pressure
Water resistivity, room temperature and pressure (MΩ)	18
Test duration (h)	500
Test Alloys	310 SS, Alloy 690, P/T 91, ODS (MA956, MA957)

TABLE II: Test Conditions for Round Robin Testing

Work is underway to characterize the mechanical properties of candidate alloys, including fracture toughness, tensile strength, and creep resistance. For in-core materials, understanding irradiation-induced changes due to growth, swelling, helium-bubble formation, dislocation microstructure, precipitate micro-structure and irradiation-induced composition changes, and demonstrating that these changes will not compromise the integrity of core components is a key requirement. Some measurements on irradiated materials have been carried out, [15] and much more work is needed in this area.

In addition to experimental programs, focused modelling effort is underway to improve understanding of materials-environment interactions within a shorter time frame. A number of key degradation processes (*e.g.*, general corrosion, pitting, SCC initiation and growth, irradiation and thermal creep) are being modelled using the latest computational techniques.

As no one alloy has yet been identified that possesses all of the properties required for critical SCWR applications (good resistance to corrosion at the surface, good resistance to SCC, creep and radiation damage in the bulk), one potential solution is to modify the surface of a material possessing the required bulk properties to impart the desired corrosion resistance [16, 17]. This approach is being explored in the third materials sub-task. While only limited work has been carried out on surface modification, there have been some promising results; for example, because the surface alloying layer can be produced after fabrication of in-core components (*i.e.*, after forming and joining operations), formability and weld ability issues can be avoided.

### III. CHEMISTRY

There is a strong interplay between coolant chemistry and materials selection in any water-cooled nuclear power plant system. The long-term viability of an SCWR will depend on the ability of reactor developers to identify a set of chemistry control specifications that will satisfy the (sometimes conflicting) requirements to minimize materials degradation and radionuclide

transport, optimize thermal performance and maximize system lifetime. The SCWR coolant will undergo a transition from “water-like” to “steam-like” densities (from  $\sim 0.8$  to  $0.1 \text{ g/cm}^3$ ) as it passes from subcritical to supercritical conditions through the reactor core. Operating experience from supercritical thermal power stations has shown that the region of most importance is the “pseudo transition zone” [18] from 275 to 450°C at 25 MPa. Few quantitative studies of aqueous solutes have been performed above 300°C; above 450°C, SCW is sufficiently steam-like that solid-gas thermodynamic models may be adequate.

Compared to the large body of work on materials testing, little work on SCWR water chemistry has yet been carried out. [19, 20, 21] The long-term goal of the Radiolysis and Water Chemistry Task is to specify a suitable water chemistry for the SCWR design. Candidate water chemistry regimes and specifications for key chemistry parameters (pH, dissolved oxygen and hydrogen concentrations, concentrations of any other additives, allowable concentrations of impurities, etc.) must be identified prior to any long-term materials testing.

The Radiolysis and Water Chemistry work package consists of four Tasks:

1. Studies of Radiolysis of SCW.
2. Understanding Corrosion Product Transport and Deposition.
3. Specification of Water Chemistry for Detailed Testing.
4. Identification of Methods for Chemistry Monitoring and Control.

As experiments at very high temperatures and pressures, especially beyond the critical point of water, are difficult to perform, computer simulations are an important route of investigation for Tasks 1 and 2. However, a large amount of fundamental experimental data will be needed in order to develop such models, and the model predictions will need to be further validated against experimental data.

Potentially the biggest challenge for the development of an SCWR water chemistry regime will be predicting and mitigating the effects of water radiolysis. [22-24] The radiolytic production of oxidizing species (*e.g.*, OH, H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub>, and HO<sub>2</sub>/O<sub>2</sub><sup>-</sup>) can increase corrosion of reactor components as well as affecting corrosion product transport and deposition. While current PWRs and PHWRs limit the formation of oxidizing species by ensuring the presence of excess hydrogen at concentrations sufficient to chemically minimize the net production of oxidizing species by radiolysis, there are insufficient data to determine whether this strategy would be effective in an SCWR. As a consequence the coolant could be very oxidizing immediately downstream of the core. Work is ongoing to develop an improved understanding of SCW radiolysis through a combination of experiments and modeling.

The release and transport of corrosion products (CPs) from the surfaces of system components has been a serious concern for all water-cooled nuclear power plants. High levels of CP transport can result in: a) increased deposition on fuel cladding surfaces, leading to reduced heat transfer and the possibility of fuel failures, and b) increased production of radioactive species by neutron activation, ultimately increasing out-of-core radiation fields and worker dose. In addition, nuclear and thermal power stations experience deposition of steam-volatile species on turbines at levels that can cause turbine failure. Supercritical thermal station experience suggests CP deposition could be significant in an SCWR. [25, 26] Some preliminary work on CP transport in an SCWR

has been performed [20, 26] with encouraging results. [27]

Several water chemistry regimes are typically used in fossil-fired SCW plants [26, 28] (Table III). However, to date most experimental work on SCWR materials has been carried out in a limited range of water chemistries, namely pure water, pure water with added oxygen (50-8 000 ppb), and hydrogen water chemistry (H<sub>2</sub> concentration ~ 30 cm<sup>3</sup>/kg water). Additional testing under a wider range of water chemistries is required. These candidate water chemistries will need to be assessed in an in-reactor loop, such as the loop currently being commissioned at the Nuclear Research Institute Řež plc in the Czech Republic, as a part of the European Union High Performance Light Water Reactor project, [29] to determine their effect on radiolysis and corrosion product transport.

It will be necessary to monitor and control relevant chemistry parameters (*e.g.*, conductivity, pH, ECP, concentrations of dissolved hydrogen and oxygen) in an SCWR and in in-reactor test loops. [19] Existing methods of chemistry monitoring, predominantly ex-situ (cooled and de-pressurized) and off-line (laboratory analysis of grab samples), will be inadequate in an SCWR, as a result of the large changes in water chemistry around the critical point. It is likely that reliable monitoring of key chemical parameters can only be achieved through the development of in-situ or on-line probes, and there is a need for more work on this topic.

Table III: Summary of Water Treatments used in Supercritical Water Fossil-Fired Power Plants

Water Chemistry	pH at 25°C	Comments
NH <sub>3</sub> + N <sub>2</sub> H <sub>4</sub>	8.5 – 9.6	
N <sub>2</sub> H <sub>4</sub> only	7.7 – 8.5	60-100 µg/kg N <sub>2</sub> H <sub>4</sub>
Chelant + NH <sub>3</sub> + N <sub>2</sub> H <sub>4</sub>		80 µg/kg chelant, 0.8 mg/kg NH <sub>3</sub> , 0.2 mg/kg N <sub>2</sub> H <sub>4</sub>
pH 7 with O <sub>2</sub>	6.5 – 7.3	50-200 µg O <sub>2</sub> /kg, conductivity <0.1 µS/cm
Combined Mode	8 – 8.5	NH <sub>3</sub> +O <sub>2</sub> - NH <sub>3</sub> provides slight pH buffering

#### IV. CONCLUSION

While there are still many unresolved issues, significant progress has been made in acquiring the data on materials properties needed to enable a short list of candidate alloys to be chosen for longer term testing. Some data on materials properties under SCW conditions are currently available for about 90 alloys. A number of out-reactor test facilities are now operating,

and some testing of irradiated materials has also been performed. The planned round robin testing and the databases under development will facilitate comparison of data from different laboratories and enable correlations to be developed (*e.g.*, effect of Cr content of alloys). While the pace is not as rapid, some progress in understanding water chemistry issues such as radiolysis and corrosion product transport in SCW has been made.

#### Acknowledgements

The author would like to acknowledge many valuable discussions with PPMB members and alternates, past and present, including L. Heikenheimo, H. Matsui, P. Arnoux, J. Jang, J. Kaneda, S. Kasahara, G. Was, S.S. Huang, W. Zheng, and to thank the technical secretariat, S. Aniel-Buchheit, for ensuring that everything stayed on track. He would also like to acknowledge stimulating and fruitful discussions with T. Allen and J. Kysela.

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