

The effect of inorganic materials on the behaviour of SCW in the vicinity of the pseudo-spinodal line

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ABSTRACT

Supercritical water is a candidate for working fluid in the new Generation IV nuclear power plants. Due to the presence of the pseudo-critical line, the thermo-hydraulics (thermal and flow properties) and the physical chemistry of the supercritical water differs significantly from the pressurized hot water used in former types of nuclear reactors. In this study we would like to analyze the effect of small amount of inorganic material (like corrosion products) on the thermo-hydraulics of the supercritical water cooled nuclear reactors.

INTRODUCTION

The Supercritical Water Reactor (SCWR) is one of the set of theoretical nuclear reactor design called "Generation IV reactors", intended to replace the present nuclear reactors after 2030 [1,2]. In SCWR, supercritical water would be used (at 25 MPa and between 550-770 K) as the working fluid. Compared to present Light Water Reactors (LWRs), the thermal efficiency would be 50% higher (45%, instead of 33%) and the structure of the reactor would be much simpler and therefore much safer. Also, phase transitions would be avoided, except during accidental condition, when the pressure drop caused by a leak can cause simultaneous vapour condensation and steam generation in various part of the cooling system [3].

Although SCW are used as working fluid for supercritical fossil fuel fired boilers too, applying it in nuclear industry would require a lot of new information, some of them is nuclear-related, while others are necessary for the higher safety standard.

One should realize that even high-purity SCW will not be pure after a few days-months-years of use (not to mention the possibility of introducing some additives). One of the possible sources of the contamination is the solid material in contact with the water. Due to the corrosion, several metal-oxides and hydroxides can be in contact with the SCW; not only ferrous ones, but - depending on the composition of the steel - cobalt, nickel, titan chromium, etc. ones. Although these materials are hardly soluble in water, one can expect that together they might have a few to few hundred ppm. Due to the lack of the miscibility data of these materials, we would like to give an estimate for the effect of inorganic contaminant for the SCW working fluid, by using data for a relatively known "model inorganic material", namely the sodium chloride.

Behaviour of aqueous NaCl solutions have been studied extensively [4–9], even in the vicinity of the stability region [10,11] and in the supercritical region [12-15]. We would like to focus on properties relevant to the flow and heat exchange related properties; here compressibility and heat capacity results will be presented and discussed.

The behaviour of supercritical water differs not only quantitatively but sometimes even qualitatively from the pressurized and hot but still subcritical one. Two of the crucial differences have to be mentioned here. First, several properties – like isotherm compressibility, isobaric specific heat, etc – have an extremum in the supercritical region, while they are monotonous functions of the temperature in the subcritical one. These extrema

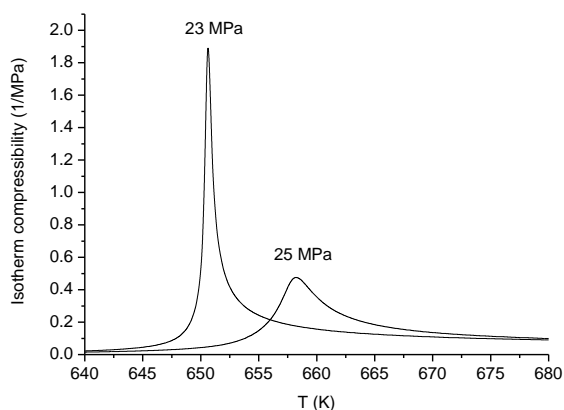


Figure 1: The extrema of isothermal compressibility of pure water on 23 and 25 MPa, calculated by the IAPWS-95 equation of state

can be very pronounced close to the critical point (Fig. 1) and still strong at 25 MPa. One can define a line connecting these extrema; the one connecting the isotherm compressibility maxima is the so-called Widom-line, often referred as pseudo-critical or pseudo-spinodal line. We should mention here that the location of these lines connecting the extrema of various properties - which strongly effects the form of tabulated data used in various codes - are not necessarily coincide; further works on that field is in progress.

The other difference is the behaviour of water as solvent; with some simplification, one can say that while the sub-critical water is good solvent for inorganic and bad solvent for organic materials, it turns into the opposite in the SC region; it could dissolve several organic materials but could not dissolve some inorganic ones. In the nuclear industry usually one does not have to worry about organic materials, but inorganic ones cannot be excluded. Even by using pure SCW, after days or months various corrosion products will dissolve into it. Although the miscibility of these inorganic materials is bad, i.e. their concentration cannot be high; they can still reach several hundreds of ppm. Even this small amount can shift the aforementioned extrema a little bit. This shift can cause measurable differences for between the expected and real quantities at a given temperature; here we would like to give an estimate for the magnitude of this effect.

Because the miscibility behaviour of various oxides in the supercritical region is not well-known and additionally we do not have proper equation of state to describe those solutions, we are using salt water as a model system. The miscibility of NaCl at 25 MPa around the Widom-line drops from 700 ppm to 300 ppm, therefore we are going to study the effect of 100 and 200 ppm contaminations on the compressibility. All calculations are performed at 25 MPa, except where other pressure values are stated.

METHODS

It is hypothesized that the aqueous solutions with small impurities obey the corresponding state principle. The Widom line up to 25 MPa is a continuation of vapor pressure line where extrema of response functions are coincided. As result the reduced pressure (P_R) for the Widom line of the aqueous solution can be expressed as a function of the reduced temperature (T_R). Our study has applied the modified Wagner–Pruss equation from [16] to express both the vapor pressures and critical parameters of aqueous NaCl.

To calculate the response functions (heat capacity, isothermal compressibility, and etc.) at different concentrations NaCl in the range 0 ... 300 ppm the Widom line was built in reduced variables $P_R = P/P_C(X)$, $T_R = T/T_C(X)$. Here the critical parameters are a function of the mole fraction of the salt (X). The Widom line for pure water at supercritical states has been calculated via a very accurate equation of state proposed by Pruss and Wagner [16]. The uncertainty in density of the IAPWS -95 equation of state is 0.0001% at 1 atm in the liquid

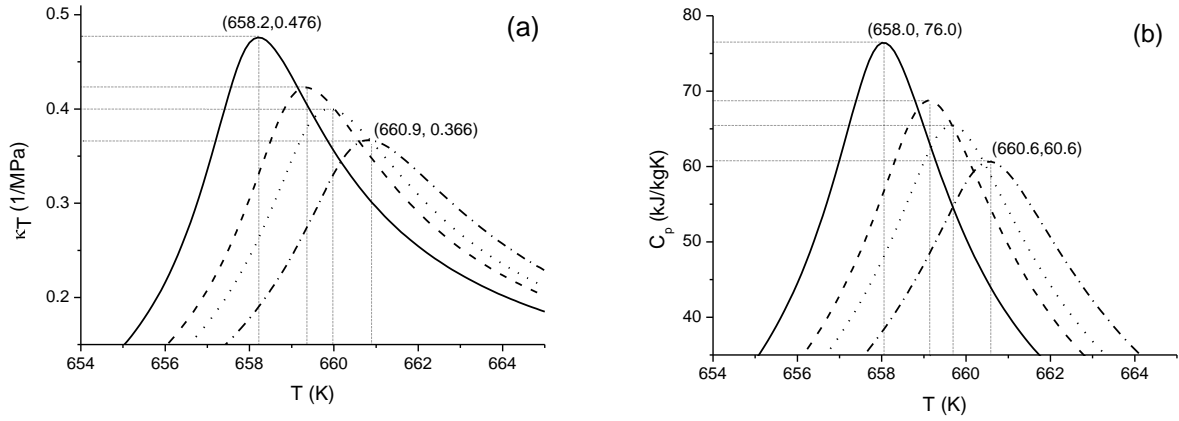


Figure 2: Isothermal compressibilities (a) and isobaric heat capacities (b) of pure water (solid) and water with 100 (dashed), 200 (dotted) and 300 (dash-dotted) ppm salt at 25 MPa with the shift of the pseudospinodal. Peak values for pure water and 300 ppm solution are marked..

phase, and 0.001% at other liquid states at pressures up to 10 MPa and temperatures to 423 K. The uncertainties rise at higher temperatures and/or pressures, but are generally less than 0.1% in density except at extreme conditions. The uncertainty in isobaric heat capacity is 0.1% in the liquid phase.

To estimate response function extrema at temperatures and pressures along the Widom line the reduced relationships “property – temperature” are used. For example, reduced isothermal compressibility is defined via scaled pure water properties

$$\kappa_R = \kappa * P_C = \kappa_{H_2O} (\Theta T_R, \pi P_R) \quad (1)$$

where the empirical factors Θ, π are calculated from condition of maximum κ_R at the Widom line. Our calculations are in good agreement with the results of Driesner who studied salty water in the range of 0-1000 Celsius and 1-500 MPa [17].

RESULTS

The changes of the compressibility and heat capacity in the vicinity of the pseudospinodal can be seen in Figure 2. It can be seen that the peak of the compressibility and of the heat capacity shifts 2.6-2.7 K; this shift is equal with a 7 bar pressure change induced shift (from 25 MPa to 25.7 MPa). This shift itself - which is coupled with the shift of other changes related to the pseudospinodal, like density change, etc. - could cause some difficulties. Thermohydraulic calculations will be more and more complex around the Widom line. Expecting stationary flow with constant temperature profile, the location of these pseudospinodal peaks can shift to another location. This can cause for example the shift of the location of the deteriorated and improved heat transfer, which can cause problem with the cooling of the wall, or - in this case - with the cooling of the core (active zone) of the nuclear reactor. Deteriorated heat transfer (causing local overheating of the wall) occurs, when the liquid bulk temperature is below the pseudospinodal temperature, while the wall temperature is above that value [18-21]. Obviously the shift of the pseudospinodal region can cause the shift of the overheated region of the wall. The knowledge of the location of these regions are necessary to design the cooling system.

The pseudospinodal (Widom line) between the critical point and 25 MPa) and the shift of the critical point by changing the concentration between 0 and 300 ppm can be seen on Figure 3. The shift of the Widom temperature (at 25 MPa) seems to be linear in the 0-300 ppm concentration range (Figure 4). From the data of Figure V, one can conclude that the concentration dependence of the Widom temperature shift is 0.0084 ± 0.0006 K/ppm. From

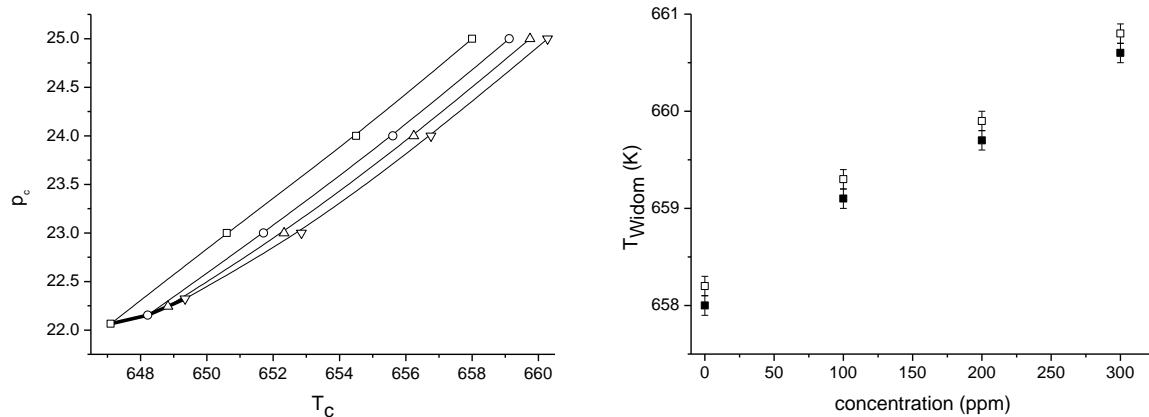


Figure 3 (right): The location of the pseudo-spinodal (Widom-line) for pure water (squares), and for various solutions of NaCl (100 ppm: circles, 200 ppm: up-triangles, 300 ppm: down-triangles). The shift of the critical point is marked by thick line.

Figure 4 (left): The location of the pseudo-spinodal (Widom-line) for pure water and for various solutions of NaCl, determined from the peak of isothermal compressibility (open squares) and isobaric heat capacity (full squares).

this value it can be seen that trace contaminations cannot cause any remarkable effect; to

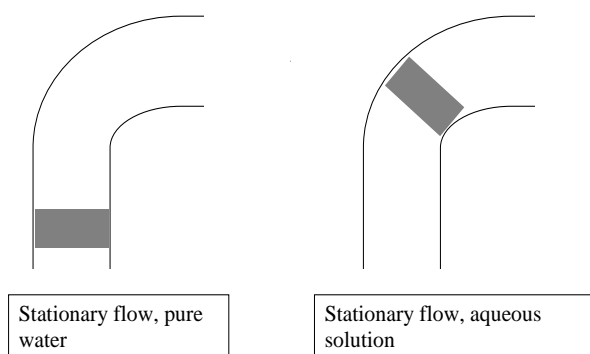


Figure 5.: Schematic representation of the shift of the pseudospinodal region in stationary flow with constant temperature profile. The various zones where the compressibility, C_p and other maxima located are shaded.

reach a few tenth K shift one need contaminant concentration around 50-100 ppm. Therefore one of the solutions to avoid these problems is the permanent cleaning of the working fluid. i.e the removal of the dissolved materials.

With stationary flow in the SCWR, the location corresponding to the C_p or κ_T peaks can be estimated. The pseudospinodal peak will be located in the so-called "Evaporator" [1,2], at the height of 2.85 m. The 2.6-2.7 K temperature shift is corresponding to a few centimeter upward shift. This few centimeter shift can cause problem when it is caused in a "bend", like on Figure 5. It can be expected that shifting the pseudospinodal location from a straight piece of pipe-part into a bended part or to a vicinity of a valve (as it might happen in any other SCW loop, but fortunately not in the SCWR) can cause remarkable changes in the flow.

Also, the change of the compressibility in fixed location can cause the change of pressure whenever pressure waves are invoked (like the so-called piston effect) [21]. In this way, the thermophysical parameters will be changed too, changing the whole local thermo-hydraulic.

The dependence of the relative changes (Figures 6-7) are less linear than for the pseudospinodal temperature vs concentration plot, but one can still approximate it in that way. The concentration dependence of the relative changes of the response function values at the pure SCW Widom-temperature are 0.0019 ± 0.0003 1/ppm for the compressibility and 0.0016 ± 0.0002 1/ppm for the heat capacity, giving 1.9 and 1.6% changes in κ_T and C_p for 10 ppm. The relative change of the peak values are smaller, 0.00074 ± 0.00009 for the

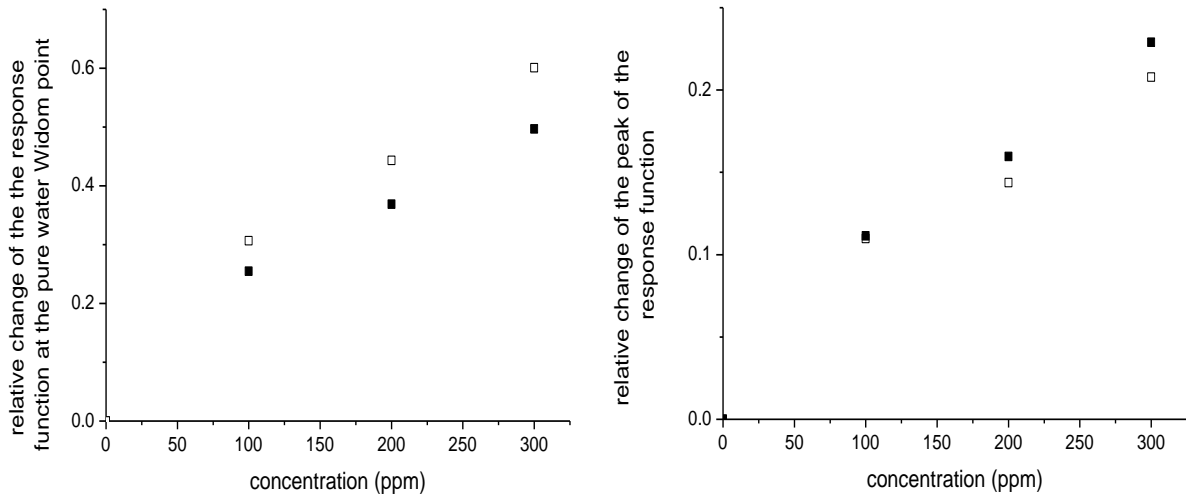


Figure 6 (left): Relative changes of the response functions (C_p and k_T) on various NaCl concentrations at 658.2 K. Isothermal compressibility is marked by open squares and isobaric heat capacity is marked by full squares.

Figure 7 (right): Relative changes of the maxima (peak values) of the response functions (C_p and k_T) on various NaCl concentrations compared to pure water values. Isothermal compressibility is marked by open squares and isobaric heat capacity is marked by full squares.

compressibility and 0.00066 ± 0.00010 for the heat capacity. Usually other errors are bigger, but these values are also not negligible.

Another problem is that various codes are using the data for pure water. Calculating the flow at 658.2 K, one would use 0.473 1/MPa for compressibility, which is correct as long as the SCW is pure. But after some time, the dissolved oxides will shift the peak and therefore the compressibility at that given temperature will be lower and lower. Although we do not have data for the corrosion products, one might expect that the shift is in the same order than in the salty water, which is around 7%. This 7% is not a negligible difference, therefore we believe that further studies are required to calculate the accurate compressibility, heat capacity etc. of SCW contaminated with very small amount of corrosion products.

CONCLUSION

The effect of small amount of inorganic solvent in the supercritical water (on 25 MPa) used as working fluid in Generation IV nuclear reactors has been studied. As a model material, NaCl was used in the calculations. The shift of the pseudocritical temperature is around 2.6-2.7 K by adding 300 ppm NaCl. The peak values for the isothermal heat capacity and isobaric compressibility changed 20-22 %, while the values of these response functions dropped 50-60 % at 658.2 K (the pseudospinodal temperature of the pure water) by changing the salt concentration from zero to 300 ppm. The effect of these changes on the thermo-hydraulic behaviours has been discussed, including the possible effect on the shift of the location of the deteriorated heat transfer region.

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