EFFECT OF FLOW CONDITIONS ON THE DEPOSITION OF PLATINUM NANOPARTICLES ON STAINLESS STEEL SURFACES

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ABSTRACT

Stress corrosion cracking (SCC) of stainless steel components in boiling water reactors (BWR) can threaten their structural integrity and leads to costly maintenance operations. A low electrochemical corrosion potential (ECP) can reduce the susceptibility of stainless steel to SCC. Injecting hydrogen into the reactor feed water lowers the ECP. The efficiency of hydrogen injection is improved in presence of catalytically active noble metals. Therefore, platinum (Pt) compounds are added to the reactor feed water and then deposit on the water-wetted surfaces. To understand the parameters affecting the application and mitigation processes, stainless steel coupons in as-received or pre-oxidized condition were exposed in a high-temperature water loop to simulated BWR water conditions with addition of Pt. Coupons were placed at three locations: i) in an autoclave with quasi-stagnant flow conditions (few mm/s), ii) in a specimen holder with a flow velocity of 0.10 m/s, iii) and in another with a flow velocity of 0.52 m/s. Independently of parameters such as Pt injection rate or water chemistry, coupons exposed to a transitional flow regime showed a lower Pt loading than the coupons exposed to a turbulent flow or suspended in the autoclave under quasi-stagnant flow.

Keywords: Stress corrosion cracking, platinum, noble metals, mitigation, nanoparticles, fluid flow, particle deposition, boiling water reactor.

INTRODUCTION

Stress corrosion cracking (SCC) in reactor internals and recirculation pipes is a well-known issue in boiling water reactors (BWRs) ¹ and different methods have been used to mitigate it.

In BWRs, the radiolysis of water with subsequent partitioning of the hydrogen into the steam is the origin of highly oxidizing conditions which are a major cause of SCC.² At first mitigation was attempted by injecting hydrogen into the feed water, a method termed hydrogen water chemistry (HWC).³ Although hydrogen injection reduces the electrochemical corrosion potential (ECP) and therefore lowers the SCC susceptibility, it has a problematic side-effect. The high hydrogen content favors the partitioning of ¹⁶N into the steam as ammonia and thus significantly increases the steam line dose rates.

A further development has been to add a catalyst to improve the recombination efficiency of the injected hydrogen with the reactive oxygen species.⁴ Consequently the amount of hydrogen needed could be reduced, which substantially decreased the amount of ¹⁶N in the steam. This catalytic technology, developed by General Electric (nowadays General Electric-Hitachi) to mitigate SCC, uses noble metals (Pt, Rh) as catalysts. Two application methods are available: *a*) either a solution containing Pt as Na₂Pt(OH)₆ and Rh as Na₃Rh(NO₂)₆ is injected into the reactor water during hot shut-down (“Noble Metal Chemical Addition”, NMCA)⁵ or *b*) Na₂Pt(OH)₆ only is injected into the feed water during operation at full power (“Online NobleChem™”, OLNC).^{6, 7} Under the influence of the elevated temperature, the injected noble metal compounds decompose to very fine metallic particles (nanoparticles) which are claimed to deposit on all water-wetted surfaces and to stay electrocatalytic over extended periods, thus providing SCC mitigation if sufficient H₂ is present.⁸ More detailed information on the NMCA technology can be found in a recently published review.⁹

In order to verify the deposition and distribution of Pt in a BWR environment, a joint research project was started at PSI (NORA, “Noble Metal Deposition Behavior in BWRs”).¹⁰ Project partners along with PSI were the Swiss Federal Nuclear Safety Inspectorate (ENSI) and the Swiss nuclear power plants of Leibstadt (KKL) and Mühleberg (KKM). Previous publications from this project have already dealt with the effect of Pt injection rate on the deposition behavior ^{11, 12} and the effect of water chemistry on the

nature of the Pt particles.¹³ The present contribution is based on a paper¹⁴ presented at the 16th Conference on Environmental Degradation of Materials in Nuclear Power Systems and describes investigations on the influence of flow conditions on the Pt deposition.

EXPERIMENTAL PROCEDURES

Figure 1 shows a schematic of the sophisticated loop in use at PSI to reproduce the water chemistry of a BWR without the radioactive component. The water chemistry can be precisely adjusted (H_2 , O_2 and Pt dosing) and closely monitored (dissolved H_2 and O_2 concentrations, conductivity, ECP, flow). Pt concentration in the loop is calculated on the basis of the Pt concentration in the feed solution, the feed flow rate and the fluid flow rate in the autoclave. This represents the maximal concentration, as deposition along the flow path will reduce it. Nevertheless enough Pt remains in the fluid to allow the deposition of high loadings in the last specimen holder (see next section). Attempts at analyzing water samples taken from the hot part of the loop for Pt content by inductively coupled plasma – mass spectrometry, did not provide reproducible results due to the very low Pt concentration (in the ppt range), but nevertheless confirmed that Pt was present in the expected concentration range.

Coupon specimens 13×10×4 mm made of AISI 304L stainless steel were used either in “as-received” (AR) condition or pre-oxidized (PO) for 2 weeks in BWR/HWC environment (275 °C, 0 ppb O_2 , 170 ppb H_2 , high-purity water).

During all experimental runs, specimens were exposed to water at three different locations of the loop: i) suspended in the autoclave with quasi-stagnant flow conditions (few mm/s), ii) in a specimen holder (SH1) with a large rectangular duct on each side of the specimens (0.10 m/s), iii) in a specimen holder similar to SH1 but with smaller rectangular ducts (SH2) (0.52 m/s). Figure 2 illustrates the configuration of the specimen holders.

The autoclave (*Parr Instruments Co.*) has an internal diameter of 95 mm for a height of 155 mm, corresponding to a volume of approx. 1 L. With a total flow of 13.3 L h⁻¹, the average residence time

of the water can be estimated to about 5 minutes. The Pt injection point is situated on the water feed pipe 200 mm ahead of the point where this pipe ends in the autoclave (see also Figure 1). The fluid takes approx. 0.7 s to flow from the injection point to the pipe end in the autoclave.

To obtain in-situ information on the electrochemical conditions inside the autoclave the potentials of an AR specimen, a Pt sheet and the autoclave were measured with respect to a Cu/Cu₂O ZrO₂-membrane electrode and referenced to the standard hydrogen electrode scale (SHE). Electrical contacts to the specimen and the Pt sheet were achieved by means of spot-welding Ni-Cr wires, insulated with tightly fitting PTFE tubing.

After eight days of pre-conditioning of the loop, loaded with the specimens under BWR-HWC conditions, Pt was injected as a solution of Na₂Pt(OH)₆. At the end of the Pt injection period, the system was kept under the same BWR-HWC conditions for three more days before shut down and removal of the specimens from the loop. Solution concentrations and injection rates for individual tests are listed in Table 1.

Pt loadings on specimen surfaces were determined by Laser Ablation – Inductively Coupled Plasma – Mass Spectrometry (LA-ICP-MS). The instrument consists of a *CETAC (LSX 3770)* ablation system coupled to an *Element 2* ICP-MS from *Thermo Fisher Scientific*. Calibration curves were established using in-house made stainless steel standards with known surface loadings of Pt (0.14 and 1.4 nm layer thickness, corresponding to 0.3 and 3 µg cm⁻² Pt surface loading).

Microstructural investigations were performed using a *Zeiss ULTRA 55* scanning electron microscope (SEM) equipped with a field emission gun and X-ray energy dispersive spectrometer (EDS) from *EDAX* for chemical analyses. A secondary electron detector was used to investigate the oxide layer topography, whereas a back scattered electron detector was used to identify Pt particles (chemical contrast) across the oxide layers. In the present case, satisfactory imaging of features (particles) below 4 nm in size was not possible. Therefore, Pt particles smaller than 4 nm need to be studied by transmission electron microscopy (TEM).¹² The size of the particles was measured using back scattered SEM pictures and the *ImageJ* software.¹⁵

RESULTS & DISCUSSION

Analysis of Specimens

After a typical Pt deposition experiment, coupons were first investigated by SEM to check for the presence of Pt particles (Figure 3) and determine their size distribution. Figure 4 illustrates the particle size distribution typically encountered when analyzing the different tests. Generally, the distributions are skewed which suggest that the distributions follow a lognormal distribution law as is commonly encountered with nanoparticles.¹⁶ The size distribution of Pt particles found on surfaces is of the same type as the one usually obtained during the formation process of such particles, and suggests that probably the deposition process does not significantly alter the particle size distribution in the system. Mean particle sizes vary between the different locations within the test but this variation is well within one standard deviation (Figure 4). However, larger variations of the particle size distribution are found between the different tests (average particles sizes ranging from below 10 up to 30 nm), when for example, the Pt injection rate or the water chemistry are varied.^{11, 13} Quantitative values for the Pt loading on the surfaces of the specimens were obtained by LA-ICP-MS. When comparing these Pt loadings for a eight tests, that have been performed under varying conditions (Pt injection rate, total Pt amount injected, temperature, and dissolved oxygen and hydrogen levels), one recurrent observation was that specimens in SH1 always had a lower Pt loading (LA-ICP-MS analyses) than specimens in SH2 and in the autoclave (Figure 5).

If one assumes that the relatively high loadings in the autoclave are related to the proximity of the Pt injection point (located in the feed water pipe to the autoclave) then SH2, which is the furthest away from this point, should have the lowest or at the least a very similar Pt loading to SH1 which is just located ahead of it. On the contrary, Pt loadings in the autoclave and SH2 are quite similar and in more than half of the experiments, the highest Pt loading was in SH2. This observation is independent of the specimens' surface conditions.

Specimens that have been pre-oxidized in BWR-HWC environment for two extra weeks prior to exposure to Pt in the loop have higher loadings (compare Figure 5a and Figure 5b). This phenomenon is being investigated and will be the subject of a forthcoming publication.

Because the Pt deposits along its path through the loop it is necessary to estimate how its concentration in the fluid will change along this path. The Pt concentration in the fluid is in the ppt (ng kg^{-1}) range (see Table 1) and attempts at analyzing water samples from the hot part of the loop did not produce fully reproducible results. Therefore, the evolution of the concentration must be based on estimation. One indirect sampling which is available is the Pt load on the specimens exposed to the loop water. Assuming that the surfaces next to the specimens (e.g., autoclave wall) will have a similar Pt loading, one can calculate the amount of Pt scavenged from the fluid by these surfaces. Table 2 lists the areas of the respective sections of the high-temperature water loop. Taking test 19 as a representative example, the following reasoning can be made. In this test, the Pt loading on specimens exposed in the autoclave was found to average to $0.3 \mu\text{g cm}^{-2}$. Assuming the same loading for all parts of the autoclave, and taking the area listed in Table 2, yields a total Pt amount of about $212 \mu\text{g}$ which is deposited in the autoclave. Therefore from $699 \mu\text{g}$ of Pt injected during this test, only an estimated $487 \mu\text{g}$ (or 70%) left the autoclave in direction of the specimen holders. This also means that the nominal Pt concentration in the fluid will have decreased by about 30%, down to 299 ppt. No actual measurement of the Pt load on the piping is available; the next point for which data is available is SH1 with about $0.1 \mu\text{g cm}^{-2}$. Assuming an average loading of $0.2 \mu\text{g cm}^{-2}$ on the 125 cm^2 of the piping another $25 \mu\text{g}$ Pt would be removed and the amount deposited in SH1 is estimated to $8 \mu\text{g}$ (80 cm^2 at $0.1 \mu\text{g cm}^{-2}$). Therefore from the initial $699 \mu\text{g}$ an estimated $454 \mu\text{g}$ (or 65%) will get to SH2 corresponding to a concentration in the fluid of 277 ppt. Despite an estimated decrease of the Pt concentration in the fluid by more than 30%, the Pt loading in SH2 is about as high as in the autoclave. This indicates that the conditions in SH2 are quite favorable for Pt deposition. A major parameter which distinguishes the three locations is the nature of the flow of the fluid across the specimens. In the following sections, this aspect will be discussed in detail to rationalize these observations.

Computation of Flow Conditions

The loop has three locations of interest. First location is the autoclave, which has a cylindrical shape. The fluid enters the autoclave via a pipe in the upper section of the autoclave and leaves it through a hole in the bottom. The reference electrode and the specimens are located in between the water inlet and outlet. Hanging from the lid of the autoclave are a Pt sheet and an AR specimen, each connected to a wire for potential measurements.

The two specimen holders are connected in series to the exit of the autoclave. They consist each of two parallel rectangular ducts. In SH1 the height of the ducts is half their width whereas in SH2 the height of the ducts is a tenth of their width. The water is flowing one each side of the specimens (Figure 2).

Flow conditions in the autoclave are difficult to analyze due to the complex geometry, the variability of the position of specimen and Pt sheet from test to test and the external heating. However, as reasonable approximation one can consider relatively slow (a few mm/s) to local stagnant flow conditions.

Owing to their well-defined geometry the specimen holders allow a more precise analysis of the flow conditions. Geometric parameters are summarized in Table 3. From this data it is possible to calculate the hydraulic diameter, D_H , as defined in Equation (1):

$$D_H = 4 \frac{A}{P} \quad (1)$$

In fluid mechanics the Reynolds number, Re , is used to categorize and compare flow regimes. The Re number, Equation (2), is non-dimensional and can be interpreted as the ratio of inertial to viscous forces (or similarly the ratio of convection velocities and diffusion velocities).¹⁷ Clearly, the higher the Re , the smaller is the influence of viscous forces, and the flow tends to be more unstable or even turbulent. Usually it is computed from the bulk velocity, U_B , a characteristic dimension of the duct, e.g. D_H and the kinematic viscosity ν (ratio of the dynamic viscosity η and the density ρ of the fluid, Equation (3), Table 4).

$$Re = \frac{U_B D_H}{\nu} \quad (2)$$

$$\nu = \frac{\eta}{\rho} \quad (3)$$

A flow is laminar at low values of Re . As the Re increases the flow exhibits a transition to an unsteady pattern, the so-called transitional flow regime. With further increase in Re , when it reaches the critical value (Re_{crit}) the flow becomes turbulent, i.e. features unsteadiness, high vorticity and a broad spectrum of scales. The value of Re_{crit} depends on the geometry of the duct. For a flow through a cylindrical pipe $Re_{crit} = 2000$.¹⁸ In the case of rectangular ducts, Re_{crit} depends on the aspect ratio α (width to height): $Re_{crit} = 2060$ for a square duct ($\alpha = 1$), $Re_{crit} = 2800$ in case of two infinite flat plates ($\alpha = \infty$). Re_{crit} goes through a minimum at 1900 for $\alpha = 2.04$.¹⁹ According to the data listed in Table 5 the flow in both specimen holders is not laminar at the temperature under consideration. The knowledge of flow regime, characterized by Re , is very important because it makes a significant impact on the effectiveness of particle deposition (*vide infra*).

When a fluid enters a duct it takes a certain distance to attain a fully developed flow profile (Figure 6). In the case of turbulent flow the entrance length can be estimated with following relation ²⁰:

$$l_e / D_H \approx 4.4 Re^{1/6} \quad (4)$$

And for laminar flow the entrance length can be calculated according to ²⁰:

$$l_e / D_H \approx 0.06 Re \quad (5)$$

Data listed in Table 5 shows that a fully developed flow in SH2 is achieved after about a fifth of its length. In the case of SH1, when assuming a turbulent regime, a fully developed flow is present only on the last third of its length and in case of hypothetical laminar conditions the flow would never fully develop (the length required being seven times longer than SH1). From this it can be concluded that the flow conditions in SH2 are turbulent for most of its length whereas in SH1 the flow conditions are in a transitional regime.

Particle Transport and Deposition Dynamics

Nanofluids, e.g. nanoparticles suspended in a fluid, have recently attracted attention due to their anomalous thermophysical properties compared to the pure fluid.²¹ In the present case the nanoparticle concentrations are too low (<1 ppb) to affect the thermophysical properties of the water in which they are suspended. Nevertheless the models developed to describe their transport behavior in the fluid will be useful in understanding the deposition behavior.²¹

The behavior of particles suspended in a fluid depends on the flow regime of the fluid. In turbulent flows, particles tend to flock to certain areas of the flow, thus leading to the disappearance of a possible initial homogenous distribution of the particles in the fluid. One of the consequences of this phenomenon is the enhanced deposition of particle on the duct walls.²² Models have been developed to describe this behavior.

The inertia of particles in a turbulent flow is given by the particle relaxation time τ_p (Equation (6)). Physically, it represents the time needed for a particle to respond to changes in the drag it experiences from the fluid as the latter's velocity varies.

$$\tau_p = \frac{\rho_p d_p^2}{18 \cdot \eta} \quad (6)$$

where ρ_p and d_p are respectively the density (21090 kg m⁻³ for Pt) and the diameter of the particle, and η is the dynamic viscosity of the fluid ²¹. This can be converted to a dimensionless relaxation time τ_p^+ :

$$\tau_p^+ = \frac{\tau_p (u^*)^2}{\nu} \quad (7)$$

using the friction velocity u^* and the kinematic viscosity ν . The friction velocity can be estimated from Re and U_B ²⁰:

$$u^* = \frac{U_B}{\sqrt{8/f}} \quad (8)$$

$$1/f = (1.8 \log(Re / 6.9))^2 \quad (9)$$

Table 6 lists estimated relaxation times for nanoparticles of different sizes for the flow conditions in SH2. τ_p^+ values span over three orders of magnitude. A correlation between τ_p^+ and the particle deposition velocity u_d^+ (non-dimensional) has been established from empirical data ²³ and is illustrated in Figure 8. This graph can be used to estimate deposition velocities for nanoparticles under the flow conditions found in SH2. The particles of interest in the present study have small relaxation times (Table 6), which means that only the curve portion left to the minimum is relevant here. The estimated deposition velocities are also listed in Table 6 and clearly indicate that smaller particles will deposit faster.

The deposition velocity, Equation (10), can be used to predict the fraction of particle of a given size that will deposit over a length of duct, Equation (11),²⁴

$$u_d = u_d^+ u^* \quad (10)$$

$$\ln\left(\frac{C_{in}}{C_{out}}\right) = u_d \frac{2l}{D_H U_B} \quad (11)$$

where C_{in} and C_{out} represent the concentration of particles (number per unit of volume) in the fluid at the entrance and exit, respectively of the portion of duct considered. Under the turbulent flow conditions in SH2, smaller particles are predicted to deposit more efficiently than larger ones (Table 6). The closer the ratio C_{in}/C_{out} is to unity the more particles that enter the duct will also leave it. Except for the smallest particles, much longer duct lengths than available here are required to radically affect the total particle concentration in the fluid. This also means that despite the serial arrangement of SH1 and SH2, the fluid will have similar particle concentrations at both locations.

To illustrate this point, details from a computation performed with parameters corresponding to test 19 are listed in Table 7. Data for four particle sizes are listed and ratios between the concentrations of each particle size have been chosen to reflect the lognormal particle size distribution found in SH1 and SH2 during test 19 (Figure 4). The data shows that about one third of the 6 nm particles entering SH2 should deposit in it whereas this should only be the case for 5% of the 15 nm particles. In total 84% of the particles entering SH2 will leave it again, carrying with them 91% of the mass of Pt that entered SH2. As already noted earlier, the concentration of Pt in the fluid at the entrance of SH2 may be estimated to 277 ppt. Considering that 91% of this Pt will leave SH2 again, an amount corresponding to the 25 ppt (9%) concentration decrease will be able to deposit in test 19. The Pt injection lasted 164.8 h with a total mass flow for the fluid of 10 kg h⁻¹ thus 1648 kg of fluid passed through SH2, more precisely 824 kg through each duct. These 824 kg of fluid are predicted to have deposited 21 µg (824 kg × 25 ng kg⁻¹) of Pt in each duct according to this model. The wetted surface area of an individual duct is 13.2 cm² (Table 3). This corresponds to an estimated surface loading of about 1.6 µg cm⁻² which is clearly higher than the actual measured value of 0.3 µg cm⁻² (Figure 5). There may be several explanations for this discrepancy. Firstly, the Pt concentration at the entry may be overestimated due to higher deposition rates in the piping between autoclave and specimen holders. Secondly, it should be emphasized again

that the model²³ used to estimate the deposition velocity is based on empirical data with a large scatter in the experimental points and where the ratio of particle density to fluid density is often larger than in the present case. A smaller density ratio seems to decrease the slope of the side left of the curve minimum in Figure 8, although the sparse experimental data in this area makes accurate predictions delicate. A less steep curve would result in smaller deposition velocities thus reducing the corresponding C_{in}/C_{out} ratios and the deposited amounts. A third point relates to the definition of deposition under the specific experimental conditions. The model used to predict particle deposition assumes that a particle is captured by the wall when it touches it.²³ In the present case, this may be too optimistic in the sense that touching the surface may not be sufficient for sticking permanently to it (formation of chemical bonds between the Pt particle and the oxide surface). If one assumes that somewhere between one to five particles out of ten that touch the wall are retained, then the discrepancy between predicted and observed loading would be minimal. This leads to the last point, namely the remobilization of Pt particles deposited on oxide surfaces. One could consider that the lower loadings observed can be explained by a remobilization rate which matches to 80% the deposition rate. However, there is evidence in the literature that noble metal nanoparticles tend to have a *strong metal-support interaction* with transition metal oxide surfaces.²⁵⁻²⁷ This strong interaction manifests itself by the rearrangement of the bonds of the atoms at the interface between the metal oxide and the metal nanoparticle resulting in chemical bonding of nanoparticles to the oxide surface. This process is probably not easily reversible and therefore the remobilization of individual nanoparticles is unlikely or at best of minor importance. On the other hand, experience from a BWR plant shows that over time the Pt surface loading on stainless steel coupons, exposed to the reactor water, decreases if no (new) Pt is injected.²⁸ As a consequence OLNC reapplications are recommended.²⁹ The Pt loss is likely to happen by erosion of oxide particles carrying the Pt on their surface. The Pt is lost for protection as these oxide particles become CRUD on fuel components or are removed by the water clean-up system. In a BWR the loss of Pt is a process which takes several weeks to months and is therefore not major relevance for the loop tests presented here, where the specimens were removed from the loop only three days after the end of the Pt injection.

Having discussed in details the particle deposition under turbulent conditions in SH2, an evaluation of the conditions in SH1 is also needed. At this location, it is difficult to make predictions because of the transitional flow conditions. However with less turbulence the particles travelling in the middle of the flow have less opportunity to reach the walls of the duct (Figure 9). The “quieter” flow means that the velocity component perpendicular to the duct walls is certainly much smaller than the parallel component and diffusion will be a more important contribution to the transport towards the wall. This is consistent with results from simulation of the deposition of nanoparticles in laminar flows.³⁰ The diffusion coefficient for a nanoparticle can be calculated using the Stokes-Einstein equation ²¹:

$$D_B = \frac{k_b T}{3\pi\eta d_p} \quad (12)$$

Using this diffusion coefficient and Fick’s second law one can estimate the time required for a particle to diffuse a distance equivalent to half the duct’s height (~1.5 mm). For Pt nanoparticles in range between 5 and 50 nm, the time scale is of order of several hundreds to thousands of seconds. For comparison the residence time of the fluid in SH1 is about 1 s ($U_B = 0.1 \text{ m s}^{-1}$, $l = 0.1 \text{ m}$). Therefore under perfectly laminar flow conditions only particles which are a few tens of μm from the wall would be able to reach it before being carried out of the duct by the fluid. A more quantitative description can be obtained by computing the time required for a particle to move a distance equal to its own diameter under the effect of turbulent transport or diffusion. (Equations (13) and (14), Table 8 and Table 9).²¹

$$\tau_t \sim d_p / u^* \quad (13)$$

$$\tau_d \sim d_p^2 / D_B \quad (14)$$

The ducts in SH1 and SH2 have a vertical orientation. Therefore gravity cannot contribute to deposition in this location but it could in the case of the autoclave. For comparison purpose, the effect of gravity has also been estimated (Equation (15), Table 10).²¹

$$\tau_g \sim d_p / V_g \quad (15)$$

The settling velocity V_g is given by following equation:

$$V_g = \frac{d_p^2 (\rho_p - \rho) g}{18\eta} \quad (16)$$

A comparison of the time scales shows that gravity (Table 10) is absolutely negligible compared to transport by diffusion (Table 8) and turbulence (Table 9). The difference between turbulence and diffusion depends on the particle size (Figure 10). For the smallest particles diffusion is the faster process but as size increases turbulent transport becomes faster (e.g. shorter transport times). This comparison also shows that in absence of turbulences the diffusion is more likely to have a sorting effect on the particles according to their size. τ_d varies by three order of magnitudes between 5 and 50 nm whereas τ_t varies by about one order of magnitude for the same particle size range.

Effect of Flow Regimes and Surface conditions on Pt Deposition

The significant difference in Pt loadings observed on specimens located in different parts of the loop can now be better understood. Locations where the flow is turbulent can accumulate more Pt because the turbulences transport the particles faster (towards the wall/specimens) and the stagnant layer is thinner. This means that the distance the particles have to travel by diffusion is much smaller than in areas of laminar or transitional flow conditions (Figure 9). Consequently more particles reach the surface per unit of time under turbulent conditions producing higher surface loadings. This is well illustrated in the case of the specimen holders. In the case of the autoclave a precise computation of the flow

conditions is not possible because of the complex geometry. However, despite the slow flow, this geometry certainly produces a complex flow pattern which still ensures an adequate mixing by convection, also the active heating of the autoclave's external wall provides an additional movement to the fluid. Another important factor, that distinguishes the autoclave from the specimen holders, is the significantly longer residence time of the fluid in the autoclave (several minutes vs. seconds) which compensate for possibly longer diffusion path of the particles. Finally, the proximity of the Pt injection point, responsible for the highest Pt concentration of the whole loop, is probably a factor that also significantly contributes to the high surface loadings observed in the autoclave.

In the present case, it was not possible to determine a statistically significant difference in particle size distribution between the different locations (Figure 4) which could be related to the flow conditions despite the prediction that smaller particles diffuse faster (Table 8) and have a higher deposition velocity (Table 6). The reason may be that the actual size distribution is too narrow for this effect to show up markedly in experimental data with its inherent error margin due to the limited particle counts (Table 7, Figure 4).

On the other hand, the nature of the surface plays an important role too (compare Figure 5a to Figure 5b). The higher loading found on PO specimens compared to AR ones at all locations indicates that this is not related primarily to the flow conditions. Often visual examination already reveals a better developed oxide layer on PO specimens. This is confirmed by microscopic investigations (Figure 7), where PO specimens have a denser coverage by oxide crystals which are also larger. This makes the oxide layer rougher, meaning also that it has a larger specific area thus providing more sites to trap the particles. This possibly translates to the higher loading found on PO specimens compared the AR ones. The idea that the particles impact better on the rougher surface of PO specimens is doubtful because the momentum of these nanoparticles is too small to break through the stagnant layer even in the turbulent regime. This mechanism is only effective for particles that have a τ_p^+ larger than 0.1 (Figure 8, right of the curve's minimum) which corresponds to particles in the μm range or larger.²² Only the part of the curve left of the minimum is relevant for nanoparticles.

CONCLUSIONS

Experiments in a sophisticated high-temperature water loop simulating OLNC applications in a BWR, together with computations of the flow conditions, have revealed that a turbulent flow regime of the high-temperature water provides the best conditions for deposition of Pt nanoparticles on stainless steel surfaces. Eddies (swirls) in the turbulent flow are an efficient way to transport the particles close to the surface. This reduces the distance they have to move by diffusion (even under turbulent conditions there is a stagnant layer) before they can deposit on the oxide film of the stainless steel surfaces. In the absence of strong turbulences the deposition will take place essentially by the slower diffusion transport (sedimentation under the influence of gravity is negligible for nanoparticles even if they consist of one of the densest materials e.g. Pt). In this context it is important to note that smaller particles diffuse faster than larger ones under the same conditions. Because stress corrosion cracks are usually too narrow for turbulences to enter them, it is important to produce by OLNC the smallest possible particles. These small particles are the most likely to be able to diffuse as deep into the crack as the reactive species do and thus develop their catalytic effect where it is most needed. Furthermore, a better developed oxide layer accumulates more Pt nanoparticles possibly due to its larger specific surface.

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LIST OF SYMBOLS

A	area of duct cross section	α	aspect ratio of duct
C	volume concentration of particles in fluid	η	dynamic viscosity of fluid
D_B	Brownian diffusion coefficient	κ	conductivity
D_H	hydraulic diameter	ν	kinematic viscosity of fluid
d_p	diameter of nanoparticle	ρ	density of fluid
f	friction factor	ρ_p	density of nanoparticle
g	acceleration of gravity	τ_d	particle diffusion time
l	length of duct	τ_g	gravitational particle settling time
l_e	flow entrance length	τ_p	particle relaxation time
P	wetted perimeter of duct	τ_p^+	non-dimensional particle relaxation time
Re	Reynolds number	τ_t	turbulent transport time
Re_{crit}	critical Reynolds number		
T	temperature		
u^*	friction velocity		
U_B	bulk velocity of fluid		
u_d^+	non-dimensional deposition velocity		
V_g	gravitational settling velocity		

REFERENCES

1. R. Kilian and A. Roth, *Materials and Corrosion* 53 (2002): p. 727-739.
2. C. J. Wood: 'Water chemistry control in LWRs', in 'Comprehensive Nuclear Materials', (ed. R. J. M. Konings), 17-47; 2012, Oxford, Elsevier.
3. R. L. Cowan, C. C. Lin, W. J. Marble, and C. P. Ruiz: 'Hydrogen water chemistry in BWRs', 5th Int. Symposium on Environmental Degradation of Materials in Nuclear Power Systems - Water Reactors (Monterey, CA, USA, NACE, 50-58, 1991).
4. S. Hettiarachchi, R. L. Cowan, T. P. Diaz, R. J. Law, and S. E. Garcia: 'Noble Metal Chemical Addition... from Development to Commercial Application', 7th Int. Conference on Nuclear Engineering (Tokyo, Japan, JSME, 1999).
5. S. Hettiarachchi, R. J. Law, T. P. Diaz, W. D. Miller, R. L. Cowan, W. Keith, L. Kriege, and R. S. Pathania: 'Application of Noble Metal Chemical Addition Technology to an Operating BWR to Mitigate IGSCC of Reactor Internals', CORROSION 98 (San Diego, CA, USA, NACE, Paper No. 142, 1998).
6. L. Oliver, B. Helmersson, G. Ledergerber, W. Kaufmann, G. Wikmark, B. Cheng, and A. Kucuk: 'Review of Water Chemistry and Corrosion Products in a NWC Plant Transitioned to Hydrogen Injection and OLNC', Nuclear Plant Chemistry (NPC) Conference (Quebec, Canada, CNS, 2010).
7. S. Hettiarachchi and C. Weber: 'Water Chemistry Improvements in an Operating Boiling Water Reactor (BWR) and Associated Benefits', Nuclear Plant Chemistry (NPC) Conference (Quebec City, Canada, CNS, Paper No. 2.04, 2010).
8. Y.-J. Kim, P. L. Andresen, S. Hettiarachchi, and T. P. Diaz: 'Hydrothermal formation and distribution of noble metal particles on type 304 SS in high temperature water', CORROSION 2007 (Nashville, TN, USA, NACE, 2007).
9. P. V. Grundler and S. Ritter, *PPChem.* 16 (2014): p. 76-93.
10. S. Ritter, V. Karastoyanov, S. Abolhassani-Dadras, I. Guenther-Leopold, and N. Kivel, *PPChem.* 12 (2010): p. 628-635.
11. P. V. Grundler, A. Ramar, V. Karastoyanov, S. Abolhassani-Dadras, I. Guenther-Leopold, N. Kivel, and S. Ritter: 'Effect of injection rate on Platinum deposition behaviour on stainless steel under simulated BWR conditions', Nuclear Plant Chemistry (NPC) Conference (Paris, France, SFEN, 2012).
12. A. Ramar, P. V. Grundler, V. Karastoyanov, I. Günther-Leopold, S. Abolhassani-Dadras, N. Kivel, and S. Ritter, *Corrosion Engineering, Science and Technology* 47 (2012): p. 489-497.
13. A. Ramar, P. V. Grundler, V. Karastoyanov, I. Günther-Leopold, S. Abolhassani-Dadras, N. Kivel, and S. Ritter: 'Platinum deposition behaviour on stainless steel under varying water chemistry in simulated BWR conditions', Nuclear Plant Chemistry (NPC) Conference (Paris, SFEN, 116 P111-145 2012).
14. P. V. Grundler, A. Ramar, L. Veleva, I. Günther-Leopold, and S. Ritter: 'Effect of flow and surface structure on the Pt deposition on stainless steel during simulated noble metal applications ', 16th Int. Conference on Environmental Degradation of Materials in Nuclear Systems - Water Reactors (Asheville, NC, USA, NACE/TMS/ANS, Paper No. ED2013-3116, 2013).

15. T. J. Collins, *BioTechniques* 43 (2007): p. 25-30.
16. J. Söderlund, L. B. Kiss, G. A. Niklasson, and C. G. Granqvist, *Phys. Rev. Lett.* 80 (1998): p. 2386-2388.
17. F. Durst: 'Flows of Large Reynolds Numbers Boundary-Layer Flows', in 'Fluid Mechanics', 463-493; 2008, Berlin Heidelberg, Springer
18. F. M. White, J. L. Hess, and C. H. Gibbson: 'Equations for fluid statics and dynamics', in 'Fundamentals of fluid mechanics', (eds. J. A. Schetz, et al.), 1-90; 1999, New York, John Wiley & Sons.
19. R. W. Hanks and H.-C. Ruo, *Industrial & Engineering Chemistry Fundamentals* 5 (1966): p. 558-561.
20. F. M. White: 'Viscous flow in ducts', in 'Fluid mechanics', 325-424; 1999, Boston, WCB McGraw-Hill
21. J. Buongiorno, *J. Heat Transfer* 128 (2006): p. 240-250.
22. J. Young and A. Leeming, *J. Fluid Mech.* 340 (1997): p. 129-159.
23. F.-G. Fan and G. Ahmadi, *J. Aerosol Sci.* 24 (1993): p. 45-64.
24. A. Dehbi, *International Journal of Multiphase Flow* 35 (2009): p. 219-226.
25. T. Schalow, B. Brandt, D. E. Starr, M. Laurin, S. K. Shaikhutdinov, S. Schauermaann, J. Libuda, and H.-J. Freund, *Angewandte Chemie International Edition* 45 (2006): p. 3693-3697.
26. S. J. Tauster, *Acc. Chem. Res.* 20 (1987): p. 389-394.
27. S. J. Tauster, S. C. Fung, and R. L. Garten, *Journal of the American Chemical Society* 100 (1978): p. 170-175.
28. S. Ritter, P. V. Grundler, A. Ramar, G. Ledergerber, and W. Kaufmann: 'Platinum deposition on boiling water reactor components: qualification of lab-scale tests with plant data', EUROCORR 2013 (Estoril, Portugal, EFC, 2013).
29. S. E. Garcia, J. F. Giannelli, and M. L. Jarvis: 'BWR chemistry control status: a summary of industry chemistry status relative to the BWR water chemistry guidelines', Nuclear Plant Chemistry (NPC) Conference (Quebec City, Canada, CNS, Paper No. 9.09, 2010).
30. A. A. Brin, S. P. Fisenko, and A. I. Shnip, *Technical Physics* 53 (2008): p. 1141-1145.
31. E. W. Lemmon, M. O. McLinden, and D. G. Friend: 'Thermophysical Properties of Fluid Systems', in 'NIST Chemistry WebBook, NIST Standard Reference Database Number 69', (eds. P. J. Linstrom, et al.), 2011, Gaithersburg MD, National Institute of Standards and Technology.

TABLES

Table 1. Experimental conditions and Pt injection parameters for tests performed at PSI.

Experiment designation	10	11	12	13	14	15	16	19
T autoclave (°C)	280	280	280	280	281	281	281	281
T sp. holder (°C)	271	271	271	271	272	270	270	270
Water mass flow (kg h ⁻¹)	10	10	10	10	10	10	10	10
H _{2in} (ppb)	79	80	40	77	77.8	81	77	75
H _{2out} (ppb)	34	74	0	28	44	42	32	34
O _{2in} (ppb)	335	38	510	310	310	320	325	322
O _{2out} (ppb)	0	0	220	0	0	0	0	0
κ _{in} (μS/cm)	0.055	0.055	0.055	0.055	0.058	0.055	0.055	0.055
κ _{out} (μS/cm)	0.097	0.103	0.145	0.098	0.141	0.108	0.082	0.096
Duration Pt inj. (h)	168.2	168.1	168.1	57.3	165.6	165.7	255.8	164.8
Pt injection rate (μg h ⁻¹)	3.9	3.8	3.5	12.1	4.1	3.6	2.1	4.2
Pt conc. in inj. solution (ppb)	94	91	84	97	100	88	95	101
Mass flow Pt solution (g min ⁻¹)	0.694	0.694	0.694	2.084	0.694	0.694	0.363	0.701
Nominal Pt conc. in water (ppt)*	392	380	350	1208	405	365	207	427
Total amount of Pt injected (μg)	660	639	589	692	688	605	529	699

*estimated on the basis of the concentration of the injection solution and the respective mass flows.

Table 2. Estimated areas of the different sections of the high-temperature loop used during the tests listed in Table 1.

Section	Area (cm ²)	Fraction (%)
Autoclave	705	71.6
Piping to SH1	125	12.8
SH1	80*	8.1
Piping between SHs	5	0.5
SH2	70*	7.0
Total	985	100.0

* These surfaces are larger than the duct areas listed in Table 3 because the internal surface of the fittings and connecting pieces are included.

Table 3. Geometric parameters for individual ducts in specimen holders (see also Figure 2).

	SH1	SH2
Width (mm)	6.0	6.0
Height (mm)	3.0	0.58
Length <i>l</i> (mm)	100	100
Wetted perimeter <i>P</i> (mm)	18.0	13.16
Duct surface (mm ²)	1800	1316
Cross section area <i>A</i> (mm ²)	18.0	3.48
Duct volume (mm ³)	1800	348
Aspect ratio α (-)	2.0	10.3

Table 4. Thermophysical properties of water.

T (°C)	P (MPa)	η ($\mu\text{Pa s}$) ^{a)}	ρ (kg m^{-3}) ^{a)}	$\nu \times 10^6$ ($\text{m}^2 \text{s}^{-1}$)
25	0.1	890.08	997.05	0.89271
25	9.0	888.19	1001.00	0.88730
270	9.0	98.573	772.45	0.12761
280	9.0	94.360	754.49	0.12506

^{a)} ³¹, <http://webbook.nist.gov/chemistry/fluid/>

Table 5. Bulk flow velocity, Reynolds numbers and entrance lengths for the specimen holders at 270 °C.

	SH1	SH2
D_H (m)	0.00400	0.001057
α (-)	2.0	10.3
U_B (m s^{-1})	0.0999	0.517
Re (-)	3131	4282
Re_{crit} (-)	~1900	~2700
Turbulent l_e (m), Equation (4)	0.067	0.019
Laminar l_e (m), Equation (5)	0.75	—

Table 6. Friction velocity for SH2 and particle relaxation times with corresponding adimensional deposition velocities estimated from Figure 8. Calculated deposition velocities and concentration ratios for SH2 ($Re = 4282$, $u^* = 0.0364 \text{ m s}^{-1}$, $D_H = 0.001057 \text{ m}$, $U_B = 0.517 \text{ m s}^{-1}$).

$d_p \text{ (nm)}$	$\tau_p \text{ (s)}$	$\tau_p^+ \text{ (-)}$	u_d^+	$u_d \text{ (m s}^{-1}\text{)}$	C_{in}/C_{out}
5	$3.10 \cdot 10^{-10}$	$3.22 \cdot 10^{-6}$	$4 \cdot 10^{-2}$	$1.5 \cdot 10^{-3}$	1.7
20	$4.97 \cdot 10^{-9}$	$5.15 \cdot 10^{-5}$	$2 \cdot 10^{-3}$	$7.3 \cdot 10^{-5}$	1.028
50	$3.10 \cdot 10^{-8}$	$3.22 \cdot 10^{-4}$	$3 \cdot 10^{-4}$	$1.1 \cdot 10^{-5}$	1.004

Table 7. Estimation of the effect of SH2 on the concentration of particles of different size. The mass of individual particles is based on a spherical shape and the density of bulk Pt (namely 21090 kg m^{-3}). The number of particles of each size is chosen to reflect a lognormal distribution similar to the one found in SH1 and SH2.

d_p (nm)	Mass indiv. particle (ng)	size distr. (C_{in}) (#part.)	Total mass (ng)	τ_p^+ (-)	u_d^+ (-)	C_{in}/C_{out} (-)	C_{out} size distr. (#part.)	Total mass (ng)
6	$2.39 \cdot 10^{-12}$	$2.4 \cdot 10^{12}$	5.7	$4.63 \cdot 10^{-6}$	0.03	1.491	$1.61 \cdot 10^{12}$ (67 %)	3.8
9	$8.05 \cdot 10^{-12}$	$2.7 \cdot 10^{12}$	21.7	$1.04 \cdot 10^{-5}$	0.01	1.142	$2.36 \cdot 10^{12}$ (88 %)	19.0
12	$1.91 \cdot 10^{-11}$	$1.9 \cdot 10^{12}$	36.3	$1.85 \cdot 10^{-5}$	0.006	1.083	$1.75 \cdot 10^{12}$ (92 %)	33.5
15	$3.73 \cdot 10^{-11}$	$1.1 \cdot 10^{12}$	41.0	$2.89 \cdot 10^{-5}$	0.004	1.055	$1.04 \cdot 10^{12}$ (95 %)	38.9
total		$8.1 \cdot 10^{12}$	104. 7				$6.77 \cdot 10^{12}$ (84 %)	95 (91%)

Table 8. Diffusion coefficients for nanoparticles and corresponding diffusion times according respectively to Equations (12) and (14). ($T = 270\text{ }^{\circ}\text{C} / 543\text{ K}$, $\eta = 98.573\text{ }\mu\text{Pa s}$).

$d_p\text{ (nm)}$	$D_B\text{ (m}^2\text{ s}^{-1}\text{)}$	$\tau_d\text{ (s)}$
5	$1.6\text{ }10^{-9}$	$1.5\text{ }10^{-8}$
20	$4.1\text{ }10^{-10}$	$9.8\text{ }10^{-7}$
50	$1.6\text{ }10^{-10}$	$1.5\text{ }10^{-5}$

Table 9. Turbulent transport times, Equation (13), for particles of different sizes.

	SH1	SH2
$D_H\text{ (m)}$	0.00400	0.001057
$Re\text{ (-)}$	3131	4282
$u^*\text{ (m s}^{-1}\text{)}$	0.00739	0.0364
	$d_p\text{ (nm)}$	$\tau_t\text{ (s)}$
	5	$6.77\text{ }10^{-7}$
	20	$2.71\text{ }10^{-6}$
	50	$6.77\text{ }10^{-6}$

Table 10. Particle settling velocities calculated using Equation (16), $g = 9.81\text{ m s}^{-2}$, $T = 270\text{ }^{\circ}\text{C}$, $\eta = 98.573\text{ }\mu\text{Pa s}$, $\rho = 772.45\text{ kg m}^{-3}$.

$d_p\text{ (nm)}$	5	20	50
$V_g\text{ (m s}^{-1}\text{)}$	$2.8\text{ }10^{-9}$	$4.5\text{ }10^{-8}$	$2.8\text{ }10^{-8}$
$\tau_g\text{ (s)}$	1.8	0.45	0.18

FIGURES

Figure 1. Schematic of the PSI high-temperature loop as used for the Pt deposition experiments.

Figure 2. Drawing of specimen holders, a) cut-away view of assembly and b-c) cross sections of SH1 and SH2.

Figure 3. Back scattered SEM pictures of PO specimens from autoclave (a & c) and SH2 (b & d) showing oxide crystals sprinkled with Pt nanoparticles (white dots). a-b) Test 13, mean particle size = 16.5 nm, Pt inj. rate = $12.1 \mu\text{g h}^{-1}$. c-d) Test 19, mean particle size = 8.4 nm, Pt inj. rate = $4.2 \mu\text{g h}^{-1}$.

Figure 4. Particle size distributions resolved by location for Test 19. Dotted lines represent position of mean values.

Figure 5. Platinum loading on specimens at different location for eight experimental runs.

Figure 6. Schematic view of the evolution of the flow regime from the duct entrance.

Figure 7. SEM pictures from test 13 specimens. First column, specimens located in SH1, second column specimens located in the autoclave. First row: AR specimens; second row: PO specimens.

Figure 8. Variation of non-dimensional deposition velocity as a function of non-dimensional relaxation time as predicted by the Fan-Ahmadi formula.²³

Figure 9. Qualitative view of particle transport under: a) laminar flow and b) turbulent flow conditions (small arrows on particle represent the random diffusion). c) In turbulent flows the flow velocity gradient is steeper than under laminar conditions resulting in a thinner stagnant layer.

Figure 10. Transport times for different processes.