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Experimental Multiscale Methodology for Predicting Material Fouling Resistance

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Abstract:	The buildup of fouling deposits in energy systems degrades their ability to transfer heat, reducing efficiency and causing operational issues such as localized corrosion. Each application presents its own challenges. In nuclear power generation, the buildup of CRUD (Chalk River Unidentified Deposits) induces unique, negative effects ranging from reduced heat transfer, to axial power shifting, to CRUD-induced localized corrosion (CILC), the last of which can cause sudden fuel failure. Knowledge of why CRUD forms and how to prevent its adhesion to nuclear fuel rods represents a major step towards eliminating it. This paper demonstrates a methodology to ascertain which materials may resist CRUD adhesion, thereby preventing its initiation and growth. It presents experiments targeted at multiple length scales: pool boiling (macroscale), which simulates CRUD initiation processes in a nuclear reactor, and atomic force microscope (AFM) force spectroscopy (microscale), which yields quantitative measurements of the adhesion between CRUD constituents and candidate CRUD-resistant materials. Early data from both sets of experiments show some correlation,

	suggesting that AFM force spectroscopy (AFM-FS) may be used to pre-screen materials for fouling resistance. So far, it appears that CRUD constituents adhere well to oxides, while carbides show both greatly reduced adhesion and no adherent CRUD in pool boiling experiments. The relationship between the AFM-FS measurements and the growth of CRUD in the pool boiling experiments may provide insight into the possible factors affecting fouling in nuclear reactors, eventually leading to its elimination.
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Dear JoVE Editors,

Enclosed please find our manuscript, entitled "Experimental Multiscale Methodology for Predicting Material Fouling Resistance," submitted for publication in JoVE. In this paper, we present a multiscale experimental methodology for quantifying and predicting the resistance of materials to fouling, a multi-billion dollar material surface degradation problem that plagues the energy production, marine shipping, and fossil fuel refining industries, as well as most applications with heat transfer and a working fluid. While we present results specific to the formation of CRUD in nuclear reactors, we believe that this methodology is widely applicable to estimating the fouling resistances of many materials in different gaseous and fluid environments.

We believe that this work deserves to be documented in JoVE's unique video format because of our initial trials and tribulations in conducting both successfully reactor-representative pool boiling studies and AFM force spectroscopy (AFM-FS) of CRUD-substrate adhesion in water. For pool boiling, numerous iterations of samples preparation technique, experimental facility design, preparation of simulated PWR water with dispersed nanoparticles, choosing appropriate nanoparticle concentrations, and confirming reliably repeatable experimental conditions took over a year to master. Tips such as using direct heat flux sensors, strongly sonicating nanoparticle solutions immediately before use, and polishing techniques for finicky Zircaloys were not told to us; we had to figure these out for ourselves. We hope to save future experimentalists this trouble. As for the AFM-FS measurements, performing them in air is relatively straightforward, while the introduction of a fluid environment presents additional challenges of laser refraction in the droplet, realignment, material selection, and using very different spring constants due to a lack of electrostatic "pop-in" and attraction in conductive water. The procedure itself is fraught with places to mess up. Breaking AFM tips is common, and the mounting/fixturing procedure takes finesse. We were lucky enough to have Alan Schwartzman (one of our authors) guiding us through this work. His expertise is not reflected in any AFM-FS papers which we have read, and deserves to be visually documented. This will help take AFM-FS from a more specialized technique to something that is more easily learned by a wider variety of researchers. In addition, AFM-FS measurements specifically, and surface adhesion measurements in general, are quite lacking

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compared to many modes of interfacial observation. A lack of easily available data can be filled by making this technique more accessible and error-free.

Pavlina Karafilis, Abdulla Alhajri, and Gabrielle Ledoux have performed AFM-FS measurements, with Pavlina and Abdulla performing the most. Pavlina, Rasheed, and Vikash have "cooked" most of our materials in the pool boiling facility. They are also responsible for redesigning the majority of the pool boiling facility after its initial conception, to make experimental measurements easier and more trouble-free. Alan Schwartzman operates the Nanolab at MIT's Department of Materials Science and Engineering. He trained Pavlina, Abdulla, and Gabrielle in AFM-FS techniques, in addition to performing a few of the measurements himself. Leigh Lin built much of the first incarnation of the pool boiling facility, and together with Pavlina and Vikash designed and built the heater control boxes, pH system, Log-O-Matic data acquisition system, and iterations of the pool boiling chamber itself. Ekaterina worked with Prof. Short at the start of the project to "cook" the first samples, and analyze CRUD adhesion to substrates by SEM/FIB. Prof. Short conceived the project, built the first realization of the pool boiling facility and its associated electronics, and designed the experimental program.

Editor Mathew Solomon assisted us in the preparation process. It was through Mat contacting us that we learned about JoVE, and we immediately jumped on the opportunity to publish with the journal. I personally believe that the mission of JoVE is highly admirable and long-overdue in the world of science. When I think back to the years I could have saved if experimental techniques were this well documented, I wonder how much faster I could have graduated!

We recommend the following peer reviewers, based on their knowledge of the problems of CRUD and fouling, pool boiling techniques, AFM force spectroscopy, and adhesion:

1. Dr. Chris Stanek
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   Dr. Stanek is an expert scientist at the MST division of LANL, specializing in thermal conductivity. He also leads the Materials Performance and Optimization (MPO) focus area of the DOE Consortium for the Advanced Simulation of Light Water Reactors (CASL). One of CASL's three main challenge problem is understanding CRUD formation in PWRs.

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2. Dr. Dennis Hussey
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   Dr. Hussey previously lead the PWR technical advisory committee (P-TAC) at EPRI, which primarily focused on operational challenges facing PWRs in the industry today. His long experience with CRUD's effects on power plants and strategies for their mitigation gives him unique scientific and industrial experience with the problem of fouling in PWRs.

3. Dr. William Byers
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   Dr. Byers holds a patent on CRUD-resistant fuel cladding, and has studied its formation in nuclear power plants for quite some time. He currently helps run the WALT loop at Westinghouse, a unique facility designed to grow CRUD in conditions (pressure, temperature, heat flux, chemistry) very similar to those found in a PWR.

4. Prof. Sung Joong Kim
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   Prof. Kim studies the formation of CRUD, and has performed numerous flow and pool boiling experiments. He will be well suited to judge the merits of the pool boiling experiments at simulating the formation of CRUD, as he has experience designing and running pool/flow boiling thermal hydraulic experiments for nuclear reactors.

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5. Prof. Sandro Macchietto
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   Prof. Macchietto has helped lead the effort to design fouling-resistant materials for the oil industry, under the CRude Oil Fouling (CROD) program of the UK Engineering and Physical Sciences Research Council (EPSRC). Prof. Macchietto's work includes AFM-FS measurements of asphaltenes on glass substrates, to simulate the initial adhesion event of these molecules, found in crude oil, on oil-facing materials. He is well-suited to judge the merits of the AFM-FS portion of this work, as well as to comment on its wider applicability to more problems of scientific and industrial interest.

6. Dr. Dalia Yablon
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   Dr. Yablon is an expert on surface characterization, having worked in the oil industry for over a decade. She has founded her own company offering surface characterization services, and is a widely recognized expert in surface science, scanning probe microscopy, and atomic force microscopy. Dr. Yablon is also qualified to judge whether the AFM-FS based methodology put forth in this paper is suited to judge the anti-fouling properties of materials.

Thank you for your consideration of our article, we very much look forward to publishing with JoVE! Please feel free to contact me if you have any questions concerning our submission.

Sincerely,

Michael Philip Short

TITLE:
Experimental Multiscale Methodology for Predicting Material Fouling Resistance

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Fouling, adhesion, CRUD, nuclear, nuclear materials, pool boiling, AFM, AFM-FS, force spectroscopy

SHORT ABSTRACT:
Fouling, or corrosion product deposition, plagues numerous fields of energy production. At its core is adhesion between dissimilar materials. Understanding and controlling adhesion could reduce or eliminate fouling. This paper demonstrates pool boiling experiments (macroscale) and atomic force microscope force-spectroscopy measurements (microscale), which when in agreement, indicate fouling-resistance.

LONG ABSTRACT:
The buildup of fouling deposits in energy systems degrades their ability to transfer heat, reducing efficiency and causing operational issues such as localized corrosion. Each application presents its own challenges. In nuclear power generation, the buildup of CRUD (Chalk River Unidentified Deposits) induces unique, negative effects ranging from reduced heat transfer, to axial power shifting, to CRUD-induced localized corrosion (CILC), the last of which can cause sudden fuel failure. Knowledge of why CRUD forms and how to prevent its adhesion to nuclear fuel rods represents a major step towards eliminating it. This paper demonstrates a methodology to ascertain which materials may resist CRUD adhesion, thereby preventing its initiation and growth. It presents experiments targeted at multiple length scales: pool boiling (macroscale), which simulates CRUD initiation processes in a nuclear reactor, and atomic force microscope (AFM) force spectroscopy (microscale), which yields quantitative measurements of the adhesion between CRUD constituents and candidate CRUD-resistant materials. Early data from both sets of experiments show some correlation, suggesting that AFM force spectroscopy (AFM-FS) may be used to pre-screen materials for fouling resistance. So far, it appears that CRUD constituents adhere well to oxides, while carbides show both greatly reduced adhesion and no adherent CRUD in pool boiling experiments. The relationship between the AFM-FS measurements and the growth of CRUD in the pool boiling experiments may provide insight into the possible factors affecting fouling in nuclear reactors, eventually leading to its elimination.

INTRODUCTION:

Fouling, or the unwanted buildup of corrosion products on a surface, complements corrosion as a surface-based material degradation mechanism. Fouling is particularly detrimental in energy systems, as the surfaces which transfer the most enthalpy are typically the most susceptible. In essence, the presence of fouling deposits, often porous and/or thermally insulating, impedes the efficient flow of heat through a system. The high flow rates and large temperature differences in the hot and cold sections of a heat transfer system or coolant loop provide ideal environments to induce flow-assisted corrosion, and subsequent transport of corrosion products from areas producing soluble & particulate species, to the areas in which deposition is most favorable. In most energy systems, corrosion is most severe in the hottest sections of a coolant loop, since corrosion rates often accelerate exponentially with temperature. In the case of systems undergoing boiling, however, the formation and cavitation of bubbles on a material surface may induce species precipitation via microlayer dryout underneath bubbles. Here the growth of fouling deposits can be particularly rapid, and the resultant effects unusually devastating. Economically, heat exchanger fouling costs many industrial countries roughly 0.25% of its gross domestic product in annual lost productivity due to fluid treatment, cleaning, component replacement, and loss of production [1], equivalent to approximately $42 billion in the United States. Figures for worldwide industries such as boilers, marine shipping, and oil/gas production are far higher.

In nuclear light water reactors (LWRs), foulants composed of soluble and particulate nickel- and iron-bearing species deposit on fuel cladding rods to form CRUD, or Chalk River Unidentified Deposits. CRUD takes the form of highly porous deposits roughly tens to one hundred microns thick, with porosities on the order of 50%. In pressurized water reactors (PWRs), CRUD is largely formed from deposits of nickel ferrites ($Ni_xFe_{3-x}O_4$) in addition to small amounts of NiO, Ni metal, and some iron and nickel chromites ($FeCr_2O_4$, $NiCr_2O_4$, and $Ni_xFe_{1-x}Cr_2O_4$) [1,19]. Images of CRUD at different length scales are shown in **Figure 1**. [2] It takes the form of brownish-grey deposits on fuel rods, which when viewed in cross section exhibits multiple, self-similar length scales of porosity. The larger pores, known as "boiling chimneys," provide a path for vaporized water to escape the CRUD, while the smaller pores throughout serve to draw water within. This porous network of CRUD normally draws water into its pores via capillary action, but dryout may occur for very high values of heat flux. The smallest constituents of CRUD are particles, some crystalline, of the iron-nickel-chromium oxides which form the nanoporous framework. Zinc oxides and zirconium oxide are also sometimes present in CRUD.

CRUD can cause multiple negative side effects in PWRs, including CRUD-induced localized corrosion (CILC), which can lead to sudden fuel failure, elevated cladding temperatures due to CRUD's additional thermal resistance, and downward axial power shifts in the reactor [9]. Previous studies [3] have shown that Zircaloys (of which PWR fuel cladding is made) corrode far more quickly at elevated temperatures. Recent multiphysics modeling efforts [4] have shown that the presence of CRUD tens of microns thick can elevate cladding temperatures by 15°C, which corresponds to roughly a doubling of the corrosion rate. The last problem of axial power shifting is due to the accumulation of boron, present to control the neutron population in the reactor, in the pores of the CRUD. Recent massively parallel, multiphysics simulations of CRUD's effects [5] demonstrated this effect by simulating CRUD formation and boron accumulation along 3,000 fuel rods in a reactor, demonstrating a downward shit in reactor power. This behavior was already known from nuclear plant measurements [6].

Previous attempts have been made to develop materials resistant to CRUD formation. Solutions have included manipulating the growth of CRUD to improve heat transfer [10], manipulating water chemistry to minimize CRUD growth and corrosion [11], pretreating zircaloy [12], and using magnetic separation as a filtration system [21]. One recent patent [7] proposed to electropolish fuel cladding surfaces, to remove nucleation sites for bubbles which can induce CRUD. However, so far no method has resulted in completely preventing the growth of CRUD. We believe that uncovering the mechanism of the initiation event of CRUD formation, the adhesion of the first particles to a substrate, is the key to preventing its formation altogether. Therefore, precise measurement of surface adhesion forces, along with proof-of-principle experiments at higher length scales, is required to predict and confirm the fouling resistance of candidate materials.

This paper presents an experimental, multiscale methodology to discover materials that can be applied to nuclear fuel cladding and prevent the growth of CRUD. In order to achieve this goal, a variety of materials are being tested, shown in **Table 1,** representing different classes of potential anti-fouling and model materials. First, sputtered or grown specimens of each material are exposed an environment similar to that of a nuclear reactor, specifically a PWR (Pressurized Water Reactor), and "cooked," or indirectly heated to induce pool boiling with excess amount of CRUD forming particulates (NiO and Fe_3O_4) to simulate the boiling process on the surfaces of nuclear fuel rods. The cooked samples containing simulated CRUD are then imaged top-down using a high-resolution scanning electron microscope (SEM) and in cross section using a focused ion beam (FIB), allowing for visualization of any CRUD-substrate bond that may be present.

The experimental pool boiling setup that has been developed possesses certain unique benefits that make experiments repeatable, effective, and more representative of in-reactor conditions. A vertically oriented sample holder, as shown in **Figure 2** prevents nickel- and iron-based particulates that fall out of solution from depositing on the surface of the sample by gravity. Strongly sonicating the CRUD-bearing solution prior to the experiment allows for longer test times and less precipitation of particulates. In addition, for each of the four samples being tested, the heat flux and temperature is recorded throughout the experiment. The pH of the simulated PWR water is also recorded throughout the experiment.

In order to quantify the bond between the CRUD deposits and the surface, we also perform AFM force spectroscopy (AFM-FS) measurements in both air and simulated PWR water on clean surfaces of the same materials. First, AFM cantilevers are functionalized with particles made of one micron spheres of compounds commonly found in CRUD (NiO or Fe_3O_4). In the MFP3D-BIO, the AFM used in this procedure, the cantilever is modeled so that the force applied to the cantilever tip is proportional to its deflection when in contact with the surface. A laser reflects off the cantilever to a photodetector to measure its deflection. In the procedure below, two constants, the spring constant and the deflection InvOLS (inverse optical lever sensitivity) must be calibrated in order to convert the deflection read by the photodetector to nanoNewtons.
In order to record adhesion of the tip to the surface, the cantilever tip is pressed against the surface of the sample with a force of 25nN. In the experiments recorded below, the tip will then remain at the surface for a period of either 0, 5, 10, 30, or 60 seconds. As the cantilever is being retracted, the tip will often adhere to the sample surface, causing the cantilever to deflect until the force of the cantilever deflection is greater than the adhesion between the CRUD particle and

the surface under investigation. Then the cantilever snaps back to zero deflection. It is this maximum deflection, and its corresponding adhesion force, that the AFM can quickly and repetitively record [18]. The area under the force-distance curve produced by AFM-FS is a direct measure of the work of separation between CRUD and a substrate, and therefore quantitatively estimates the adhesion of that CRUD particle to each surface. Using the same AFM cantilever on multiple samples eliminates variability in particulate size and composition.

This unique combination of simulated CRUD growth and AFM measurements provides multiple, coupled datasets that allow us to understand how and why CRUD may develop on certain material surfaces. Rather than undergo time-consuming pool boiling experiments, which can take up to a day to complete, a large number of materials can be pre-screened using AFM-FS to estimate their fouling resistance. We also show initial results confirming the efficacy of this procedure, whereby materials which exhibit little to no CRUD adhesion in pool boiling also show very low values of CRUD-substrate adhesion in AFM-FS. Conversely, materials which grow large amounts of adherent CRUD in pool boiling also adhere strongly to CRUD particles in the AFM.

PROTOCOL:

1. **Material Preparation**

1.1. Using a suitable machining method, section 1 cm x 1 cm coupons of the base substrate material (here, Zircaloy-4) from a sheet approximately 1 mm thick. The exact thickness is not important.

1.2. Using a manual or automatic polishing machine, polish the base substrates to an optically smooth, mirror finish.

1.2.1. Mount specimens to a flat sample holder using a hot plate and a shear-resistant wax, for insertion into an automatic grinding/polishing machine. Here, mount twenty at once.

1.2.2. Grind the faces of the mounted samples smooth on a rough diamond grinding disc (DGD) or with coarse sandpaper mounted to a very flat platen.

1.2.3. Remove the samples from the sample holder by carefully chiseling the side of each sample with a flathead screwdriver. The mounting adhesive should cleave and break off with very little force.

1.2.4. Sonicate the samples in acetone for 5 minutes, then in 100% ethanol for 5 minutes to remove any trace of the mounting adhesive.

1.2.5. Mount the newly flattened faces of the same samples to the flat sample holder using the mounting adhesive.

1.2.6. Using successively finer grit sandpaper or diamond solutions, polish the faces of each sample.

1.2.6.1. First, flatten the exposed faces of the samples using the DGD or coarse sandpaper.

1.2.6.2. Next, use ~240 grit sandpaper to remove all the scratches from the previous polishing step. Polish for at least one minute using water as a lubricant, or until all scratches from the rough grinding stage are removed.

1.2.6.3. Remove the sample holder with samples from the polishing machine. Sonicate the entire assembly for at least two minutes, to remove any embedded sandpaper grit. If the entire assembly does not fit in the sonicator, rotate the assembly in the water, sonicating each section for at least two minutes. Return the assembly to the polishing machine.

1.2.6.4. Repeat steps 1.2.6.2-1.2.6.3 with 400 grit and 800 grit sandpaper.

1.2.6.5. If not wearing gloves, put them on at this stage. Diamond particles and silica nanoparticles can lodge under the skin, and are very uncomfortable!

1.2.6.6. Use a 9 μm diamond suspension on a suitable polishing cloth, without additional water lubricant, to continue polishing the specimen. Squirt or pour a small amount (5-10 mL) of diamond suspension on the spinning platen once every 15-30 seconds. Repeat step 1.2.6.3.

1.2.6.7. Repeat steps 1.2.6.6-1.2.6.7 for 3 μm and 1 μm diamond suspensions.

1.2.6.8. Using a 0.05 μm silica suspension and a clean, appropriately chosen polishing cloth, polish the samples to an absolute mirror finish. This may take up to 30 minutes.

1.2.6.9. Clean any excess silica suspension from the samples using squirt bottles of ethanol and lint-free wipes or lens cloth.

1.2.7. Repeat steps 1.2.4-1.2.5.

1.3. Using a suitable surface deposition method for each of the materials, deposit the chosen potentially CRUD-resistant materials onto the mirror-finished sides of the base substrates. Here, use sputtering for the materials. Sputter the materials to test to a thickness of approximately 50 nm. The exact thickness is not important, as long as it is sufficiently thick to discount any changes in surface chemistry from its underlying substrate.

2. Cooking sample

2.1. PWR Water Preparation

2.1.1. First, prepare simulated PWR reactor water. Measure 5 L of deionized water, 0.06 g of boric acid and 0.03 g of lithium hydroxide. Mix together and shake vigorously. This ‘simulated PWR water’ can be used in later experiments.

2.2. Measure 0.18 g of NiO nanoparticles (10-50 nm), 0.18 g of Fe_3O_4 nanoparticles (10-50

nm), and 300 mL of deionized water. Mix together these CRUD particulates in a beaker.

2.3. Add 200 mL of simulated PWR reactor water to the solution with CRUD particulates. Strongly sonicate the solution for 5 minutes.

Note: The simulated PWR water consists of 10 ppm of H_3BO_3, 5 ppm of LiOH, 100 ppm of NiO and 100 ppm of Fe_3O_4 and 1.8 L of deionized (>15 MΩ) water. These measurements may change depending on desired ratios of particulates and experimental chamber size. Normal concentrations of NiO and Fe_3O_4 in PWRs are 10's to 100's of ppb. [4]

3. Cooking Preparation

3.1. If the simulated PWR water is not freshly mixed, turn the container of simulated PWR water on its head. This helps eliminate the acidity gradient that tends to develop when the simulated PWR water sits for long periods of time.

3.2. Cover both sides of each heat flux sensor with a thin layer of conductive silver paste. This helps ensure good thermal conduction into the sample. Use as little as possible, to prevent the entry of silver paste into the simulated PWR water in the pool boiling facility. Remember to check for silver's presence in the CRUD using a suitable technique (SEM/EDX) later.

3.3. Place a clean, sample on top of each heat flux sensor. If not all heat flux sensors will be used, cover these unused ones with a thin piece of rubber.

3.4. Place and clamp down an insulating material on all exposed metal surfaces in contact with the heating element to prevent boiling on surfaces other than sample itself.

3.5. Place O-ring on experimental body. Put some silicon grease in the O-ring groove to keep the O-ring in place while the nuts are beings tightened. Tighten the nuts.

3.6. Insert pH probe and water bath thermocouple.

3.7. Pour in the sonicated nanoparticle solution and an additional 1.3 L of the simulated PWR water. Make sure that there is a vent for the displaced air to exit. Once the sample holder and pump intake has been completely covered by PWR water, seal off the experimental body.

4. Cooking

4.1. Turn on the data collection system and the circulation pump to a flow rate of approximately 130 mL/min.

Note: The pump promotes sub-nucleate boiling by preventing the formation of a vapor film with a steady stream of water. The data collection system records heat flux for each sample, bath temperature, each sample temperature, and the system pH. A credit card sized data logging circuit board and its carrier board with screw-type terminal block connections is used as a data collection device, and K-type thermocouple measurements are amplified by a simple circuit

presented in **Figure 3**.

4.2. Turn on the Proportional Integral Derivative (PID) bath heater controller, with a set point of 97 °C.

Note: The circuit diagram of the control box that houses the pH meter, and the PID bath and sample controllers is presented in **Figure 4**. The bath water should not reach over 97 °C. The bath water temperature and the sample temperature difference should not be greater than 10 °C while the sample heater is off. A large temperature discrepancy during heating can cause excessive CRUD growth and affect the repeatability of the results.

4.3. After the water has reached a temperature of 90 °C, turn on the PID sample heater controller. The sample should quickly stabilize at 125 °C.

4.4. Create new file in the data collection system to record experimental conditions of sample & bath temperatures, pH, and heat flux. Begin data collection as soon as the samples stabilize at 125 °C.

4.5. Let the experiment run for the desired amount of time. Typically, runs last from 15 minutes to 8 hours.

5. Clean-up

5.1. At the end of desired run time, turn off all heaters.

5.2. Drain the experimental body, collecting a sample of water for records and possible future chemical analyses. Label properly.

5.3. Place paper towels underneath the experimental body, untighten, and remove nuts.

5.4. Unscrew the rubber cover at the center of the sample holder. Unclamp and remove Teflon cap.

5.5. Carefully retrieve and store cooked samples. These samples are ready to be examined using the SEM, or any other analysis technique.

6. Atomic Force Microscopy Force Spectroscopy in PWR Water

6.1. Calibrate the Spring Constant Photodiode Resonse of the Cantilever

6.1.1. Load a CRUD-functionalized tip into the cantilever holder.

6.1.1.1. To do so, loosen the screws on the spring clip. Using two tweezers, hold the cantilever and raise the spring clip. Slide a CRUD-functionalized AFM cantilever under the spring clip and tighten the screws on the spring clip. Make sure that the cantilever tip is one

half to two thirds up the trapezoidal window on the cantilever holder and parallel to the top of the trapezoidal window.

6.1.1.2. Load the cantilever holder into the AFM head.

6.1.2. Turn on the top-down optics system to view the top of the AFM cantilever.

6.1.3. Clean a glass slide with MeOH (methanol). Place it onto the stage and return the AFM head back on the stage.

6.1.4. Align the laser on the cantilever tip and maximize the reported sum.

6.1.5. Adjust the photodetector until the deflection reads zero volts.

6.1.6. Select 'engage' to electronically lower the cantilever. Slowly lower the front of the AFM head manually until the cantilever tip engages with the surface of the glass slide. Continue to lower the front of the AFM head until the voltage of the z-piezo is 70 V at the surface of the slide.

6.1.7. Withdraw the cantilever and adjust the photodetector until the deflection is 0 V +/-0.09 when the tip is withdrawn. Repeat steps 6.1.6 and 6.1.7 until the correct voltages are achieved.

6.1.8. Calibrate the photodiode response or (volts) per nanometer of cantilever deflection. Complete a single force curve and a linear fit to find the inverse slope of the force curve while the cantilever is in contact with the glass slide. The reciprocal of the slope is the photodiode response.

6.1.9. Disengage the tip from the surface.

6.1.10. Begin capturing thermal data. During this process, the thermal vibration of the cantilever is recorded. The AFM software analyzes a power spectrum of the thermal vibration and plots it in a new window.

6.1.11. Wait for the sample collection count to reach over 100, then stop the data collection. Use the AFM software to specify the center and width of the lowest-frequency (fundamental resonance) peak.

6.1.12. Perform a fit to determine the spring constant.[23]

6.1.13. If AFM-FS measurements in air are desired, skip to step 6.3. Otherwise proceed with step 6.2 first to perform AFM-FS measurements in water.

6.2. Calibrating AFM in Water

6.2.1. Raise the AFM head, take it off the stage, and place it cantilever-side up. Use a pipette incremented to at least 20 µL to place one or two drops of the simulated PWR water on the cantilever tip, but no more than 20 µL.

6.2.2. Place no more than 60 µL of the simulated PWR water on the glass slide. Return the AFM head to the stage. Make sure the water on the sample and the water on the cantilever form one droplet.

6.2.3. Realign the laser beam on the back of the cantilever tip and maximize the reported sum. Due to Snell's law, the laser will refract in the water and will therefore have to be realigned.

6.2.4. Repeat steps 6.1.5 through 6.1.8 to engage the tip with the surface and calibrate the photodiode response.

Note: The simulated PWR water in this procedure has a pH greater than 5.5 and less than 8. If the water pH exceeds this range, a different cantilever holder must be used.

6.3. Collecting Force Maps

6.3.1. Raise the AFM head by more than the height of the sample to make sure the cantilever won't crash with the sample surface when the AFM head is reinstalled. Remove the AFM head and glass slide from the stage.

6.3.2. Clean a glass slide with MeOH and secure the sample to the surface with double sided tape. Place the sample on the stage. For AFM measurements in water, place no more than 60 µL of simulated PWR water on the surface of the sample and one or two drops of simulated PWR water on the cantilever. Reinstall the AFM head making sure that the water droplets on the tip and on the sample surface meet and coalesce.

6.3.3. Engage the AFM tip with the sample surface as described in 6.1.6.

6.3.4. If ringing occurs, where the deflection oscillates quickly over large ranges, particularly from positive to negative, decrease the integral gain.

6.3.5. Set the force distance and start distance by engaging the tip with the surface, and right-clicking the red bar on the force calibration screen. Select the dwell type 'towards surface' and a desired dwell time. Set the velocity to approximately 2 µm/sec and the trigger point (the force applied by the tip to the surface) to 25 nN.

6.3.6. Define a 6 x 6 grid (or greater grid for better statistics) with a scan size to be 15 µm.

6.3.7. Click 'Do Scan' to collect the number of force curves specified in the grid.

6.3.8. Repeat steps 6.3.6-6.3.7 at different locations at least 30 µm apart with varying dwell times.

7. Clean Up

7.1. Remove the AFM head, the sample, and the glass slide from the stage. Store the sample and clean the glass slide.

7.2. Remove the cantilever holder and carefully wick up the remaining solution off the cantilever, if desired. Remove the cantilever and place it in a gel pack or reusable storage container.

7.3. Clean the cantilever holder with MeOH.

REPRESENTATIVE RESULTS:

Initial results show that experiments in both the pool boiling facility and the AFM-FS measurements show some correspondence. Materials which grew visually adherent CRUD in pool boiling exhibited high values of adhesion in AFM-FS, while materials on which CRUD did not grow exhibit low values of adhesion in AFM-FS. In addition, the average adhesion force vs. dwell time increased for materials on which CRUD grew, while potential CRUD-resistant materials did not exhibit this increase.

Section 1.1: SEM/FIB Images

Figure 5 shows an SEM image from the FIB of CRUD grown on a sample of TiO_2, cooked in the experimental facility shown similar to **Figure 2,** except the sample was oriented horizontally, and there was only one sample in the chamber rather than four. This image clearly shows adherence between the simulated CRUD and the TiO_2 substrate. **Figure 6** shows an image of a sample of CRUD-like particles deposited on ZrC. This image shows the limited bonding between the ZrC and the CRUD. In particular, one should notice that the CRUD on TiO_2 is strongly adherent to the substrate, leaving no porosity between CRUD and TiO_2. By contrast, the CRUD particles on ZrC are clearly not adhered to the substrate, rather they simply sit on the exposed surface. No adhered CRUD particles were present on this sample. The horizontal orientation of the sample surfaces presented in this paper explains the presence of large pieces of CRUD that are sitting on but not adhered to the surface of the sample. These particles likely deposited from the simulated PWR water with nanoparticles clustering and settling out of solution, without adhesion. During the experiment, CRUD particles can come out of PWR solution and drift down to the sample surface when the sample is horizontally oriented. The vertical orientation should eliminate this problem. **Figure 7** shows evidence that the larger sediments on the sample surface are not adhered to the surface, as an omniprobe in the FIB easily moved them with a little prodding.

Section 1.2: AFM-FS Measurements

Figure 8 shows a single sample force curve [13]. The x-axis reflects the tip distance from the surface of the sample, and the y-axis records the force felt by the tip, which is proportional to the deflection of the cantilever. A positive force corresponds to the tip being pushed by the sample surface and a negative force to the tip being pulled by the sample surface, but still held on by

adhesion forces. The black line records the approach, while the red line records the retraction of the sample from the surface. This graph also presents effects of electrostatic forces as the sample approaches. Particularly for the AFM tips with NiO in air, electrostatic forces had a significant effect on the force during the approach, causing significant deflection away from (negative force) or towards the sample surface (positive force) until it contacted the surface. Therefore, data using Fe_3O_4 functionalized AFM cantilevers will be presented in this section, as these electrostatic effects were not observed as strongly. The adhesion data recorded is the difference between zero deflection, and the minimum force felt by the cantilever.

Figures 9 and **11** present the AFM-FS in-air data based on dwell time at the surface for TiO_2 and ZrC surfaces with Fe_3O_4 tips. For TiO_2, average adhesion increases with increasing dwell time, while the ZrC presents the opposite result. In addition, the measured adhesion forces, in both air and water, are visibly greater for TiO_2. **Figures 10** and **12** present similar data, but performed in a droplet of simulated PWR water. Here, the average adhesion of the ZrC is also consistently less than in adhesion of the TiO_2. It is important to note the change of scale on the y-axis and the significant decrease in adhesion force between air and water. All AFM data points, except those with a dwell time of 60 seconds are the average of 36 adhesion measurements. Data points with dwell times of 60 seconds are the average of 16 adhesion measurements.

Table 1: Materials and surface modifications considered in this study. Materials referred to in this study are shown in bold.

Figure 1: Multiscale Images of CRUD in PWRs [2], showing (a) Appearance of CRUD on fuel cladding rods as a brownish deposit layer (b) Microporous CRUD structure showing boiling chimneys (dark) and porous structure, and (c) Examples of CRUD crystalline particulate constituents

Figure 2: Pool Boiling Experimental Facility Diagram

Figure 3: Pool Boiling Facility Control Box Diagram

Figure 4: Thermocouple Amplification Circuit Diagram

Figure 5: SEM/FIB Image of CRUD Growth on TiO_2, 20,000x & 150,000x

Figure 6: SEM/FIB Image of CRUD Growth on ZrC, 5,000x

Figure 7: SEM/FIB Image of CRUD. These images show an Omni Probe in the FIB rolling a large piece of CRUD that had deposited, but not adhered to the surface.

Figure 8: Example AFM-FS Single Force Curve [13]. The black curve represents loading, while the red curve represents unloading. The green area gives a quantitative estimate of adhesion energy.

Figure 9: AFM-FS measurement of the adhesion of Fe_3O_4 tip to TiO_2 in Air. Data are averages of 36 measurements at times of 0-30 s dwell time, and 16 measurements at times of 60 s. Error bars show the minimum and maximum of all measurements taken at each dwell time.

Figure 10: AFM-FS measurement of the adhesion of Fe_3O_4 tip to TiO_2 in Water. Data are averages of 36 measurements at times of 0-30 s dwell time, and 16 measurements at times of 60 s. Error bars show the minimum and maximum of all measurements taken at each dwell time.

Figure 11: AFM-FS measurement of the adhesion of Fe_3O_4 tip to ZrC in Air. Data are averages of 36 measurements at times of 0-30 s dwell time, and 16 measurements at times of 60 s. Error bars show the minimum and maximum of all measurements taken at each dwell time.

Figure 12: AFM-FS measurement of the adhesion of Fe_3O_4 tip to ZrC in Water. Data are averages of 36 measurements at times of 0-30 s dwell time, and 16 measurements at times of 60 s. Error bars show the minimum and maximum of all measurements taken at each dwell time.

DISCUSSION:

This facility has several features that will produce reliable and useful results. First, the vertical orientation of the sample surface prevents solution precipitates from depositing on the surface, as was observed in **Figures 5-6**. Particularly important are the heat flux sensors, used to directly measure heat flux by differences in thermocouple height vs. temperature, rather than back-calculating a heat flux just from temperature measurements. This helps to further ensure experimental repeatability. Finally, the small water circulation pump prevents film boiling from occurring and promotes sub-cooled nucleate boiling, which is the true condition under which CRUD develops in reactors. Sonicating the simulated PWR water also prevents particles from falling out of solution during boiling. Once again, while this facility is specialized to work with CRUD, many of its traits could be used in other fouling growth experiments. The use of the small amplifying circuit in **Figure 4** and a credit-card sized datalogger is a small, simple feature that is applicable for any experiment that collects data electronically, replacing an entire computer and monitor with a circuit board the size of a credit card.

The use of AFM for force spectroscopy can provide repeatable experimental data of adhesion between varieties of dissimilar materials quickly and efficiently. In the procedure shown here, the AFM is outfitted with a tip specifically suited for our research needs. While this procedure is applied to the adhesion of CRUD on a sample, with a variability of tip sizes, shapes, and materials, the procedure shown here is applicable to any problem where the adhesion between two materials at the atomic level in air or in any optically transparent fluid may be useful. AFM-FS has already been used to quantify adhesion and debonding forces between cells [14], organic molecules on glass [15], and between dissimilar solids [16].

For each installation of the chip with the cantilever and tip, the deflection InvOLS and the spring constant will be slightly different, in part because of slight differences in how it is mounted, and in part because the ambient humidity and temperature may also have changed. Recent experimentally validated models have quantified the change in adhesion of AFM-FS measurements as a function of humidity and surface/tip compositions [17]. However, with the ability of the AFM to complete large numbers of measurements quickly, statistically significant results can easily be ascertained.

Figures 9-12 all show a significant decrease in adhesion measurements from air to water. This is

to be expected as the decrease of AFM measurements in water with respect to air is a well-documented phenomenon [22]. The presence of conductive water, which contains H_3BO_3 and LiOH, likely eliminates any electrostatic forces present in the AFM-FS in-air measurements. The in-water data also represent conditions more realistic to those found in a PWR. Even so, the data in air and in water show relative correspondence, even though the absolute magnitudes of the in-water data are lower. Because these measurements represent the critical, quantitative data in this procedure, proper measurement techniques in Step 6 are critical to acquiring the data in this procedure. In particular, calibrating the individual spring constants of each tip, in air and in water, represent the largest potential sources of experimental error, and should not be omitted.

Looking at the results from the AFM and the FIB together, it is clear that the adhesion force is likely a significant factor in the growth of CRUD on each substrate. In both air and simulated PWR water, the TiO_2 AFM-FS measurements are consistently higher than those on ZrC. In **Figure 5,** the CRUD is tightly bound to the TiO_2 substrate, while in **Figure 6**, the CRUD sits on a few nanoparticles that appear to rest on the surface of the ZrC substrate, creating a far weaker bond if any at all. These preliminary data suggest that the AFM-FS measurements can predict relative bond strength of CRUD, or any fouling deposit, to candidate anti-fouling substrates. Here, the AFM-FS results have been corroborated by simulated growth of CRUD. The AFM-FS measurements can be extremely useful in providing an initial screening test for coatings or surface modifications that can limit CRUD growth in nuclear reactors. While this method of AFM measurement and accelerated fouling growth is used here for fouling in nuclear reactors, it can be easily applied to find protective coatings for fouling in many other applications, or to find a substrate the will promote growth of a mineral or crystal.

DISCLOSURES:
The authors have nothing to disclose.

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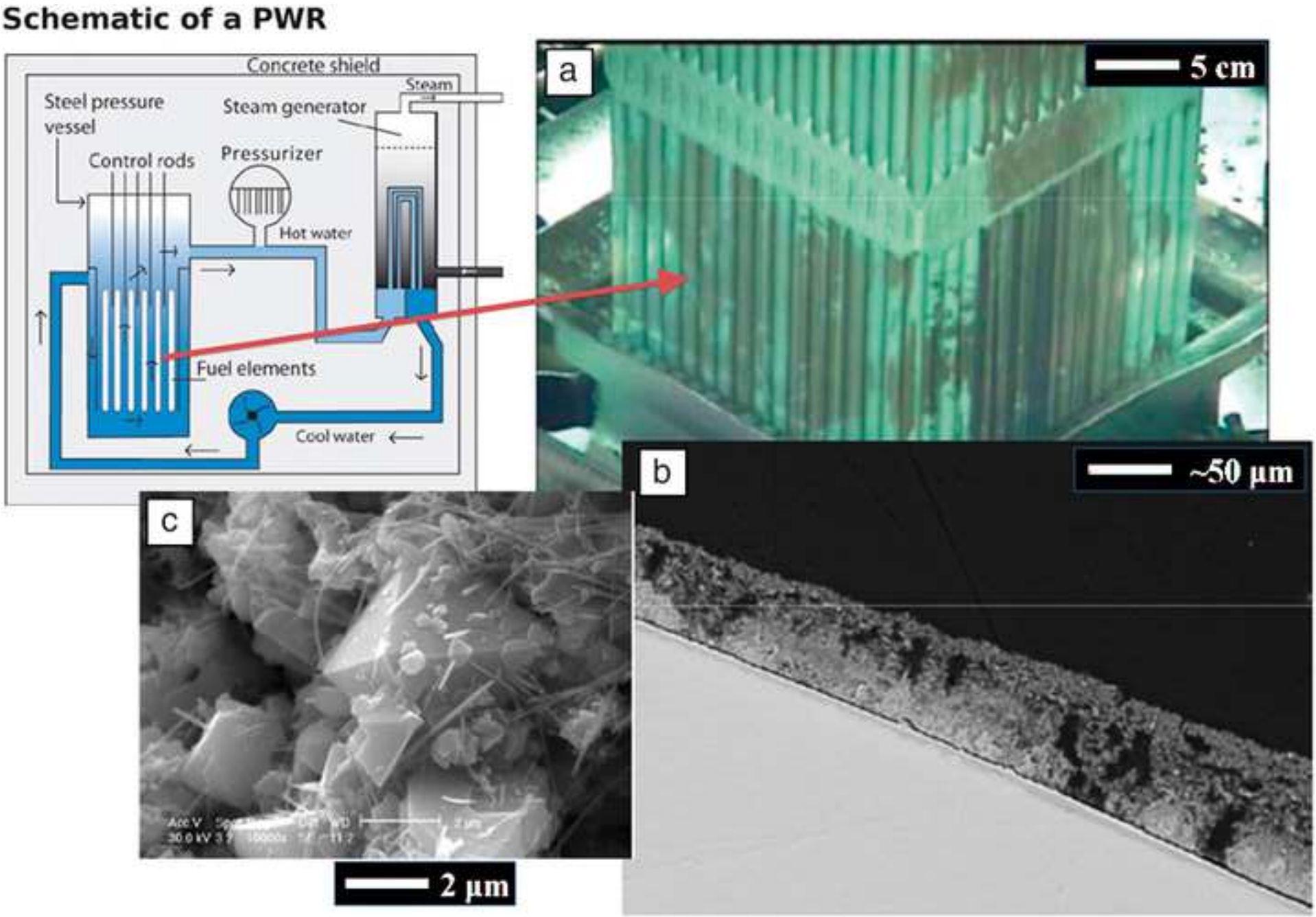

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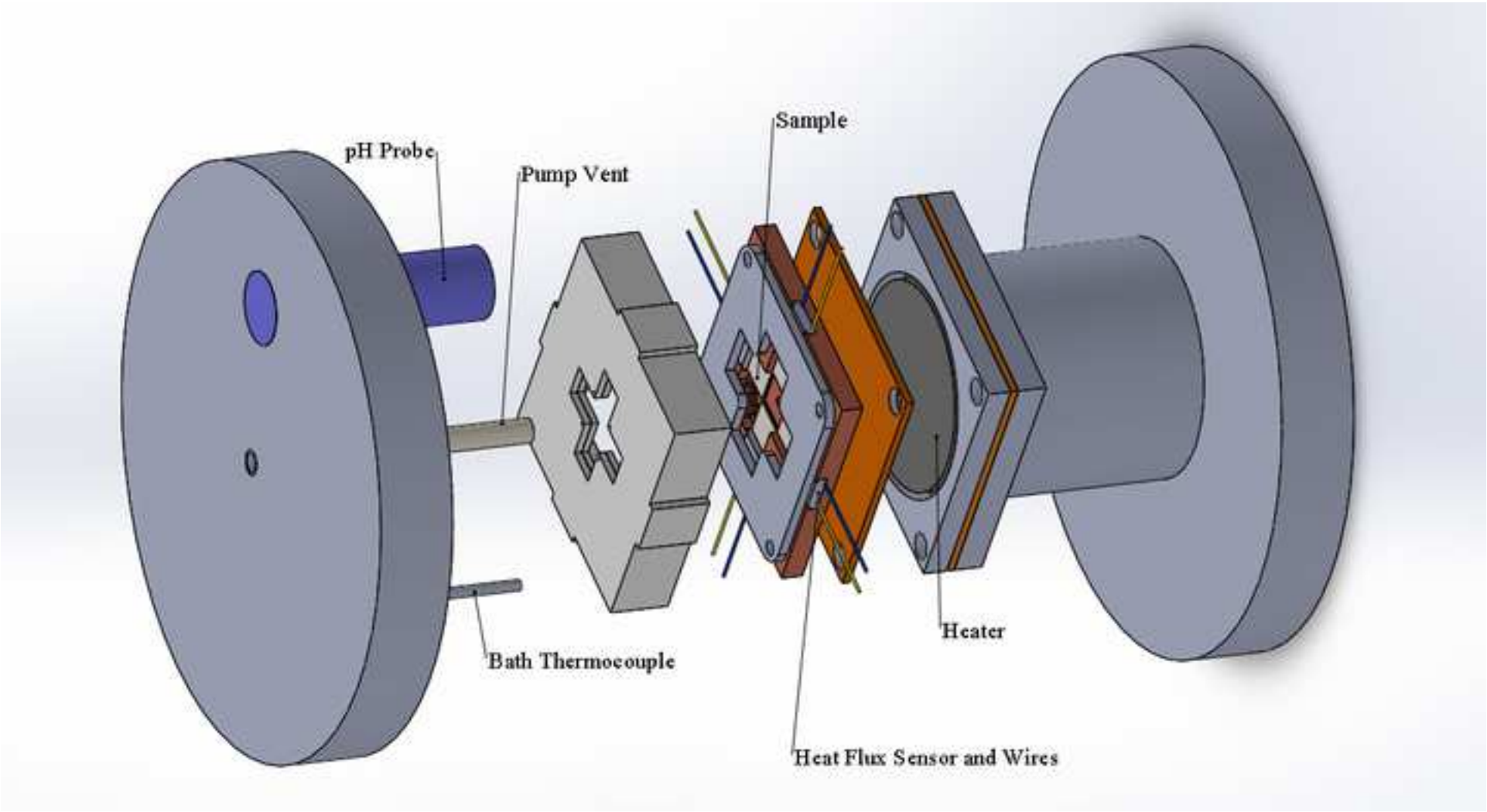

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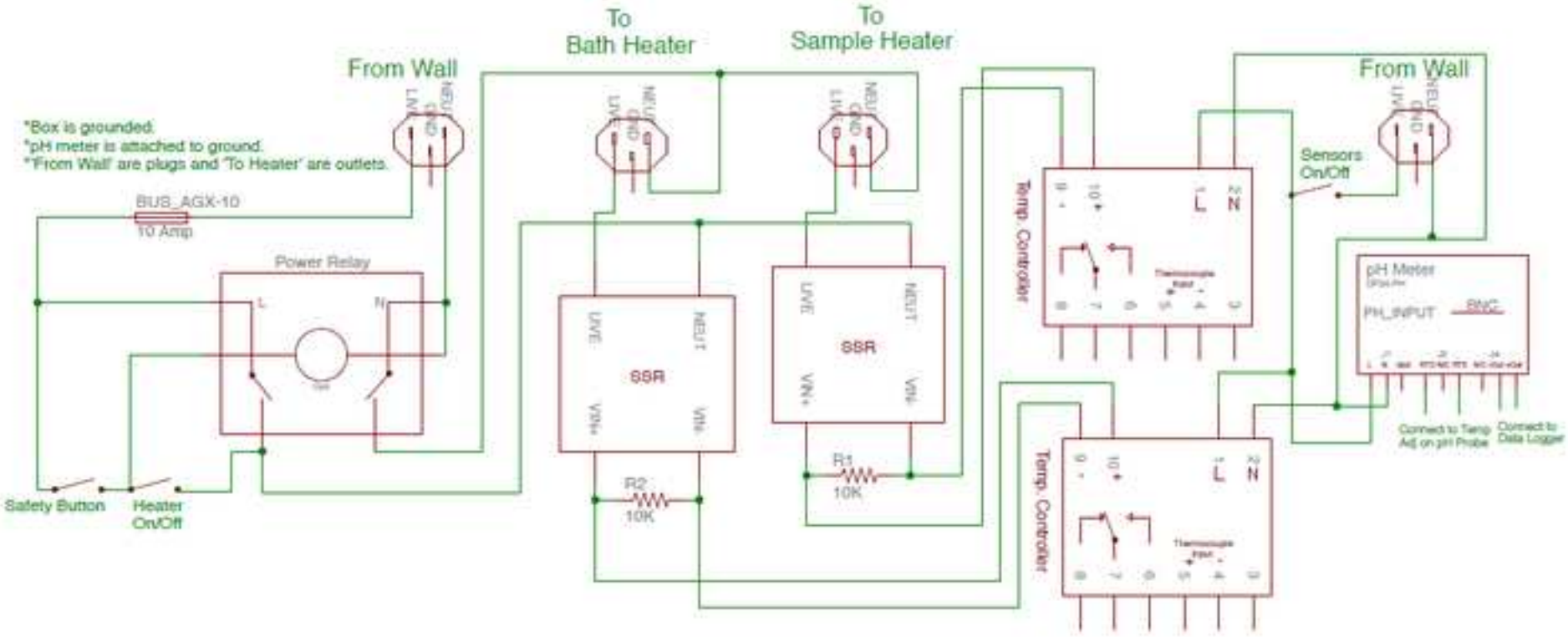

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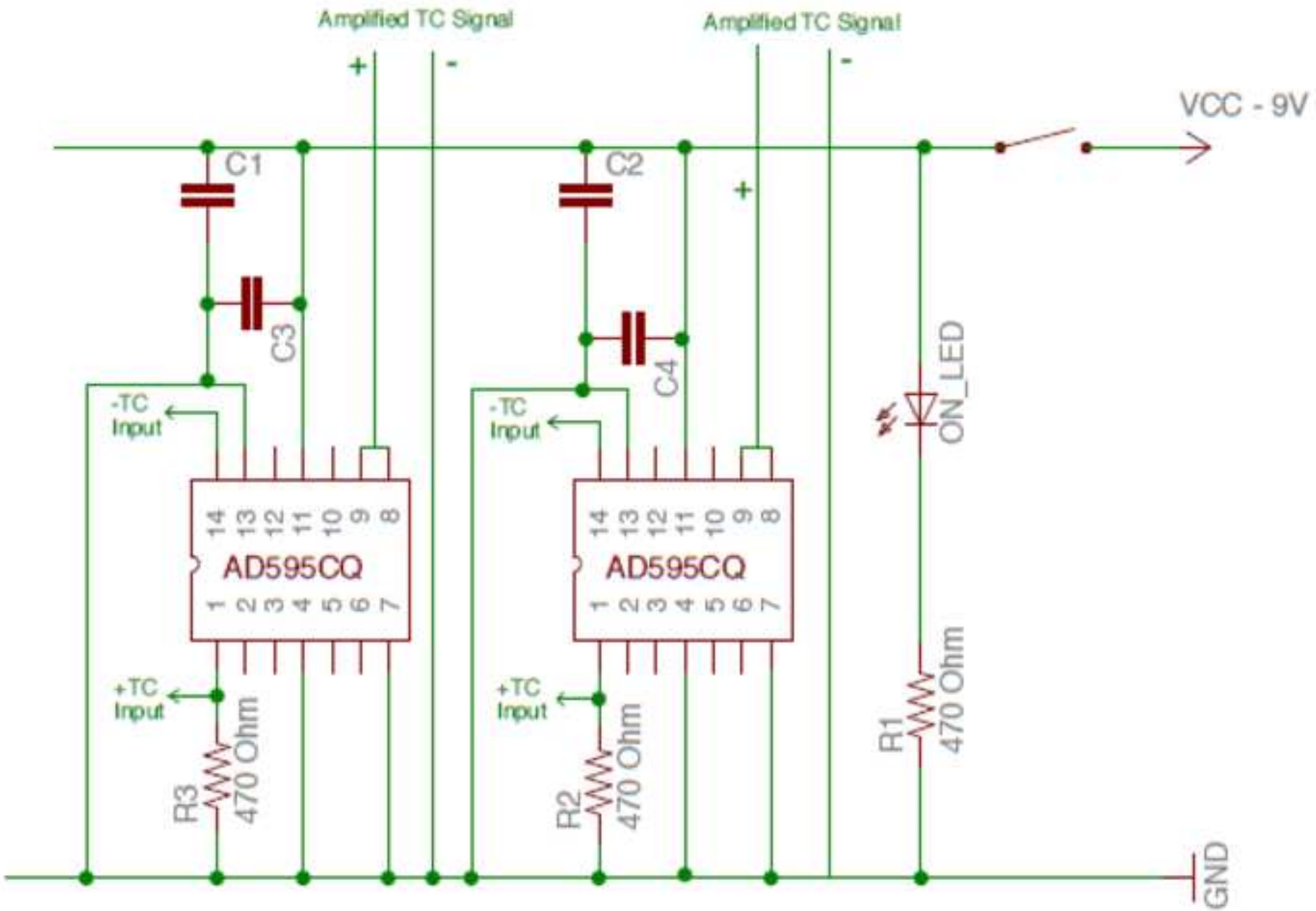

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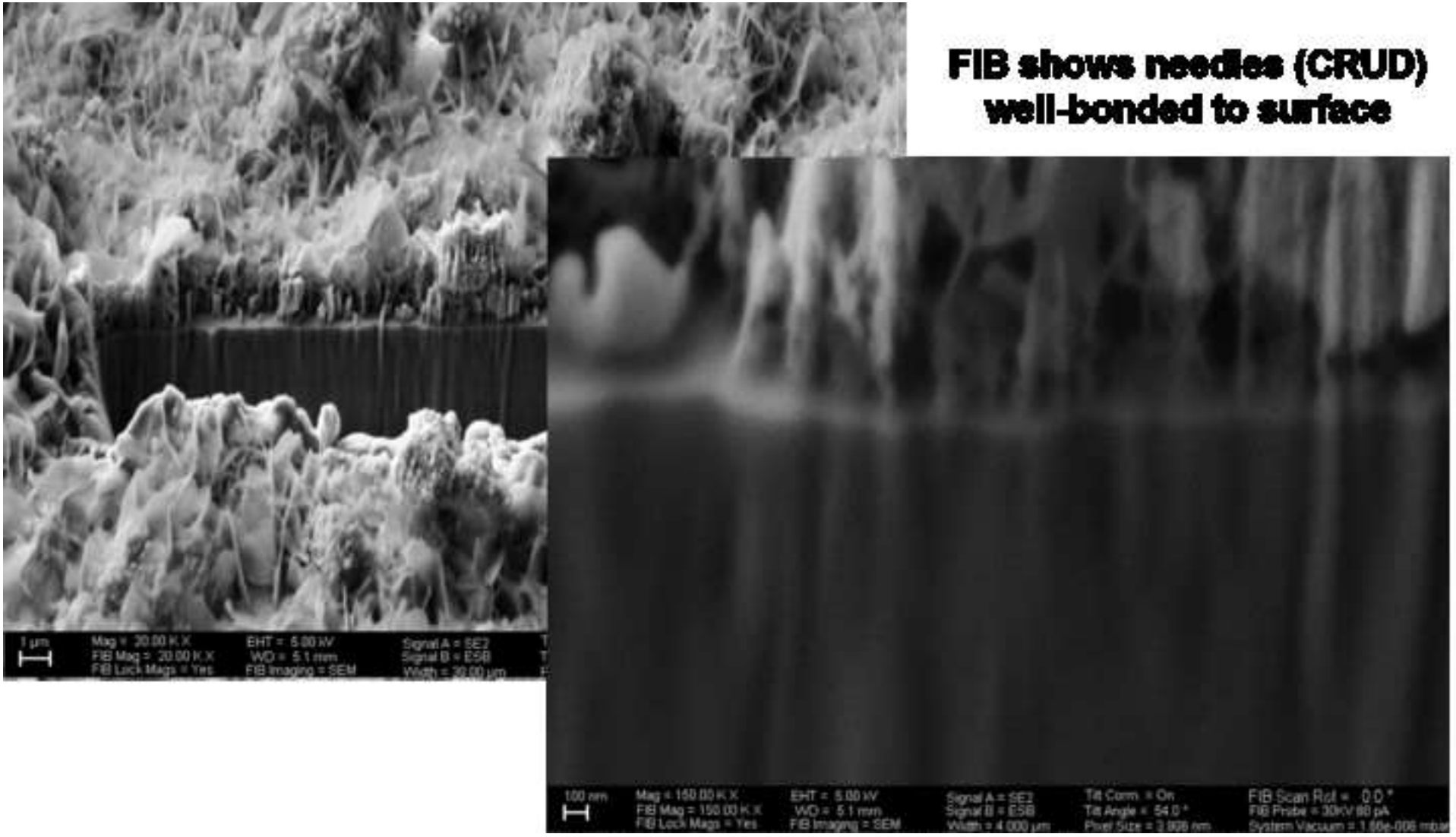

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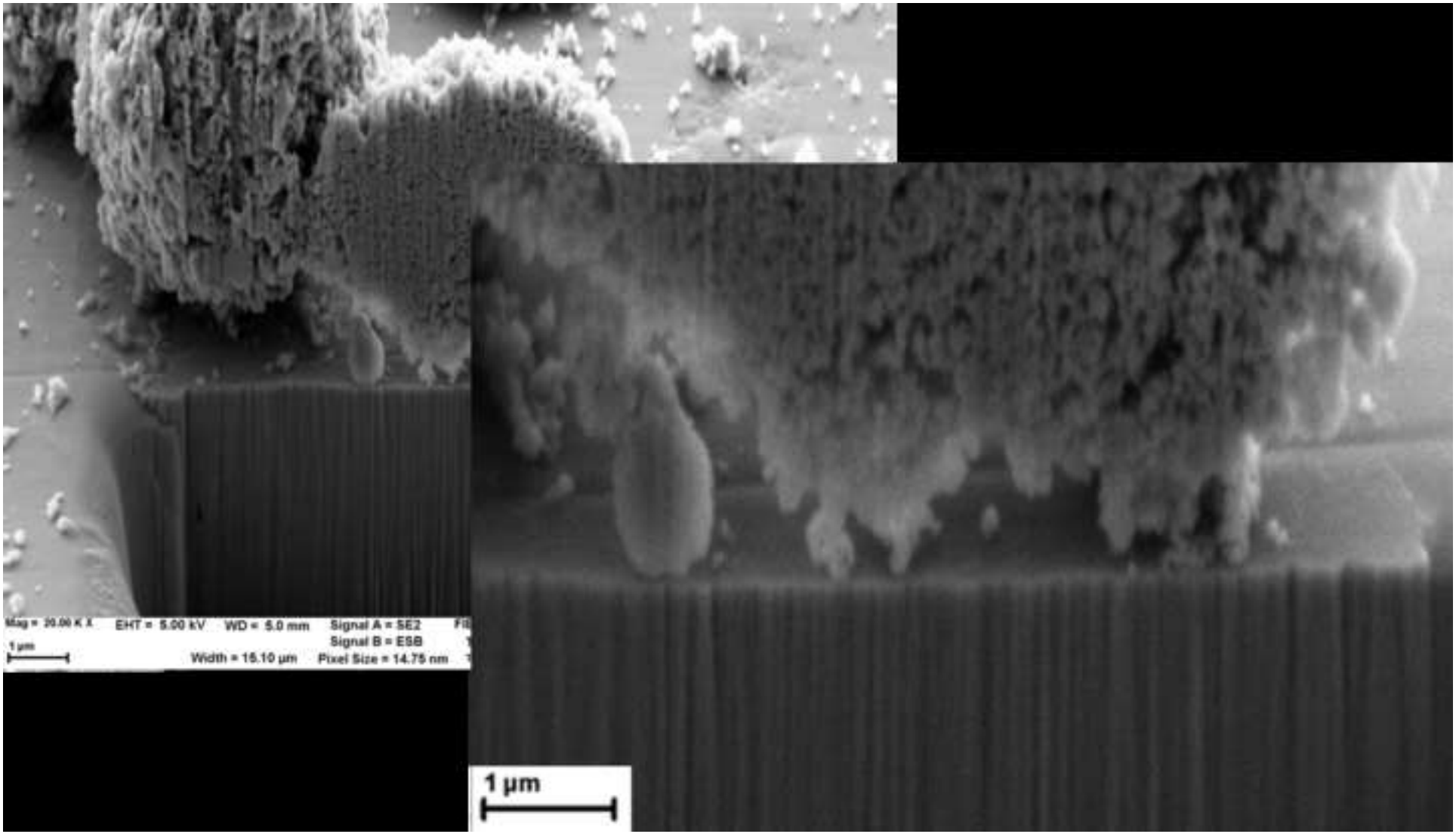

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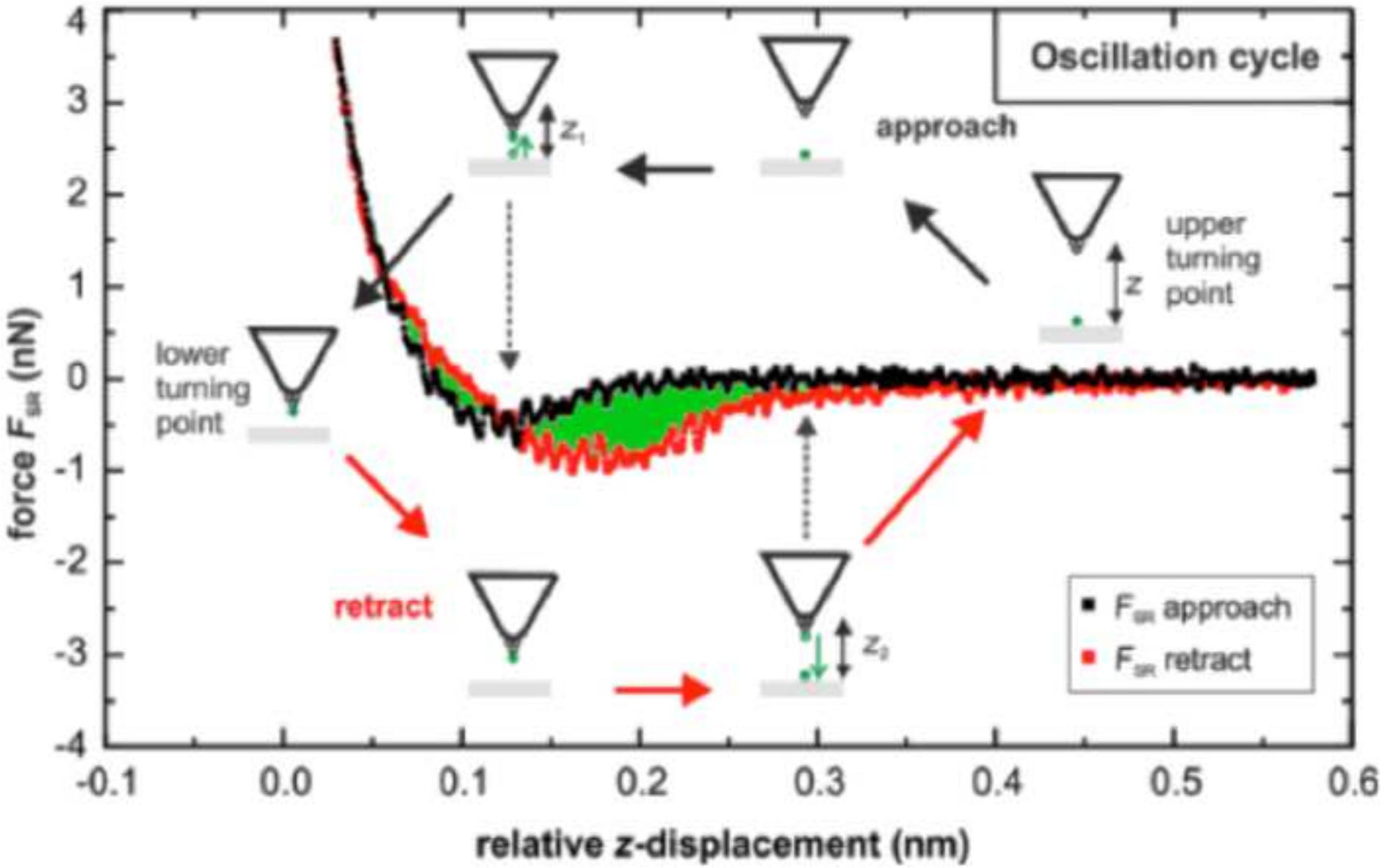

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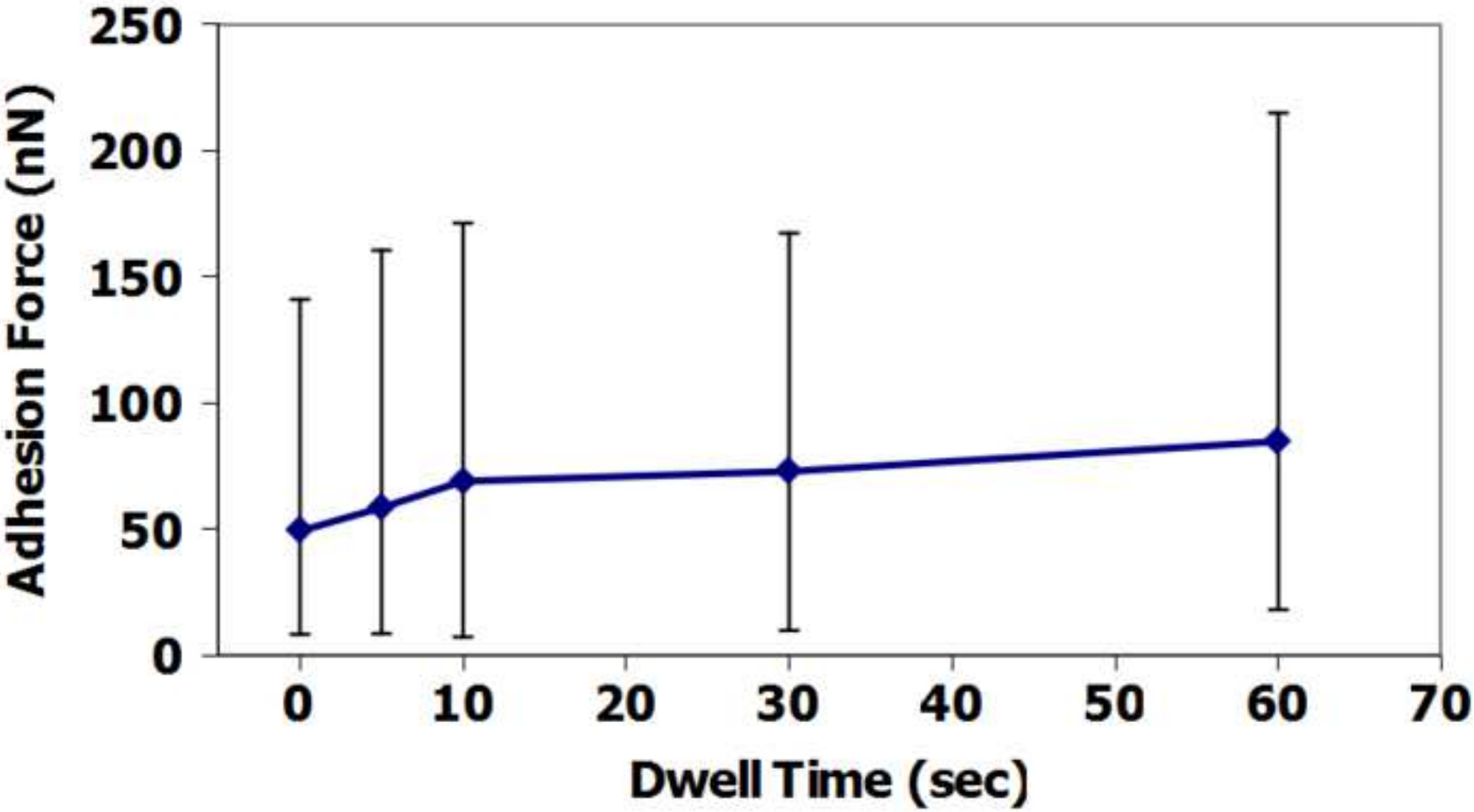

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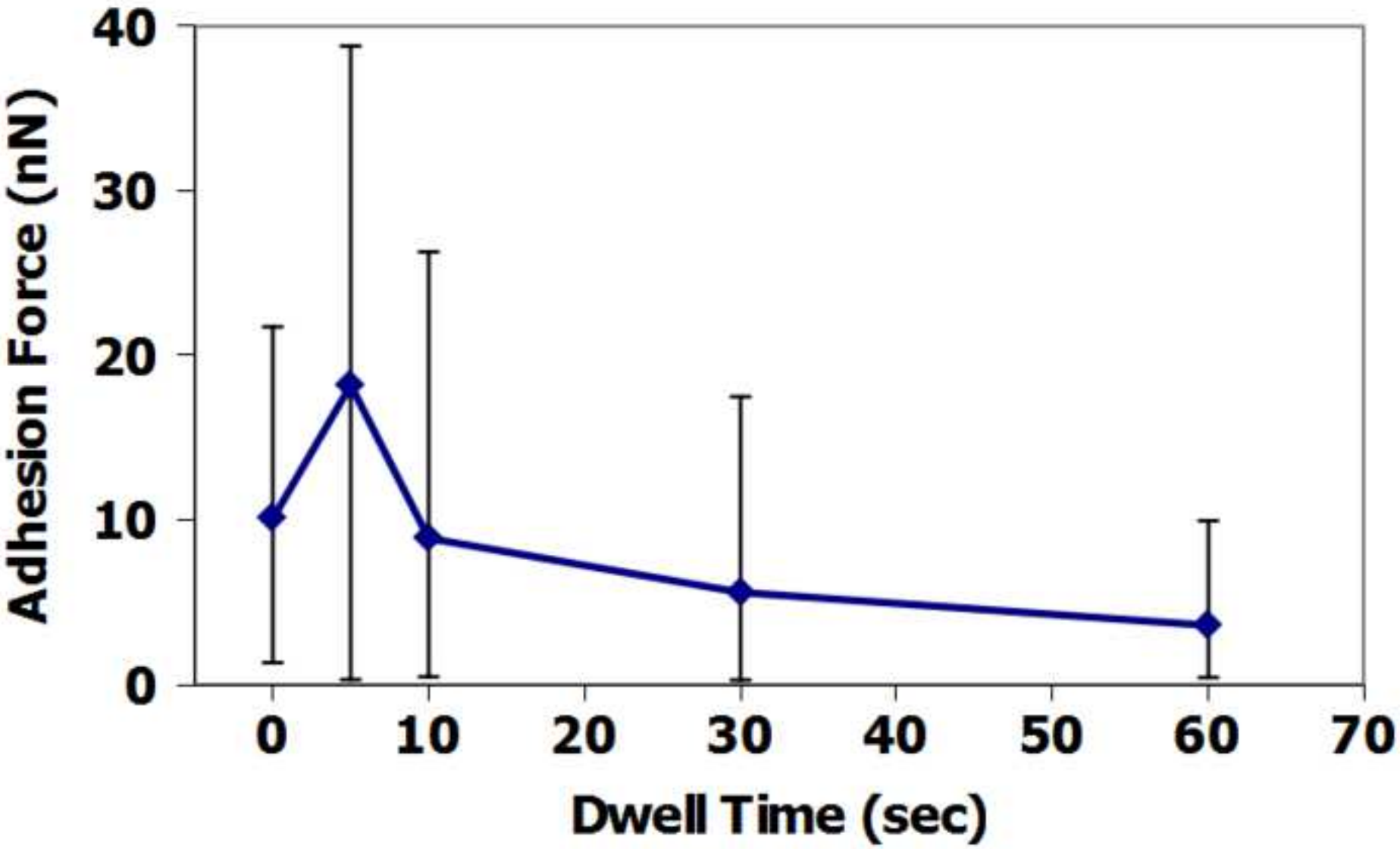

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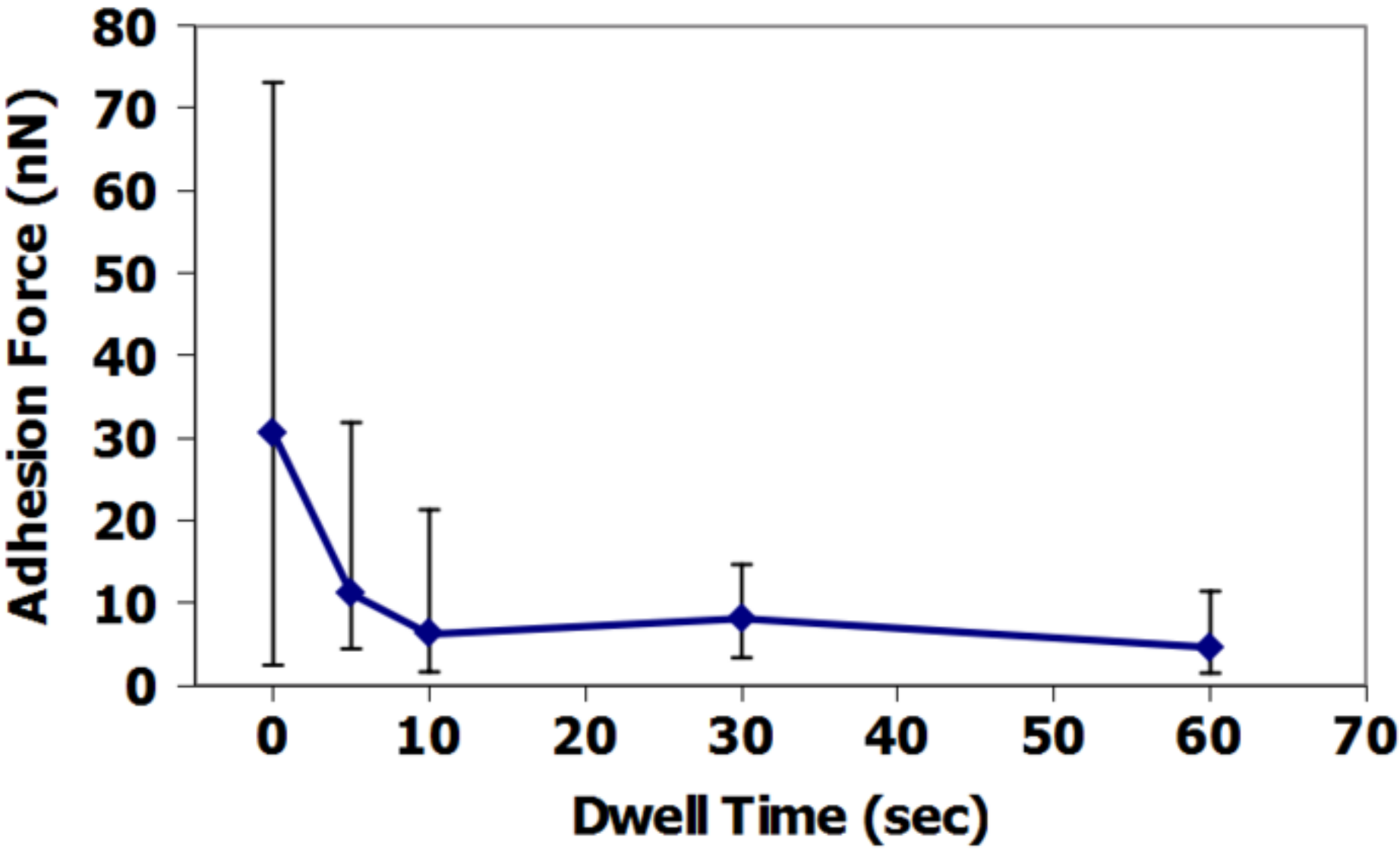

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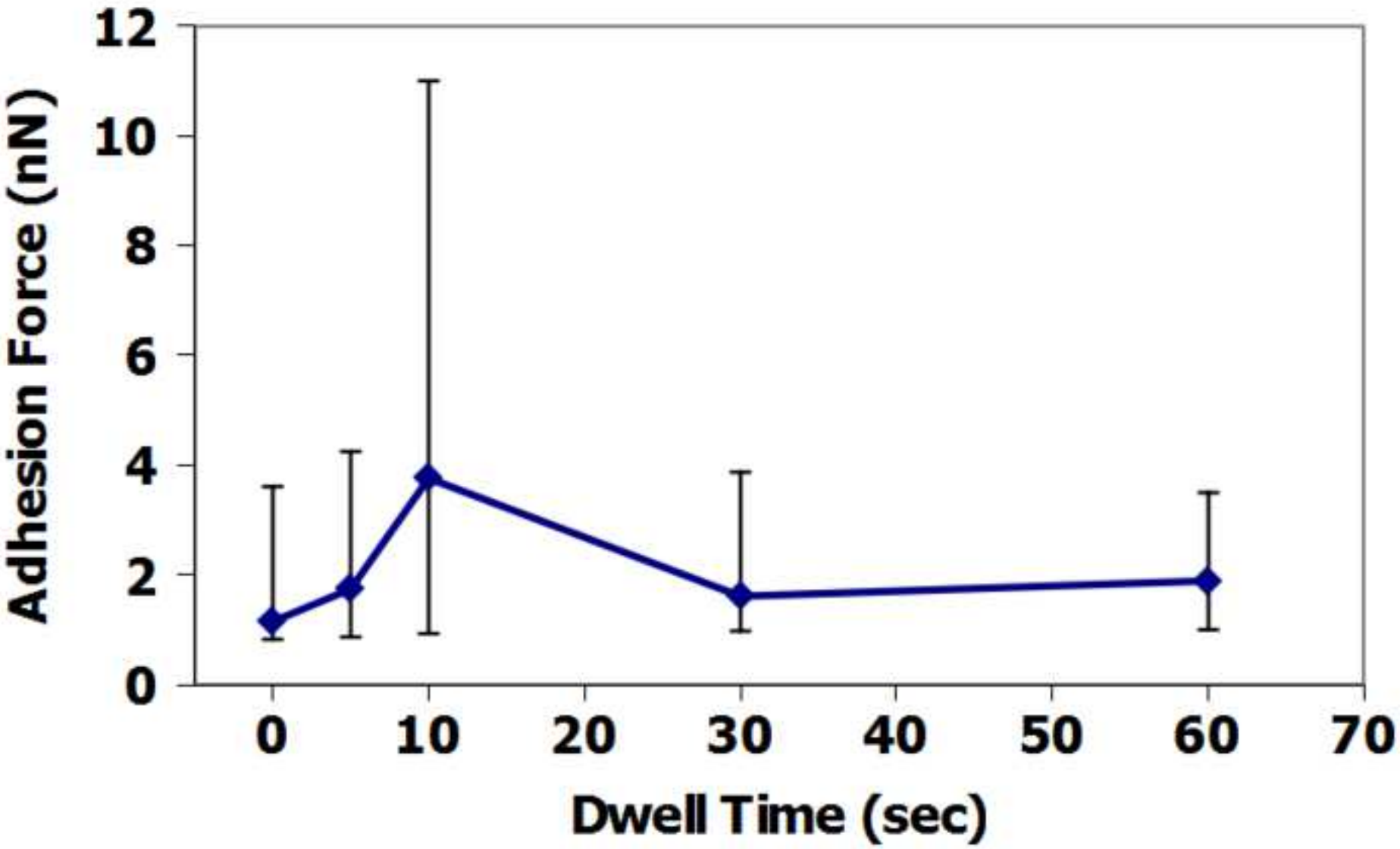

Table

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LWR Materials	Model Materials	New Materials	Geometric Mods
	Au	**Tetragonal ZrO_2**	
	Ag	Monoclinic ZrO_2	**Nucleation sites**
Native Zircaloy-4	**SiO_2**	**ZrN**	**Micropillars**
100nm ZrO_2	**Al_2O_3**	**ZrC**	Hydrophobic coatings
2μm ZrO_2	**MgO**	**ZrB_2**	Hydrophilic coatings
	Diamond-like carbon (DLC)	**Ti-equivalents (TiN, TiC, TiB_2)**	Biphilic coatings
	Graphene	**CeO_2**	

Excel Spreadsheet- Table of Materials/Equipment

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Name of Material/Equipment	Company	Catalog Number	Comments/D
Atomic Force Microscope	Asylum	MFP3D-BIO	
AFM Functionalized Cantilevers	Novascan		1 micron sphe
NiO Nanoparticles	Alfa Aesar		8-20nm avera
Fe3O4 Nanoparticles	Alfa Aesar		20-30mn aver
Silver conductive grease with silicone base	Chemtronics		The higher th
H3BO3	Mallinckrodt		99.945% pure
LiOH	Alfa Aesar		99.995% pure
Heat Flux Sensor (500kW/m2)	Captec Enterprise		1cm x 1cm
PID Temperature Controller	Omega	C9000A	Configured fo
Logomatic V2 Serial Data Logger in Enclosure	Ocean Controls		Acquires 0-3.3

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Changes made by the Science Editor:

1. There have been edits made to the manuscript.

Changes to be made by the Author(s):

1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues. The JoVE editor will not copy-edit your manuscript and any errors in the submitted revision may be present in the published version.

We have read though and fixed any typos, thank you.

2. Please highlight 2.75 pages or less of the Protocol (including headings and spacing) that identifies the essential steps of the protocol for the video, *i.e.,* the steps that should be visualized to tell the most cohesive story of the Protocol. The highlighted steps should form a cohesive narrative with a logical flow from one highlighted step to the next. Remember that non-highlighted Protocol steps will remain in the manuscript, and therefore will still be available to the reader.

Currently, there are just over 3 pages of highlighted protocol text.

We have un-highlighted all sub-steps from Step 1 (material preparation), as this is a much more standard procedure. This brings us down to 2.5 pages of highlighted text, and will make for a more focused, compact video.

3. Additional detail is required in a number of places:
-3.4: Place the insulating cap where?

Clarified, thank you.

-4.2: Spell out the first instance of “PID”

Fixed, thank you.

-Line 480: Spell out SEM/FIB at first instance

These were already spelled out for the first time in lines 159 and 160.

-Figures 8-11: Please include a description of the error bars in the figure legends.

Figure captions for 8-11 were updated to show both the number of averaged data points making up each plotted point, and an explanation of the sizes of the error bars.

4. In the Discussion, what are the critical steps of the procedure?

Clarified on page 14, to say that the calibration of each AFM-FS tip, both in air and in wáter, represent the most critical steps in the procedure. Otherwise the data are meaningless, relative at best.

Reviewers' comments:

Reviewer #1:

Manuscript Summary:

The submitted manuscript entitled to "Experimental Multiscale Methodology Predicting Material Fouling Resistance" deals with the detailed experimental methods to prescreen the CRUD-resistant materials and to characterize the CRUD resistance with multiscale methods. The experimental procedures established by the authors will definitely benefit the readers as all the procedures were performed very rigorously based on accurate information and evidences. The results are expected as reliable as to be used in relevant research area efficiently. Also the manuscript was written very clearly and succinctly and certainly satisfies the journal criterion for the publication. Therefore this reviewer recommends the submitted manuscript for the publication in JoVE. However, to improve the quality of the manuscript this reviewer suggests following comments:

Major Concerns:

(1)Lines 266-270: This is the last process to prepare potentially CRUD-resistant materials and the authors recommended a sputtering technique. The sputtering process may involve variety of operating conditions of vacuum pressure and temperature, which may affect the surface morphology significantly. So it is necessary to address the desirable pressure and temperature range to properly simulate the PWR CRUD morphology.

The sputtering technique used by our outside vendor was in a high vacuum environment, and is not actually set up to recreate conditions and morphology found in PWR CRUD. Rather, we designed this suite of experiments to separate out effects of morphology, surface chemistry, and everything else to study only the effects of surface chemistry on the AFM-FS data. For reference, our vendor was PVD products, and we independently purchased high-purity, 2” diameter sputtering targets for this work. We believe that if down the line, our predictions of CRUD-resistance are different from those observed in larger, more integrated tests, then we will have

to come back and investigate whether film morphology played a role in fouling resistance. However, we won't know until we perform some of the studies in the Future Work section, where we both predict which materials should be CRUD-resistant, and test them in a PWR-equivalent flowing water loop.

(2) Lines 330: Temperature set point of the bath is 97 oC and this reviewer assumes that the pool boiling experiment was conducted under atmospheric pressure. Considering the PWR is operated at 15.5 MPa, a big gap exists between the PWR CRUD formation condition and authors' experimental condition. So please justify that the authors' experimental condition is reasonable for the CRUD formation of the typical PWR.

Admittedly these experiments are not at PWR pressures. The experiment is designed this way in part to simplify the experimental setup and in part because this experiment is meant to help develop a baseline understanding of CRUD growth. Materials that perform well in these tests will be placed in another experimental setup under pressure.

(3) It is curious whether repeatability of the adhesion force data was satisfied. Please explain how the repeatability test was conducted. If not, please also explain how the test results can be accepted.

Repeatability was ensured by averaging between 16 and 36 points for each AFM-FS measurement. We have updated the figures captions for Figures 8-11 to reflect this suggestion by the reviewer, thank you. The force measurements are taken at a fixed spacing grid, so that local morphology effects, if any, are averaged out.

Minor Concerns:
(1) Line 132: please give the specific value for the corrosion rate.

This is a rule of thumb, not a true calculation. An accurate number can be found by taking the ratio of two diffusion coefficients, each with the same value of D_0 and activation energy, but one with a temperature *T* and another with a temperature *T+15K*. We have added the word "roughly" on line 132 to mention that this is not a precise number.

(2) It is recommended to treat Figure 3 as a table. The authors might as well make a list of variety of materials being tested and name it as Table 1.

Good suggestion, thank you. This has been updated. Figure numbers have also been updated accordingly.

(3) Lines 286-289: please give a reference for the simulate PWR water chemistry.

This reference has been added, thank you, on line 294 immediately adjacent to a description of real PWR water conditions.

Reviewer #2:

Manuscript Summary:

This manuscript draws a correlation between macroscale CRUD adhesion on particular materials using faster measurements on the nanoscale with AFM force spectroscpy to measure the adhesion of 2 different materials in air and water.

Major Concerns:

The force curve in figure 7 looks a bit strange. Why does the approach curve overshoot the retract curve at point of contact with the surface and in first part of the repulsive wall?

This curve, by a different study from the literature, illustrates all the possible features in an AFM-FS curve. The overshoot region at the point of contact on the approach curve represents what is known as "pop-in," where longer-range attractive forces, such static electricity, cause the tip to move towards the surface before making contact. Therefore, the force-distance curve registers this as an overshoot, as the tip deflects to contact the surface, while the z-piezo controlling the cantilever back is still registering the tip as above the sample. By the way, this is now Figure 6 due to the figure renumbering.

there is also quite a bit of noise in the adhesion dip, so it is important to explain how that adhesion is being measured.

Yes, thank you. This is done briefly in the introduction and a sentence has been added at line 515.

Due to the very large error bars of the measurement, no conclusions can be drawn with respect to function of dwell time. Finally, although the ZrC does seem to have lower adhesion than the TiO2 in water, that is not conclusive due to again, the large error bars of the measurement. The error bars need to be tighter to reach the conclusions drawn in the paper.

The data represented here are only preliminary. While their error bars are indeed quite large, in this paper we are reporting representative data and trends and trying to explain what we think these trends mean. Extra qualifying words have been added throughout the paper to make sure this is clear.

Minor Concerns:

Why not conduct the force curves also at temperature? Since the macroscale CRUd measurement is being done in heated water, one could do a more appropriate simulation with the AFM.

This is something we also have considered. Unfortunately, the AFM at our disposal does not have this functionality. We have two active proposals out, to build a high-pressure, high-

temperature AFM stage to conduct these measurements at both temperature and pressure. To our knowledge, only one other group has crossed the 100 bar pressure threshold so far, and they did their measurements in high pressure CO_2.

The AFM calibration is described with vendor (Asylum Research) jargon that is not appropriate to a generic audience. Suggest the calibration be stripped of jargon and written in more general terms (i.e. terms like inVOLS, LDX, etc.)

Removed, thank you.

No information is provided on the functionalization of the tip, how robust it was, and how it was confirmed.

All procedures we complete with the tip are described in this paper. Any other procedures were completed by Novascan, the company from which we purchased the tips. We examined the tips by SEM after analysis, to ensure that the particle remained attached to each tip.

How many force curves went into each measurement?
For all data points except those with a dwell time of 60 seconds there are 36 force curves. For data points with dwell times of 60 seconds there are 16 force curves. This information has been added in lines 525 and 526.

Reviewer #3:
Manuscript Summary:
A smart technique for predicting material fouling resistance in energy systems is presented in this paper. The method will be of interest to scientists active in this field and that wish to apply this technique.
The principle of the technique (AFM tip modification for measurement of adhesion force) can be successfully applied to other fields of scientific research.
The paper is clear and well written. The procedure is clearly described.

Major Concerns:
Table in Figure 3 presents a number of different materials investigated during the research. However, it appears that only AFM data related to the adhesion of Fe3O4 tip to TiO2 in Air/Water and Fe3O4 tip to ZrC in Air/Water are presented (Figure 8, 9, 10, 11).
If possible, it would beneficial for the sake of completeness to present data related also to other material combinations.
Eventually, a ranking of material fouling resistance based on the proposed method could be made and possibly compared with results from other methods.

This is indeed the ultimate goal of our research. Here we have presented preliminary and representative results alone because some of the data and images for a complete dataset

analysis have not yet been taken. In addition, the full dataset of AFM-FS measurements, along with a theoretical analysis of the data, will be the subject of a future paper in preparation for submission.

Minor Concerns:
Figure 2 and 3 should be inverted in the text (lines 152 and 163).
Moreover, the rest of Figure references appear on a not-ordered sequence (e.g. Figure 12, line 328, and Figure 13, line 333, appear before reference to Figure 4 at line 482).
Order of references to Figure should be corrected for the sake of clarity in the final version of the paper.

Figures have been reordered, so that they appear in order in the paper.

Image quality of Figure 3 and 4 should be improved for the sake of clarity.
Please avoid red text on a black background (see Figure 1) as well as black text on a red background (see Figure 3).

Thank you for these suggestions. We have re-implemented Figure 3 as a Table in text, removing the blurriness altogether. Figures have been renumbered accordingly throughout the text. We have also changed the red scale bars to white ones in Figure 1.

Additional Comments to Authors:
N/A