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Assessment of Modelling Methodologies in Predicting Creep-Fatigue Damage of Alloy 617

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A number of Very-High-Temperature Reactors (VHTRs) have operated routinely with reactor outlet temperatures of 700-850°C but only two VHTRs operated at 950°C – this is effectively a limit using present structural alloys. All modern VHTR designs feature passive decay heat removal capability to produce inherent safety. The initial focus in Generation IV International Forum (GIF) VHTR R&D was to develop a reactor capable of hydrogen production using the thermochemical iodine-sulphur cycle, requiring reactor outlet temperature of about 1000°C. However, driven partially by recent market research showing that there is a significant demand for 'clean' process heat, mostly in the form of steam < 600°C (which today is almost entirely fossil-fuelled) most current commercial designs are predominantly Small Modular Reactors (SMRs) and have reactor outlet temperatures of 750-850°C.

The Ni-based alloys, 800H and 617, have been identified as suitable for VHTR heat exchanger and steam generator applications and both are being studied within GIF. The most significant outcome of this work was the development and submission of an ASME Code Case for the use of Alloy 617 as a new construction material for high temperature nuclear components at temperatures up to 950°C for 100,000 h. Design and construct codes rules, such as those embodied in ASME are typically conservative, particularly when creep-fatigue is considered. Thus, it is important to develop, validate and test models capable of accurately predicting creep and creep-fatigue damage in VHTR system materials that can be utilised to support the operational sustainment of VHTR plant throughout its life. This paper assesses present predictive models of creep and creep-fatigue damage of alloy 617 using data obtained through collaborative GIF R&D.

Traditional, conservative, methods for prediction of the cumulative damage under creep-fatigue conditions are based on the time-fraction (TF), and the ductility-exhaustion (DE) approaches. Stress modified ductility exhaustion (SMDE) and strain energy density (SED) methods are novel creep damage models, which have been shown to give more accurate predictions. The SMDE approach is of note as it has recently been included in the UK fitness for purpose code, R5 as an alternative to DE for stainless steel. SMDE is an extension of the original R5 DE method, is based on consideration of cavity growth mechanisms, where both stress and ductility are considered. SED is also a modification of the original DE model. However, rather than using the strain-to-failure, the strain energy-to-failure is used. SED uses an empirical expression that assumes that the creep damage is directly proportional to absorbed internal energy density in a creep rupture test. Fatigue damage is evaluated separately from creep and linear summation of creep and fatigue damage is used to predict creep-fatigue life. Contrary to this traditional approach of evaluating creep and fatigue damage separately before combining it into creep-fatigue damage, the so-called ϕ (phi) method predicts creep-fatigue damage using a single creep-fatigue term, which directly quantifies the combined creep-fatigue damage.

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Characterisation of Na⁺ dynamics in cation stabilised γ -Na₃PO₄

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Solid-state ionic conductors have been increasingly looked towards as an alternative to liquid electrolytes in energy applications including sodium-ion batteries. Whilst much progress has been made in the design and development of promising candidate materials, complex structures and difficulties in probing dynamics beyond the bulk picture has meant that understanding the mechanism(s) involved in Na⁺ diffusion in these materials remains a challenge. Quasi-elastic neutron spectroscopy (QENS) is one avenue which provides an opportunity to gain insight into these mechanisms at an atomic level.

This work focuses on characterising sodium self-diffusion mechanisms using QENS in cation stabilised γ -Na₃PO₄. From a dynamics perspective, γ -Na₃PO₄ is of interest since its structure features multiple inequivalent sodium sites, forming non-Bravais sublattices.[1] Since it cannot be known *a priori* which site(s) are involved in the diffusion mechanism, the model of the dynamic scattering function from the construction of a jump matrix has been used.[2,3]

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Corrosion at the Glass-HIP Canister Interface in Nuclear Waste Immobilisation

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Nuclear Wastes created from fission reactions such as the production of Molybdenum-99 can be immobilized in borosilicate glasses and disposed in geological repositories. These materials are known to corrode in water over thousands of years and as such immense effort has been made to study the mechanisms of glass dissolution and corrosion in order to understand and predict the fate of the radionuclides. ANSTO has been developing hot isostatic pressing (HIP) as a method for consolidating nuclear waste into an appropriately designed wasteform as it has several benefits over other technologies. However, it is unknown how the temperature and the pressure of the hot isostatic pressing process may affect the corrosion of the glass, particularly at the interface of the glass and the specially designed stainless-steel container that contains the glass during the HIP process and subsequent disposal system.

This Honours project, a collaboration between ANSTO and UNSW, will investigate the corrosion and stability of the glass-metal interface of three nuclear waste glasses when subjected to HIPing. The first candidate is International Simple Glass (ISG) because of its recent use worldwide as a benchmark for glass corrosion experiments. The other two glasses are the UK Mixture Windscale Glass (MW), and French R7T7 Glass (otherwise known as SON68). Both are used internationally but show varying corrosion kinetics with MW showing corrosion at a rate 10 times higher than R7T7.

The glass frits were prepared by mixing, drying, and calcining of the appropriate precursor powders, and subsequently formed into simulant wasteforms by both melting in a furnace and HIPing.

They were characterized using scanning electron microscopy (SEM) to determine the microstructural characteristics and homogeneity and by energy dispersive spectroscopy (EDS) to determine their elemental distribution. Corrosion experiments will be performed on sections of the HIPed samples in water over the time periods of 7, 28 and 90 days, using a temperature of 90°C to accelerate the corrosion. Once they have corroded, they can be examined and compared with uncorroded control samples to determine the effect of the corrosion at the HIP canister-wasteform interaction zone. The surface will be characterized using SEM/EDS and X-ray photoelectron spectroscopy (XPS). The interfacial regions will be sectioned and then polished and then milled into a thinner section using focused ion beam (FIB) milling for transmission electron microscopy (TEM). Nuclear magnetic resonance (NMR) spectroscopy will also be used to determine structural changes in the glass particularly in terms of Si species. The combined results will provide valuable data for the safety case for disposing nuclear waste glass in HIPed canisters underground for thousands of years.

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Disorder by Design: Energy, Pyrochlores, and the Art of 'Stuffing'

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In accordance with the Paris Climate Agreement, Australia will reduce its carbon emissions to 28% of its 2005 levels by 2030, with 24% of Australia's electricity production to come from renewable sources. Two technologies being developed in Australia to assist with this transformation include next-generation oxygen ion conductors and long-term storage for radioactive waste. The former is an attractive candidate, as it does not generate carbon dioxide in hydrogen gas fuel cells, and the latter is particularly important in closing the nuclear fuel cycle as Australia is a major exporter of uranium. However, significant technical issues have arisen in the development of these technologies, such as their lack of efficiency and short equipment lifespans.

Pyrochlores of the structure $A_2B_2O_7$ have found immense applications in each of the above areas: oxygen ion conductors and for radioactive waste storage. However, this appears to be an apparent contradiction in requirements, with one requiring flexibility and movement in its anionic sublattice and the latter needing a robust lattice from which ions cannot escape. It is believed that the oxygen vacancies present in the pyrochlore structure allows for short-range disorder, whilst keeping the long-range order consistent.

In this work, we are concerned with looking at the oxygen-vacancy disorder, and 'tailoring' it to improve the applications of pyrochlores. We have done this by looking at 'stuffed' pyrochlores of the form $A_2(A_{0.67-x}B_{1.33+x})O_{6.67+x/2}$. Increasing the amount of the larger A-type cation that normally occupies the eight-coordinate sites results in some of this occupying the six-coordinate B-site, in a process known as stuffing. It is envisaged that this increase in disorder in the cation sublattice will allow the possibility of engineering these for specific applications.

The presentation will focus on two parts: the synthesis and characterisation of the stuffed pyrochlores, and their physical applications.

Two series of eleven stuffed pyrochlores, namely $Yb_2(Yb_{0.67-x}Ti_{1.33+x})O_{6.67+x/2}$ and $Tm_2(Tm_{0.67-x}Ti_{1.33+x})O_{6.67+x/2}$ with $x = 0-0.67$ have been synthesised using conventional solid state methods and their structure characterised by Rietveld Refinement of conventional X-ray diffraction. The local short-range order has been characterised by Raman and infra-red spectroscopy.

Over the coming months, further characterisation will be undertaken using soft x-rays and x-ray powder diffraction at the Australian Synchrotron. It is also planned to determine the displacement

of oxygen ions using the ECHIDNA Diffractometer at ANSTO. Since synthesising the two series of stuffed pyrochlores, various measurements have also been undertaken regarding their photocatalytic, associated band gaps and magnetic properties, showing promising results.

These results will be presented, along with a judgement as to whether inducing certain types of disorder within the pyrochlore structure can lead to them being purposely-built for their applications.

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Dye Anchoring in Dye-sensitized Solar Cells

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Dye-sensitized solar cells (DSCs) are photovoltaic devices that are manufactured from low cost and tuneable materials. The organic components and thin film technologies allow flexible, coloured and transparent DSCs with good efficiency in ambient conditions, making them candidates for solar-powered windows, wearable devices and powering the "Internet of Things". At the interface between the dye molecules and the titanium dioxide (TiO₂) semiconductor, the adsorbed dye molecules harvest energy from light and enters an excited state. The photoelectron is injected into the TiO₂ conduction band, where the electrical circuit begins. The dye – TiO₂ interface is vital to the efficiency and performance of DSCs, but their structure is poorly understood. This study investigates dye adsorption and packing arrangements at the TiO₂ interface using X-ray reflectometry (XRR) and atomic force microscopy (AFM) instruments at ANSTO for a range of organic dye structures. The dyes bind to the TiO₂ surface via carboxylic acid and nitrile groups in a monolayer, and bulky, hydrophobic groups point away from the surface to form a protective barrier. By minimising gaps in the monolayer, the TiO₂ surface is less susceptible to electron recombination to the electrolyte solution in DSCs and the device efficiency can be improved.

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Examining the effects of surfactants on the structural and mechanical properties of a thermoresponsive polymer brush

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Layers of densely tethered polymers (polymer brushes) are of interest due to their unique lubricating, antifouling, and/or biocompatible properties, which stem from their diffuse 'brushy' conformation. When these brushes are constructed from stimuli-responsive polymers, their properties can be modulated via a stimulus-induced conformational change, allowing for control of interfacial properties. The brush architecture also affords insight into general polymer behaviour due to the range of powerful techniques that can be used to study planar thin films.

Here the interactions between a range of surfactants and a poly(N-isopropylacrylamide) (PNIPAM) brush layer are explored. Using a combination of ellipsometry, Neutron Reflectometry (NR) and quartz crystal microbalance techniques the structure of the layer and the location of the surfactant within the interface are quantified. By subjecting the brush to a confining force and measuring its conformation with NR the mechanical implications of the presence of surfactant are determined. As part of this work, new modelling techniques for the analysis of NR data from diffuse interfaces were developed.

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Figure 1. *Left:* PNIPAM volume fraction profiles at 40°C as determined by NR, showing SDS swelling the brush and suppressing its thermoresponse. *Centre:* Anionic surfactants (blue) bind to PNIPAM, charging the brush layer, cationic surfactants (red) do not. *Right:* Charge modifies the mechanical properties of the layer.

A rich surfactant-specific behaviour is observed and found to be headgroup dependent, consistent with prior work on other PNIPAM architectures. Those surfactant species that do interact are found to swell the brush layer, even at concentrations well below the CMC, as micelles decorate the ordinarily neutral PNIPAM with charges. These charges are also found to modify the mechanical properties of the brush, assisting it in resisting confinement. Specific surfactants were found to control brush properties at low concentration (<0.1 wt%); as such this system is a promising multi-responsive interface.

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Fabricating dense semiconductor nanowire coatings with helium plasma

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Materials engineering at the nano-scale is a promising area of research as it holds the potential to simultaneously enhance material performance while reducing the amount of material required. Recently, we have demonstrated a new technology that enables dense nanowire coatings to be developed on silicon and germanium that may have broad technological applications such as low-reflectivity surfaces for solar panels and high-density anodes for lithium-ion batteries. This process is made possible by the peculiar way in which helium interacts with materials it is implanted into. Being a noble gas helium is insoluble in most materials so has a strong tendency to associate with vacancy-type defect sites and precipitate into bubbles once a critical helium cluster size is reached. Under high-flux helium plasma the helium-material system exists in an extreme non-equilibrium state which can produce significant morphological changes, including the production of bubbles, surface pits, and nanowires. The exact features that form are very sensitive to the sample temperature and plasma conditions. The process was first observed by nuclear fusion researchers investigating the influence of plasma exposure on tungsten tokamak wall tiles.

Here, we discuss our recently work in applying this technology to semiconductor systems and how this technology could provide a feasible pathway for scalable, low-cost fabrication of nanostructured surfaces. We propose a model where nanowire growth occurs due to helium-enhanced Frenkel-pair formation, and the subsequent suppression of recombination due to helium atoms binding to

vacancy-type defects. Surface changes then occur progressively due to differences in the behaviour of vacancies and self-interstitial-type defects, and in particular the way surface adatoms interact with surface morphology.

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Factors contributing to the iso-elemental fingerprinting of Giant tiger prawns (*Penaeus monodon*).

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Demand for seafood has steadily increased as demonstrated by the growth in aquaculture production. By contrast, wild fisheries (i.e. wild-caught) production has plateaued. However, wild-caught and farmed seafood products are often sold alongside each other. Allowing for the substitution of higher value seafood products with those of lesser quality and value to occur. There are also reported cases involving human health risks associated with pathogens and banned substances present in fraudulently-marketed imported seafood. Accurate and reliable methods of seafood provenance are necessary to protect human health, improve biosecurity and maintain consumer confidence in seafood. Several methods are currently used for seafood provenance; however, there are drawbacks associated with some of these methods. A pilot study was conducted to scope the utility of isotopic and nuclear techniques to determine seafood provenance. Stable isotope analysis (SIA) and x-ray fluorescence (XRF) through Itrax were used to determine the isotopic and elemental fingerprint of giant tiger prawns (*Penaeus monodon*), a species that is traded globally. These fingerprints were then used to create a seafood provenance model based on multiple statistical methods. The pilot study showed that these methods could determine the provenance of seafood with over 80% accuracy. To further improve the accuracy of the models, the factors causing the isotopic and elemental variability, in the seafood products, need to be understood. Quantifying these factors will help develop more robust and reliable models. The current seafood provenance model development research examined the role of feed, water and sediment to the overall isotopic and elemental fingerprint of *P. monodon*. Replicate feed, water, sediment and *P. monodon* samples (n=9) were collected from nine different ponds in four farms around Queensland and New South Wales, Australia. These samples were then processed and analysed using SIA and XRF through Itrax to determine the isotopic and elemental composition of each individual sample. The results were then analysed using mixing models to quantify the isotopic and elemental flow from different feed and environmental components to the prawns. The analysis found that the feed and water are the major factors controlling the isotopic and elemental composition of *P. monodon*. Findings of these analyses will contribute to developing a scientifically robust and accurate model that can determine the provenance of seafood. This will allow for regulatory bodies to bolster consumer confidence, protect human health and allow for quarantining of seafood that could threaten local biodiversity and fisheries and aquaculture industries.

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Fundamental Studies of Sulfuric Acid Baking of Rare Earth Ores

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Rare earth elements are used in a myriad of technological applications that underpin modern civilisation. These applications span industry, defence and private sectors, creating a strong dependence in developed nations on a consistent supply of this group of 16 elements. In the last decade, the supply risks associated with a Chinese domination of the global market has driven strong interest in developing commercially viable extraction processes for other rare earth deposits around the world. Processes for extraction of rare earth elements from rare earth ores are typically complex due to low concentrations of rare earths, the presence of radioactivity in the ore and the large number of co-occurring rare earth elements which must be separated before use. Processing can be broken down into three main stages: (a) physical separation of gangue (unwanted) minerals to produce a rare earth mineral concentrate, (b) chemical decomposition of the rare earth mineral and (c) purification and separation of individual rare earths to produce saleable products.

The major industrial process for the chemical decomposition step, used by both China and Australia, is the sulfuric acid bake. This simply involves mixing the mineral concentrate with concentrated sulfuric acid and heating to over 200°C. The rare earths are converted into soluble sulfates and are dissolved in a subsequent water leach to produce a rare earth containing solution ready for further purification. Although the sulfuric acid bake process is well established in industry, a fundamental understanding of the chemistry involved is severely lacking. Improving this understanding could have great value in assisting development of economic extraction processes for new rare earth deposits.

In this study, the effects of variables such as ore composition and bake temperature on reaction processes was examined using XRD, SEM-EDS and FT-IR. The impact of reaction processes on extractions of rare earths and impurities was also explored. The effect of ore composition was studied by addition of specific common gangue minerals to a rare earth mineral concentrate.

In the absence of gangue minerals it was found that rare earth and impurity extractions were high for bake temperatures of <300°C. For bake temperatures >300°C the extraction of impurities decreased sharply, while the extraction of rare earths decreased slightly. The decreased extractions were found to be due to formation of insoluble phosphate phases, which partially incorporated rare earths.

Addition of apatite, a calcium phosphate, exacerbated this effect by acting as a source of additional phosphate, and led to large decreases in rare earth extraction for bake temperatures of >300°C. Addition of iron oxide minerals had the opposite effect, acting to increase rare earth extractions. The mechanism was through incorporation of iron into the insoluble phosphate phase in preference to the rare earths, thereby allowing the rare earths to remain as soluble sulfates.

These results highlight the strong effects of ore composition and bake temperature in determining rare earth and impurity extractability and are key to understanding and improving extraction processes for rare earth ores.

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How stable isotopes reveal energy flow and trophic connections of size-structured ocean habitats. Implications for fisheries management and ecosystem monitoring.

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Open ocean fisheries depend on vast and diverse assemblages of pelagic crustaceans, molluscs, squid, and midwater fish (known as micronekton). These assemblages form complex, size-structured food web interactions that dictate the availability and flow of energy throughout the ecosystem. As ecosystems vary from one another in terms of community structure and biodiversity, the flow of energy through a food web also changes, creating quantifiable metrics that can describe the ocean habitats. The East Australian Current (EAC) produces two types of ocean habitats in the form of gyres, or eddies. Cyclonic eddies have a strong upwelling current which promotes higher productivity and creates a more favourable habitat for micronekton than the surrounding waters. Anticyclonic eddies are characterised by a downwelling force and therefore tend to have lower production.

We sampled four ocean eddies off the coast of eastern Australia from the Research Vessel Investigator in September 2017. Fish, zooplankton and other micronekton were sampled from the top 100 m of the eddies using trawl and plankton nets. The catch was sorted into size classes and broad morphological groups representing all trophic levels from producers to predators. 256 samples, consisting of individuals from each size class and group, were selected for stable isotope analysis to model food chain length and trophic interactions in these size-structured eddy habitats.

The stable carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) isotopes identified relationships between body size and trophic level of species. Predator-Prey mass ratio (PPMR), Food Chain Length (FCL) and energy transfer efficiency varied within each of the eddies, with more productive habitats within the cyclonic eddies showing a much larger PPMR and shorter FCL compared to anticyclonic eddies.

The application of stable isotopes to quantify food web metrics is beneficial for the estimation of fish populations throughout the food web by identifying the extent of productivity within ocean habitats. Traditional methods of managing fisheries are often based on the population and growth of individual target species, but by understanding the flow of energy through the whole habitat we can interpret satellite-derived data and more effectively and manage Australia's \$3.1 billion fisheries from a perspective that considers the ecosystem as a whole.

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Investigating Carbon Molecules with Pressure-Volume-Temperature Equations of State

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We are interested in intermolecular interactions which determine thermodynamic stability in crystalline solids and their response to changes in the external conditions.

In no area is this information of more importance than in planetary materials science, where scientists are trying to understand the fate of carbon in the context of the origin of life and/or the varied planetary surfaces observed. Molecules of high astrobiological and astrophysical relevance, such as amino acids (1), polyaromatic hydrocarbons, and N-heterocycles (2), have been identified across the Universe but how they behave under such varying conditions is a question yet to be answered.

Key to our approach is the determination of the internal-energy, entropy and the Gibbs free energy - not only computationally but also, and for the first time, experimentally. We have developed a new method that transforms variable-pressure (P)-temperature (T) crystallographic data into thermodynamic information. Equations of State (EoSs) are the models of choice to fit these data, describing how pressure, temperature, and volume (V) are inter related in solid phases. Although it is quite common to model thermal expansion at ambient pressure with a VT equation of state (EoS), and compression at ambient temperature using a PV-EoS, determinations of PVT-EoSs are much less common, particularly for molecular materials (3). The paucity of PVT-EoSs reflects the difficulty in varying pressure and temperature simultaneously in crystallographic experiments, especially at reduced temperatures. These difficulties are addressed by the variable temperature insert for the Paris-Edinburgh press available on the PEARL instrument at the ISIS Neutron Spallation Source (4) and by the cryofurnace for the Merrill-Bassett cell available on the KOALA instrument at the ANSTO OPAL reactor (5). The results can then be combined with Periodic DFT and other semi-empirical calculations, where pressure and temperature can be included at little time cost, enabling the stability profile of a material to be understood, right down to the level of individual intermolecular interactions.

Many classes of structure-directing intermolecular interactions involve hydrogen atoms: hydrogen bonds are an obvious example, but hydrogens can also be involved in dispersion and electrostatic interactions. The responses of different kind of crystalline organics containing these interactions, such as hexamethylenetetramine, naphthalene, histidine, and alanine are to be studied using powder and single-crystal neutron diffraction up to 5 GPa and between 105-480 K. We are specifically using neutron diffraction for the experiments because of its sensitivity to locate hydrogen atoms. Additionally, the penetrating nature of neutron radiation means that complete, high-quality data can be obtained for samples in elaborate extreme-conditions environments.

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Investigating the effects of helium plasma on tungsten recrystallisation under fusion-relevant conditions

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Society is now at a critical point for action on climate change and energy security as the global demand for energy, and the associated greenhouse gas emissions, continue to rise. Nuclear fusion is a promising energy source with real potential to provide a safe, reliable and virtually inexhaustible base load supply without producing long-lived radioactive waste. The ITER experimental fusion reactor, due to begin operating in 2026, has the goal of demonstrating the feasibility of fusion power. However, many materials challenges must be addressed before this becomes a reality.

Our study focuses on materials used the divertor region of the reactor, which serves to remove waste and impurities generated from the core of the fusion reaction above. For the ITER reactor, the divertor will be made of tungsten, which is expected to withstand temperatures up to 1500 K and huge fluxes ($> 10^{23} \text{ m}^{-2} \text{ s}^{-1}$) of low energy ions, such as helium, originating from the core plasma of the fusion reaction.

Under the expected heat flux, the tungsten material will undergo recrystallisation – a process where the deformed and strained grains of the material are replaced by new defect-free, and typically larger, grains. This presents critical problems for the ITER operation as recrystallisation leads to a modification of material properties, including reductions in hardness, strength and resistance to crack formation from thermal shocks. In addition to the heat flux, the divertor will also experience helium plasma exposure, which has been found to induce the formation of helium nano-bubbles, on the order of nanometers in diameter, underneath the surface of tungsten.

A detailed understanding of the recrystallisation kinetics of tungsten under fusion-relevant conditions is essential for the operations of the ITER reactor. Until now, no comprehensive study existed on the synergistic effects of helium plasma exposure and heat on the recrystallisation of tungsten.

Our study was conducted using the MAGPIE linear plasma device, which is able to simulate the particle bombardment conditions expected in the ITER divertor. We have developed unique capabilities at the ANU to study the distribution of helium nano-bubbles in tungsten with grazing-incidence small-angle X-ray scattering using facilities at the Australian Synchrotron. Extensive microscopy

studies were conducted to identify changes in tungsten surface morphology and to quantify the extent of recrystallisation.

The results of the study were the first to establish a definitive link between the presence of sub-surface nano-bubbles following plasma exposure and the retardation of recrystallisation in tungsten. We discuss the effects of plasma exposure conditions on the size distribution of nano-bubbles in tungsten. This strongly influences the kinetics of recrystallisation at different temperatures and the mechanical properties of the tungsten. These findings are crucial to understanding and achieving safe and efficient reactor operation, which brings us one step closer to the future powered by nuclear fusion.

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Metal pollution during pulse stormwater events: bioaccumulation kinetics of cadmium and zinc in a freshwater decapod crustacean

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Stormwater runoff has been identified as a major source of metal pollutants in urban waterways, where organisms that access these environments tend to be exposed to multiple pulses, rather than a constant exposure, of contaminants. Current water quality guidelines (WQGs) are generally derived using data from continuous exposure toxicity tests, where the assumption is that chronic exposures provide a meaningful way of assessing metal bioaccumulation kinetics and effects in an organism. In this study the radioisotopes ¹⁰⁹Cd and ⁶⁵Zn were used to explore the uptake, depuration and organ distribution of a non-essential and essential metal in a decapod crustacean over the course of three short-term (< 10 hours) pulse exposures followed by a 7-day depuration. The freshwater shrimp (*Paratya australiensis*) was exposed to radiolabelled cadmium only, zinc only and a mixture of cadmium and zinc at environmentally relevant stormwater concentrations. Whole-body metal concentrations were determined by daily live-animal gamma-spectrometry. Anatomical distribution of the radioisotopes was visualised using autoradiography at multiple time points throughout the depuration period. Metal uptake and efflux rates were similar in the individual and mixed-metal exposures, where both metals accumulated to a greater extent when presented individually. Interestingly, the rate of cadmium uptake in the whole-body of the organism over the course of the three 'pulses' decreased with each successive pulse. The rate of zinc uptake remained linear over the course of the three pulsed exposures. The efflux rate for cadmium regardless of exposure treatment (single or multi-metal) was close to zero. Zinc concentrations decreased in the whole-body of the organism over the course of the depuration period, with the efflux rate being greater for zinc exposed individually. Autoradiography indicated the presence of both metals in the gills and hepatopancreas of the animals regardless of depuration time. This study reveals how cadmium bioaccumulation kinetics may differ between repeated 'pulse' exposures where, unlike zinc, the rate of uptake decreases with each successive pulse. This demonstrates how repeated exposures, rather than a constant exposure, can influence the bioaccumulation kinetics of metals, highlighting the important consideration for incorporating pulsed toxicity tests in frameworks when deriving WQG values.

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Molten Salt Corrosion (FLiNaK) and Mechanical Behaviour of Ni-Mo-Cr Alloy (GH3535) Weldments for Application in Energy-Generation and Energy-Storage Systems

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The threatening presence of climate change has stimulated investment in development of low-emission energy-generation systems utilising both nuclear and renewable energy sources. Molten salts (fluorides, chlorides, etc.) are being extensively explored as heat transfer media for application in these next-generation systems due thermo-physical properties superior to those for traditional heat transfer fluids – leading to significant improvements in safety and efficiency. Reignited interest in Molten Salt Reactor (MSR) technology—a Generation IV reactor system—has led to considerable advances, with commercial deployment the goal. A major obstacle, however, hampering deployment of MSR technology, is development and standardisation of suitable structural materials required to withstand highly corrosive molten fluoride salts. Further, given the importance of welding in fabrication of these systems, an understanding of the corrosion performance of welded joints, is crucial. The present study focuses on corrosion behaviour of Ni-Mo-Cr alloy (GH3535), and its weld (matching filler metal), in FLiNaK molten salt.

Corrosion testing was performed in FLiNaK salt at 750 °C for 500 h, whereby four isolated weld-metal and four isolated parent-metal specimens were extracted from a custom-built GH3535 multi-pass weldment and collectively immersed. Present results indicate that, on average, GH3535 weld-metal is less affected by exposure to FLiNaK salt than GH3535 parent-metal (i.e. parent metal loses more mass, per unit surface area). Material mass loss was primarily driven by the presence of trace impurities in the salt (e.g. SO_4^{2-} , H_2O), promoting thermodynamically driven redistribution of individual alloying elements at corrosion-affected surfaces. EDS analysis showed weld and parent metal to be depleted of Cr, Mn, Si and Mo, while enriched in Fe and Ni. Given the identical composition of weld and parent metal, the observed difference in mass loss is attributed to disparate microstructures – weld metal is characterised by large, elongated grains, while parent metal features much smaller, equiaxed grains. It is shown that the extent of molten salt corrosion is predominantly dictated by the presence of high-angle grain boundaries, with intergranular corrosion dominant. That is, enhanced corrosion of parent-metal GH3535 is a result of its greater grain-boundary density.

Morphology and distribution of Mo-rich (M_6C) carbides differed significantly for both regions, with parent metal characterised by larger, more uniform M_6C carbides, as opposed to the finely dispersed M_6C carbides common to welded regions. It is suggested that these carbides play a secondary role in corrosion behaviour, whereby their cathodic nature promotes depletion of surrounding (anodic) alloy matrix, via galvanic corrosion. This led to noticeable pitting on parent metal surfaces—largely absent from post-corrosion weld metal—contributing to increased mass loss.

Further, mechanical testing (tensile, small punch and hardness testing) suggested a weld region of greater yield and tensile strength. It is concluded that finely dispersed M_6C carbides in weld metal promote dispersion strengthening, while the much larger M_6C carbides in parent metal undergo brittle fracture, limiting alloy strength. A weld region of greater strength and superior corrosion resistance, compared to its parent material, would suggest GH3535 weldments to be suitable for design of molten-salt-based energy-generation and energy-storage systems.

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Recovery of ion irradiation damage during annealing in nuclear graphite

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The project concerns recovery of ion irradiation damage in nuclear graphite during annealing. Nuclear graphite is employed as a moderator material in generation IV nuclear reactors such as Molten

Salt reactors, to slow fast neutrons and sustain the fissile chain reaction. Ion irradiation produces a similar cascade damage effect to neutron irradiation and is more convenient to control for experimentation.

Interstitials and vacancies in crystalline graphite cause anisotropic microstructural distortions which cause shrinkage and expansion as well as electrical property changes. Annealing at high temperatures has been shown to recover these changes to some extent and is used to manage the release of potentially destructive Wigner energy in current reactor operation. The research of this project endeavours to improve the understanding of the recovery process in PCIB nuclear graphite, which is a candidate material for current generation reactor designs. With greater understanding of the recovery process and improved estimation of damage, moderator and hence reactor operational lifetime may be extended.

Raman, TEM and XRD techniques were used to characterise samples that had been irradiated with Carbon ions accelerated at 35MeV at a fluence of 4.50×10^{17} ions/cm². Using SRIM to predict the damage profile allowed the correlation of crystallite size to dpa reflecting the highly concentrated maximum damage at 30dpa at approximately 40 μ m from the irradiated surface. TEM images showed the arrangement of binder matrix and rosette-shaped filler particles with pores at a range of scales from the microscopic to nano-scale Mrozowski cracks between basal planes. Qualitative evidence of increasing disorder with damage was seen in HRTEM images of filler particles. The trend in d-spacing, measured by diffraction patterns, supported this observation between 2dpa and 30dpa. Dislocations were identifiable in the IFFTs.

Raman spectroscopy will also be conducted in-situ during annealing to give a time-dependent kinetic model at 200oC and a temperature dependent model for a range of temperatures up to 600oC, approximating molten salt reactor conditions. Activation energies for the expected fast and slow processes will be deduced and compared with literature values for HOPG, PCIB and other nuclear graphite grades.

A Molecular Dynamics simulation is being run to independently predict activation energies and gauge the validity of assumptions regarding which defect arrangements are involved under the given conditions.

Using multiple characterisation techniques the present inquiry seeks to enrich the body knowledge of nuclear graphite and clarify the microstructural mechanisms of irradiation damage recovery.

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Structural basis for importin alpha 3 specificity of W proteins in Hendra and Nipah viruses

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There are seven human isoforms of importin α that mediate nuclear import of cargo in a tissue- and isoform- specific manner. Understanding how nuclear import adaptors differentially interact with cargo harbouring the same nuclear localisation signal remains poorly understood since the recognition region is highly conserved. This talk will focus on providing a structural basis for the nuclear import specificity of W proteins in Hendra virus and Nipah virus. Hendra and Nipah are both zoonotic biosafety level 4 pathogens with an ~70% mortality rate and have no available approved therapeutics.

The W proteins from these viruses hijack nuclear import adaptors to enter the nucleus of infected cells and block innate immune responses. To better understand how this hi-jacking occurs, the

structural interfaces of both W proteins with importin $\alpha 1$ and $\alpha 3$ were determined using the MX1 and MX2 Australian Cancer Research Foundation detectors. Through the design of importin $\alpha 1$ and $\alpha 3$ chimeric and mutant proteins, together with structures of cargo-free importin $\alpha 1$ and $\alpha 3$ isoforms, the molecular basis of specificity was found to reside in the differential positioning of importin α armadillo-repeats 7 and 8. Overall, the mechanistic insights into important nucleocytoplasmic transport processes reliant on isoform adaptor specificity and the virus life cycles of Hendra and Nipah will be presented.

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Structure and property changes of ambient-cured fly ash/slag geopolymer following gamma irradiations

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Geopolymers are a class of materials formed by reacting alkali solution with aluminosilicate rich sources – fly ash, blast furnace slag, and metakaolin. Geopolymers share many similar properties to that of ordinary Portland cement (OPC) including good compressive strength, high thermal stability, and fire resistance. They can also be cured at ambient temperature while achieving high compressive strengths.

At present, OPC mortars are used for the immobilisation of low-level waste (LLW) owing to its low costs, reasonably desirable properties such as durability and mechanical strength. However, there are a number of disadvantages of using OPC mortars for intermediate-level waste (ILW). These include radiolytic hydrogen gas build-up in the pores during storage and disposal and poor aqueous durability. Geopolymers could be used as an alternative; however its performance under gamma irradiation needs to be assessed. In the present work, ambient-cured 60 wt% fly ash and 40 wt% slag geopolymer were exposed to 0 KGy, 1 574 KGy, 4 822 KGy and 10 214 KGy gamma irradiation using a Co-60 source and the bulk properties were characterised. The effects of the irradiations were examined using various mechanical and characterisation techniques such as ²⁹Si NMR, SEM-EDS, XRD, and compressive strength. In addition, the geopolymers were subjected during leach testing using standard aqueous durability regulatory tests, such as the PCT-B, ANSI tests.

Compressive strength for paste samples, increased from 50MPa to ~85MPa before decreasing to 68 MPa and 45 MPa respectively. The authors postulate that the sudden increase in strength between 0 and 1 574 KGy was a result of precursors abruptly breaking down and providing samples with activation energy to accelerate the geopolymerisation process. Single source geopolymer produces a Na-A-S-H gel network. Au contraire, a hybrid geopolymer that contains fly ash and slag, forms (Ca, Na)-A-S-H gel network that is responsible for high strength. However, with further radiation, the SEM micrograph shows that the inside of the fly ash particle which contains quartz and mullite degrades to form a high number of concentrated closed pores encapsulated in unreacted fly ash particles. This could have been responsible for the decrease in compressive strength.

The slag particle is also broken down following irradiation, as was observed on the SEM micrograph. It was found using EDS, that the matrix is highly rich in calcium, forming the Ca-S-H gel. The results are backed up by the XRD pattern which illustrated a growing crystalline peak from the amorphous region about 30° (2 θ) and identified as calcium silicate (C3S). Moreover, the ²⁹Si NMR signal detected an increase in Q2 species. This result is more consistent with slag geopolymer than that of fly ash geopolymer which produces smaller amounts of Q2 species.

Changes in the aqueous durability of the geopolymer will also be discussed in relation to the structural changes that are occurring as a result of the gamma irradiations. The results of this study will provide valuable information for the use of fly ash/slag geopolymer for the storage and disposal of ILW nuclear waste.

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The effects of temperature and moulting on metal concentrations in decapod crustaceans

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The predicted rise in sea surface temperature due to climate change may affect the uptake and depuration of contaminants by crustaceans, affecting their survival and reproductive success. Decapod crustaceans are routinely used as bioindicators in environmental research as they are commonly found in aquatic environments, have an omnivorous diet and an important position in food webs. They may also be exposed to a wide range of contaminants present in aquatic ecosystems from urban and industrial processes. Both ambient temperature and moulting of the exoskeleton are known to influence contaminant regulation in these taxa. This study used the radiotracers ¹⁰⁹Cd, ⁵⁴Mn and ⁶⁵Zn to investigate the internal concentrations of these metals in three ambient temperature treatments, 21 °C, 23 °C and 25 °C, based on predicted increases in sea surface temperatures for Australia. Spotted shore crabs (*Paragrapsus laevis*) were exposed to two pulses of a mixed radiotracer solution, each followed by a depuration stage of five days. We found no significant effect of ambient temperature on uptake or depuration rates of the three metals. However, across temperatures the rate of uptake was significantly higher than that of depuration for ⁵⁴Mn and ⁶⁵Zn. Of 21 crabs, 15 moulted throughout the study and no significant difference was found in the amount of metal taken up pre- and post-moult. However, there was a significant difference in whole-body metal burden between non-moulted crabs and moulted crabs immediately after moult. It was determined there was no significant difference in internal metal concentrations of ¹⁰⁹Cd, ⁵⁴Mn and ⁶⁵Zn over the elevated sea surface temperatures predicted by climate change models and that moulting only significantly affected depuration of the metals.

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To D or not to D – an in vitro/mass spectrometry screening method to confirm improved metabolic stability in deuterium-labelled radiotracers

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Deuteration, where hydrogen within molecules is switched with the non-radioactive and naturally occurring isotope deuterium, can lead to enhanced material properties. For example, the deuterium kinetic isotope effect is well known to improve the metabolic stability of molecules such as drugs, as the C–D bond is stronger and more difficult for enzymes to break than the C–H bond. However, the specific molecular location to deuterate to gain a metabolically favourable outcome may not be clear, without undertaking separate assays of both the deuterated and non-deuterated molecules, followed by separate HPLC-UV/radiometric measurement. In the case of compounds which also contain a radiolabel (e.g. radiotracers for diagnostic medical imaging), specialist infrastructure and teams are required, and chemical synthesis and bioanalysis are time-critical.

Our ongoing work with the radiotracer [18F]PBR111, a TSPO ligand showing potential for imaging neuroinflammation^{1,2,3}, demonstrated that [18F]PBR111-d4 (where d4 is incorporated at a specific site) has slower metabolic breakdown^{4,5} and a decreased rate of formation of polar metabolites *in vitro* (rat and human liver microsomes) relative to non-deuterated^{5,6}.

Our recently published MS/MS method⁴ demonstrates the relative difference in metabolic stability without radiolabelling, by analysing different time points from a liver microsome assay which has been administered a 50:50 mixture of deuterated/non-deuterated compound. Pharmacokinetic parameters can also be determined from the data. Deuteration adjacent to the fluoro-alkyl group in PBR111 showed ~50% improvement in the stability of the intact radiotracer relative to non-deuterated using a ratio determination of the analogous MS transitions unique to the deuterated/non-deuterated compounds⁴. As a control, a second deuterated analogue was also synthesised⁴ with deuterium purposely incorporated at a site significantly less metabolised than the first site⁵, which our newly developed method was also able to confirm.

We expect this simple and rapid method could be applied to deuterated and non-deuterated analogues of other biologically important molecules to determine the suitability of the chosen site of deuteration. For radiotracers, there is no requirement to radiolabel until studies progress to *in vivo* PET imaging.

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Two birds with one stone: leaching of alkaline mineral wastes enhances CO₂ sequestration and concentrates trace metals

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The mineral wastes produced by ultramafic mines (i.e. Cu-Ni-PGE, podiform chromite, diamondiferous kimberlite and historical chrysotile deposits) are ideal material for sequestering CO₂ via mineral carbonation, which is a natural process that involves weathering of Mg or Ca-rich silicate and hydroxide minerals to form Mg-carbonate. Due to a higher surface area, mineral carbonation of mine tailings typically occurs at rates 2-3 orders of magnitude above background rock weathering rates, and at the Mt Keith Ni Mine, WA, offsets 11% of the mine's annual CO₂ emissions.(1) If geochemical treatments were applied to these materials, reaction rates could be further accelerated such that a mine could potentially achieve carbon neutrality. In order to encourage uptake of mineral carbonation technology at mine sites, treatments will ideally make use of relatively conventional technology and expertise within the minerals industry. As such, in situ heap leaching is proposed as a potential strategy to accelerate mineral carbonation.

Here, we simulate this process in column experiments, by leaching ultramafic tailings from Woodreef Chrysotile Mine (NSW, Australia) with dilute sulphuric acid (pH ≈ 1). A high-pH leachate rich in Mg is produced with the potential to sequester 21.4 kg CO₂ m⁻² of treated tailings per year, which is approximately 1-2 orders of magnitude higher than estimates of passive carbonation that has occurred within these tailings over the past three decades.(2)

Importantly, synchrotron X-ray fluorescence microscopy shows concentration of Ni, Co and Cr within Fe-(oxy)hydroxides at the neutralisation horizon, and geochemical modelling indicates that with continued acid leaching this horizon would become enriched in transition metals over time, concentrating metals of potential economic benefit in distinct zones within the vertical profile.

Acid heap-leaching technology could therefore not only be useful for accelerated mineral carbonation but also for ore processing and recovery of base metals from tailings, waste rock, or low-grade ores.

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Unlocking past climate signals in speleothems using chemical clues in cave drip waters

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The Snowy Mountains alpine region is vulnerable to extreme rainfall variability associated with the El Niño Southern Oscillation (ENSO). As the Snowy Mountains are the headwaters for Australia's largest water catchment, the Murray-Darling basin, this has had profound impacts on water resources, ecosystems, regional agriculture and the economy. Tucked away in underground chambers in the Snowy Mountains, speleothems, or natural calcium carbonate formations in caves, are a pivotal land-based record providing a valuable opportunity to reconstruct past climates. A continuous climate record, spanning thousands or tens of thousands of years, is preserved in the stable isotope and geochemistry of successive layers of calcium carbonate. However, the geochemistry of cave drip waters, from which speleothems precipitate, is influenced by climate, surface, soil and karst hydrological processes. Since speleothem records are sensitive to site-specific sources and processes, developing the requisite understanding of the modern cave system are quintessential to correctly interpret speleothem-based proxies. Therefore, this research examined geochemistry and bi-monthly drip water hydrochemistry in Harrie Wood Cave, Yarrangobilly over the last 10-years, capturing contrasting rainfall conditions of ENSO phases, to identify suitable palaeoclimate proxies for interpreting speleothem records. This research presents the first high-resolution rainfall and drip water δ¹⁸O, aerosol, soil, bedrock and inorganic drip-water geochemical datasets for the Snowy Mountains alpine region, to develop a comprehensive understanding of sources and processes that influence solute variability. The main contributors of aerosols to this montane study site were: automobile, secondary sulfate, smoke, soil and aged sea salt. This research established that long-distance transport of bushfire smoke emissions and aeolian Na and soil from Australia's desert interior to the

study site increased during below-average rainfall and El Niño conditions. The source of solutes to the drip waters was quantified using hydrochemical mass balance modelling, where the local bedrock was identified as the main source of solutes, followed by aerosols. The clay-rich soil zone was recognised as a significant factor influencing the retention and transfer of metals from soil solution to the cave drip waters. During the transmission of water from the surface to the stalactite tip, processes within the soil zone involving clay minerals and colloids were demonstrated to modify the chemical composition of the resultant drip waters. The flow paths feeding the drip sites were also demonstrated to be from a network of fissures in a zone of greater porosity and permeability. In addition, the long-term monitoring results revealed distinctive hydrological processes, and therefore changes to the drip water hydrochemistry occurred due to variations in the site cumulative water balance during ENSO events. This research revealed that trace elements can potentially be very useful in examining past ENSO patterns and are currently being validated in modern speleothems. Speleothems located in this key water resource region in SE Australia will enable us to extend our understanding of climate patterns beyond the past few hundred years to support future climate predictions and, therefore, provide practical insight regarding natural-resource policy and management.

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Vacancy Generation and Oxygen Uptake in Cu doped Pr-CeO₂ Materials Using Neutron and In-Situ X-Ray Diffraction

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Applications of CeO₂ based materials in solid oxide fuel cell, catalyst and oxygen separation technologies require high oxygen storage capacities (OSC), for which the O₂ uptakes are largely dependent on the concentration of oxygen vacancies. Neutron diffraction carried out at the Australian Centre for Neutron Scattering (ECHIDNA instrument) was used to determine the oxygen occupancies of CeO₂, Pr-CeO₂ and 5% Cu-doped Pr-CeO₂, and related to the oxygen uptake measured using thermal gravimetric analysis. Refinement was carried out by allowing the formation of Frenkel defects in CeO₂ (Fm $\bar{3}$ m) via movement of the 8c tetrahedral oxygen anions to the 48i interstitial site. The 5% Cu doped Pr-CeO₂ material possessed lower oxygen occupancy than Ce_{0.85}Pr_{0.15}O_{2- δ} , and CeO₂ had the highest oxygen occupancy. This work shows that the formation of vacancies is encouraged by the addition of Pr to CeO₂ and further increased with Cu. Oxygen occupancies could not be determined for the 10% Cu and 15% Cu materials due to segregation. Evidence of vacant tetrahedral sites did not correlate with oxygen uptake at 420 °C, indicating that a minimum temperature is required to generate sufficient vacancies/+3 cations. At 600 °C, 15% Cu doped Pr-CeO₂ had the highest oxygen uptake (120 $\mu\text{mol.g}^{-1}$) followed by 5% Cu doped Pr-CeO₂ (92 $\mu\text{mol.g}^{-1}$) then Ce_{0.8}Pr_{0.2}O_{2- δ} (55 $\mu\text{mol.g}^{-1}$). Cation reduction commenced at ~300–400 °C as shown through an exponential increase in the lattice parameter determined by in-situ X-ray diffraction. Our results show that both Pr and Cu introduce vacancies and promote the O₂ uptake of CeO₂ that is necessary for the development of high OSC materials.