SLATT UNDERGRADUATE RESEARCH FELLOWSHIP
FINAL REPORT

SCHOLAR NAME:	Nicholas Anthony Poole
FACULTY ADVISOR:	Dr. Peter Burns
PROJECT PERIOD:	Spring 2022
PROJECT TITLE:	Humidity Induced Carbonation of Uranyl Triperoxide Monomer Salts
CONNECTION TO ONE OR MORE ENERGY-RELATED RESEARCH AREAS (CHECK ALL THAT APPLY):	**(x) Energy Conversion and Efficiency (x) Sustainable and Secure Nuclear** **( ) Smart Storage and Distribution ( ) Transformation Solar** **( ) Sustainable Bio/Fossil Fuels ( ) Transformative Wind**

MAJOR GOALS AND ACCOMPLISHMENTS

Summarize your research goals and provide a brief statement of your accomplishments (no more than 1-2 sentences). Indicate whether you were able to accomplish your goals by estimating the percentage completed for each one. Use the next page for your written report.

RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Collect Raman Data for All Compounds at Humidity	Collect Raman spectroscopy data for uranyl triperoxide monomer salts from 0% to 85% humidity as they convert from their initial states. This was completed for salts with cations K, Ca, Li, and Na.	100%
Determine the Crystal Structure of All Compounds at Humidity	Determine the crystal structure of the initial compounds and the final products they convert to. Due to the homogenous nature of final products at high humidity, crystal structure data cannot be collected using single crystal. Powder crystal xray diffraction must be used. Most of the conversion compounds are known for K and Ca (Ca doesn't change), but more data is needed for Li and Na. The Raman data we have is suggestive of the converted products' crystal structures, but not conclusive.	50-75%
Synthesize Unknowns (may not be necessary depending on how effective PXRD is)	Due to the issue with determining the crystal structure of some components as discussed above, I attempted to synthesize the conversion products chemically, instead of through humidity. This would allow a better examination of intermediates with Raman spectroscopy, since there's really no published data on any of the Li products. A lot of different techniques were utilized in an attempt to products these compounds, but mostly to no avail. There is now a list of what recipes don't work though, which will hopefully help narrow down a correct synthesis.	10%

RESEARCH OUTPUT

Please provide any output that may have resulted from your research project. You may leave any and all categories blank or check with your faculty advisor if you are unsure how to respond.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS SUBMITTED	
EXTERNAL AWARDS RECEIVED	
JOURNAL ARTICLES IN PROCESS OR PUBLISHED	
BOOKS AND CHAPTERS RELATED TO YOUR RESEARCH	
PUBLIC PRESENTATIONS YOU MADE ABOUT YOUR RESEARCH	• College of Engineering - Ireland Study Abroad, *Uranium Crystal CO_2 Adsorption*, March 8, College of Dublin • ND Energy Research Symposium, *Humidity Induced Carbonation of Uranyl Peroxide Monomer Salts*, March 31, University of Notre Dame
AWARDS OR RECOGNITIONS YOU RECEIVED FOR YOUR RESEARCH PROJECT	Outstanding undergraduate research in materials science or technology, William D. Manly Award, March 1 2022
INTERNAL COLLABORATIONS FOSTERED	Daniel E. Felton, Burns Group – University of Notre Dame, Graduate Student Advisor, interacted daily during research and was an essential mentor throughout the project

EXTERNAL COLLABORATIONS FOSTERED	Dr. John Loring, Pacific Northwest National Laboratory, Aided in the design of the humidity control system and provided the program for its operation, communicated via email about once a week during the first month of the project
WEBSITE(S) FEATURING RESEARCH PROJECT	
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	

RESEARCH EXPERIENCE

Please let us know what you thought of your research experience: Did this experience meet your expectations? Were lab personnel helpful and responsive to your needs? What else could have been done to improve your experience or achieve additional results?

I've been with the Burns group since the spring of 2019, and have loved my time there. Having the hands-on experience of conducting chemistry research on uranium compounds was both incredibly interesting and just really cool. I had a lot of fun with the people I worked with, too. As a graduating senior, it was very sad to say goodbye to the grad students and faculty I'd grown to know. Conducting research on a project of my own was incredible. Next year I'll be attending graduate school at NC State, looking to get my PhD in Nuclear Engineering. So much of my desire to attend grad school came from the joy of working on my own project under the guidance of those in the Burns group. The only wish I have towards this research experience is that I could have spent more time doing it outside of being in lab. I would read papers and work on code for research on my own time, but with balancing classwork and other activities it was difficult to fully dive into research. But again, that's just another reason I'm so excited for grad school. I don't think anything else could be done to achieve additional results other than time. The last data needed for this project will be collected over the summer.

FINAL WRITTEN REPORT

With the ever-growing threat of climate change, CO_2 sequestration is becoming an increasingly popular topic. By switching to renewable sources of energy and increasing industrial efficiencies, the amount of CO_2 being emitted can be reduced. But to reduce the amount of CO_2 already present in the atmosphere, something else needs to be done. This is the focus of CO_2 sequestration, the umbrella term for methods that take CO_2 from the atmosphere and turn it into more useful products. Currently, CO_2 sequestration is very costly and energy intensive. [1] To make CO_2 sequestration both energy efficient and economically competitive, research into advanced sequestration materials is required. My project demonstrates the ability of uranyl peroxide monomer salts to absorb CO_2 from the atmosphere, and the mechanism by which this process occurs. And although it is unlikely for a uranium compound to be implemented as an industrial CO_2 sequestering material, the knowledge gained from this project may lead to the design of more applicable materials.

This project began in the fall of 2020 when members of the Burns group noticed that the potassium uranyl triperoxide monomer (KUT) would convert from its initial state when left out on a bench top. From crystallographic studies, they determined that KUT was absorbing CO_2 from the air! [2] The initial and final states of KUT from this process are shown in Fig 1 below. These structures were constructed using single crystal x-ray diffraction data.

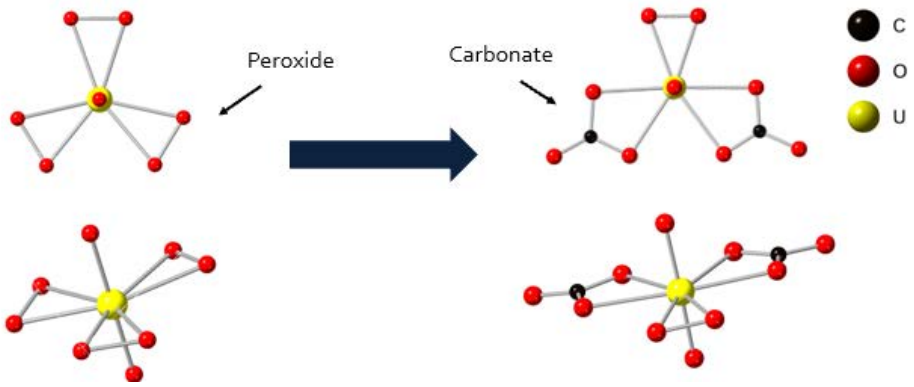

Fig 1. Monomer Conversion

From this observation, I set out with the goals of determining the mechanism by which this happens and the rate at which it occurs. To do so, I designed a humidity control system in conjunction with PhD candidate Daniel Felton in the Burns group and Dr. John Loring from the Pacific Northwest National Laboratory. The schematic of this system alongside its real counterpart are shown in Fig 2 below. Essentially, CO_2 gas enters from a tank into the system, and two flow controllers are

adjusted by a program until the humidity setpoint is reached. This allows for the long-term humidity stability that is required of this project, since some compounds (the sodium monomer, NaUT, for instance) take three or more weeks to convert.

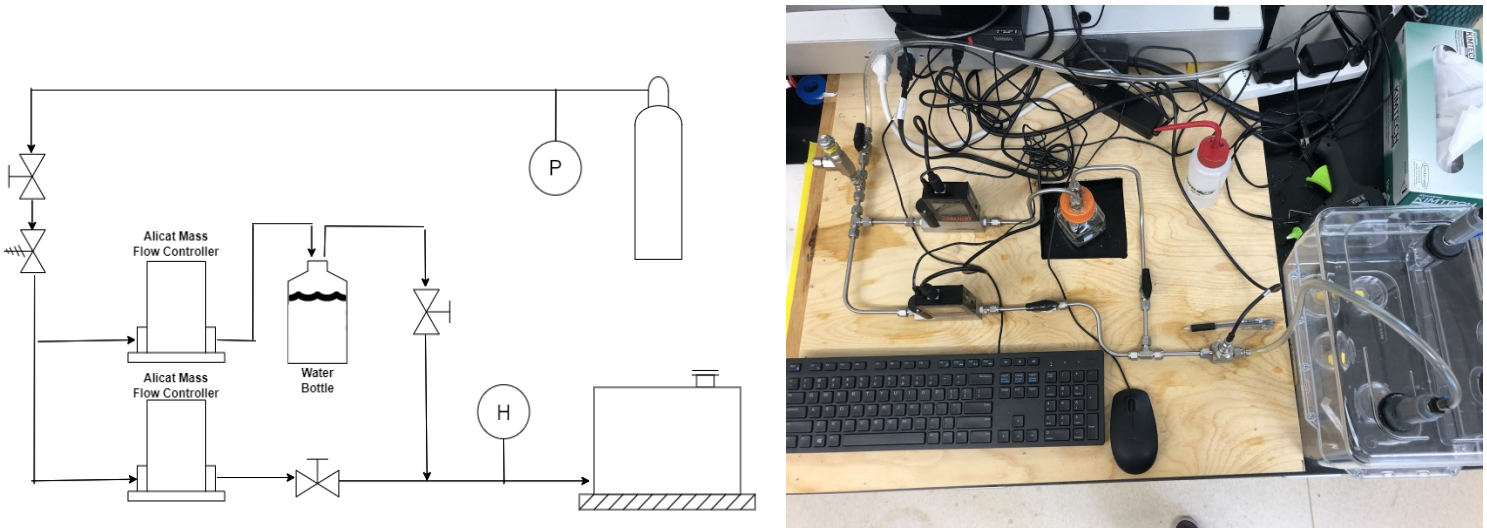

Fig 2. Humidity Control System

We were curious about the effects of humidity, since it was believed from the beginning that water played a role in the conversion mechanism. This was very quickly confirmed by doing a zero percent humidity test. KUT did not absorb CO_2 in the two weeks where that test was run, indicating that water is either necessary for the conversion to occur, or significantly speeds up the process.

Due to the physical limits of the control system, humidity levels over a range of 0-85% were chosen for my experiments. Four different starting monomers were chosen, with the difference between them being the element that neutralizes the structure's electrical charge. So, in addition to KUT, the sodium (NaUT), calcium (CaUT), and lithium (LiUT) monomers were chosen as well. From there, samples were placed in the humidity chamber. They would be taken out the chamber briefly every other day to be examined spectroscopically, then quickly placed back in the chamber. The analysis would continue until conversion was reached, which would take up to days or weeks depending on the humidity level and initial compound. Raman spectroscopy was used as the chief tool to measure this process, and an example of KUT at 40% relative humidity (RH) converting over time can be seen to the right in Fig 3.

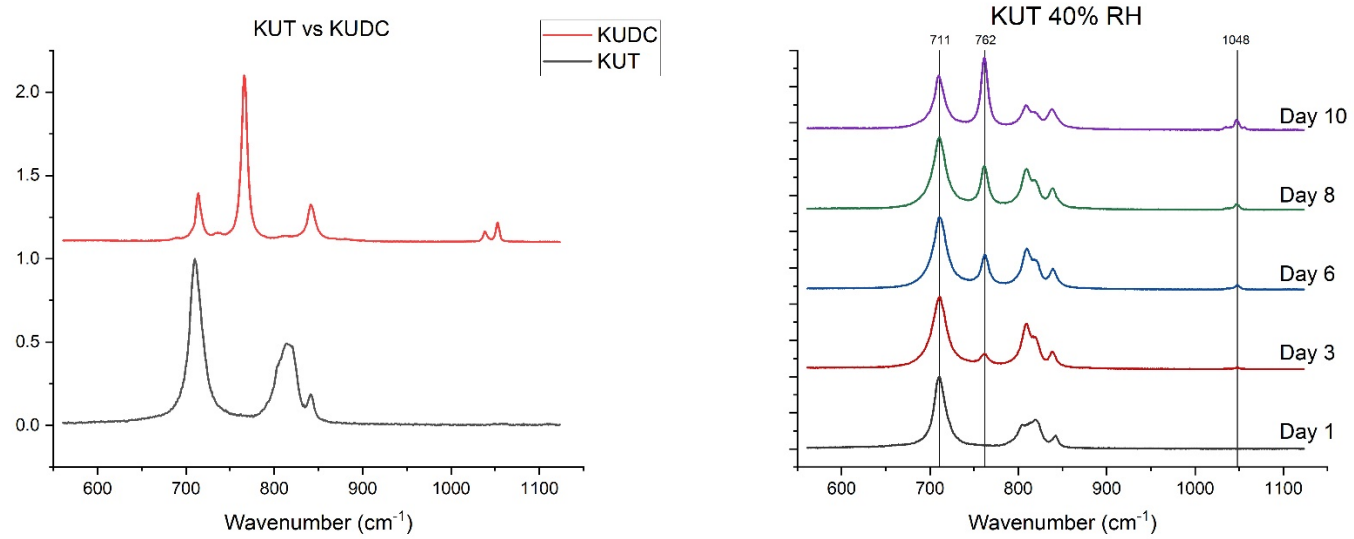

Fig 3. KUT – 40% RH Conversion

The left of Fig 3 shows the pure spectra of the initial KUT and final product, potassium uranyl monoperoxide dicarbonate (KUDC). As can be seen, the initial peak on the left of the spectra at 711 cm^{-1} shrinks as one to the right at 762 cm^{-1} grows in, along with a small peak at 1048 cm^{-1} that also emerges. [3] This is the essential process of this research, with the guiding questions of discovering what happens in between the initial and final states, and how long it takes to happen. The process at 40% RH takes around 10 days to completely convert the initial KUT to only KUDC. When increasing the humidity to 60% RH, the process

only requires 3-5 days, further indicating the presence of water as a mechanistic driving force for conversion. This trend was seen for all materials tested, except for CaUT. CaUT did not absorb CO_2 at any humidity, but this was expected since CaUT tended to be insoluble in water and was therefore unlikely to absorb CO_2 through a water-based mechanism.

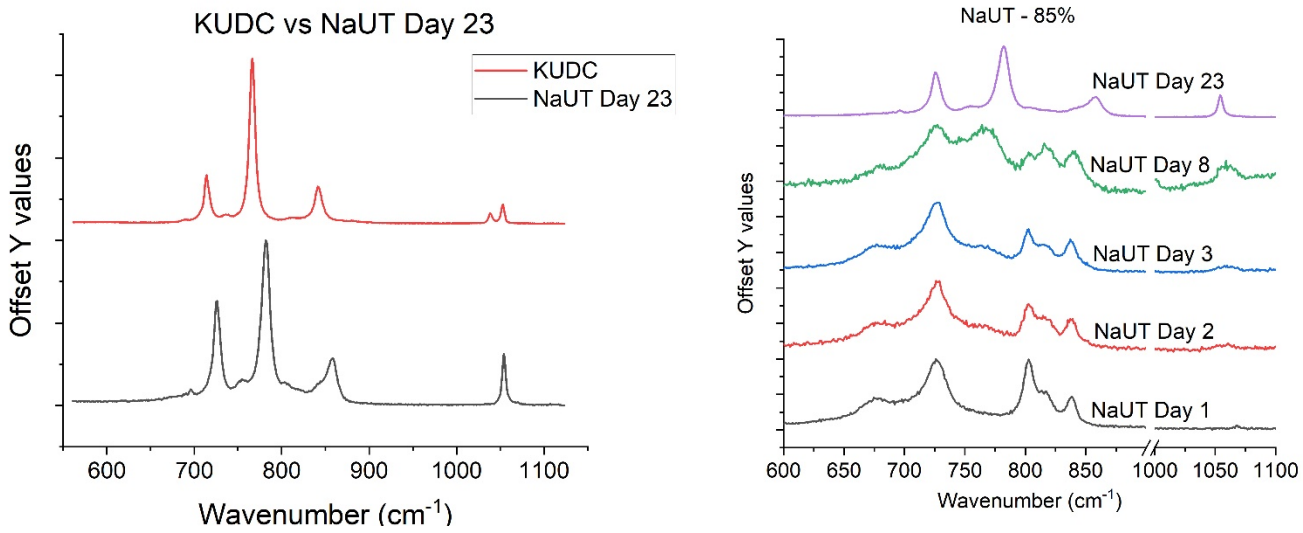

Fig 4. NaUT – 85% RH Conversion

In contrast to KUT, the NaUT monomer doesn't quickly convert at low humidity. Almost no effect is seen until 85% RH, seen to the right in Fig 4 above. The NaUT compound doesn't change much for the first few days. After a week however, it completely dissolves, indicated by the waviness of the Day 8 spectra. It becomes an amorphous, viscous substance until three weeks later, where the compound recrystallizes. This compound displays a spectrum incredibly similar to the KUDC product, compared to the left of Fig 4. This data is therefore incredibly indicative of there being at sodium uranyl monoperoxide dicarbonate (NaUDC) product, but more conclusive evidence is still required to confirm this. Because it recrystallizes as a polycrystalline compound, single crystal xray diffraction is unable to determine its crystal structure.

This same issue is extremely prevalent in the experiments with lithium, since there is little to no published data on lithium uranyl carbonate compounds. Additionally, LiUT doesn't form compounds with spectra similar to KUDC like the NaUT compound did, so it's difficult to even guess what compounds might be forming. To subvert this, I attempted to synthesize lithium carbonate compounds chemically as a different path of finding their crystal structures. This would enable me to determine what lithium compounds are produced in the humidity chamber just by looking at their Raman spectra. Unfortunately, all attempted methods to synthesize these lithium compounds failed to yield the desired product. But hopefully the list of unsuccessful methods I've generated will be useful to narrowing down an effective synthesis method in the future.

Additional future work includes utilizing powder xray diffraction (PXRD), since this method has the ability to analyze polycrystalline compounds such as those formed in the NaUT and LiUT conversion processes. PXRD also provides better rate information on the rate of conversion than Raman spectroscopy. Because PXRD can examine the bulk properties of a compound, an accurate rate can be determined from the incremental carbon entering the crystal as it converts. A PXRD machine is expected to arrive at the Burns lab this summer. After this PXRD data is collected, all that remains is to wrap up the analysis and publish the results. This will be continued remotely after this semester.

REFERENCES

[1] Yu, C.-H.; Huang, C.-H.; Tan, C.-S. A Review of CO2 Capture by Absorption and Adsorption. *Aerosol Air Qual. Res.* **2012**, *12* (5), 745–769. https://doi.org/10.4209/aaqr.2012.05.0132.

[2] Dembowski, M.; Bernales, V.; Qiu, J.; Hickam, S.; Gaspar, G.; Gagliardi, L.; Burns, P. C. Computationally-Guided Assignment of Unexpected Signals in the Raman Spectra of Uranyl Triperoxide Complexes. *Inorg. Chem.* **2017**, *56* (3), 1574–1580. https://doi.org/10.1021/acs.inorgchem.6b02666.

[3] Goff, G. S.; Brodnax, L. F.; Cisneros, M. R.; Peper, S. M.; Field, S. E.; Scott, B. L.; Runde, W. H. First Identification and Thermodynamic Characterization of the Ternary U(VI) Species, UO2(O2)(CO3)24−, in UO2−H2O2−K2CO3 Solutions. *Inorg. Chem.* **2008**, *47* (6), 1984–1990. https://doi.org/10.1021/ic701775g.

(both the presentation and poster I've presented are attached to the bottom of this report)

Humidity Induced Carbonation of Uranyl Peroxide Monomer Salts

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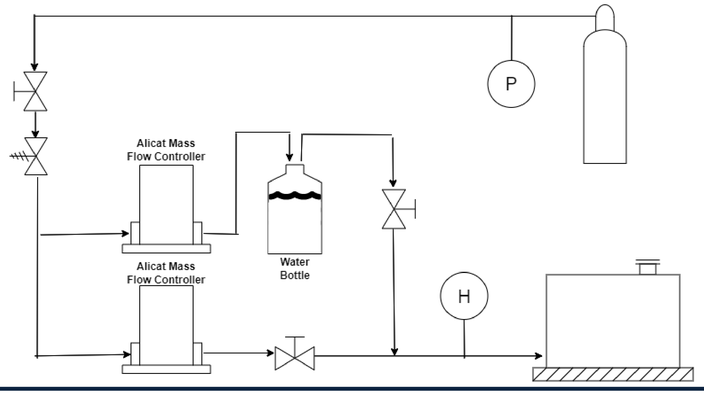
INTRODUCTION

In previous studies[1,2], it was noticed that potassium uranyl triperoxide monomer [$K_4UO_2(O_2)_3$, KUT] crystals alter when left exposed to atmospheric conditions. After two weeks, the light yellow or bright orange crystals lose their hue as a duller orange product takes their place. Over time, the characteristic 712 cm^{-1} uranyl Raman peak of KUT diminishes as a new peak at 766 cm^{-1} grows in alongside another peak at 1051 cm^{-1}, signifying a carbonate species[3]. This conversion product was identified as the uranyl dicarbonate, monoperoxide monomer [$K_4UO_2(CO_3)_2O_2$, KUDC].

GOALS

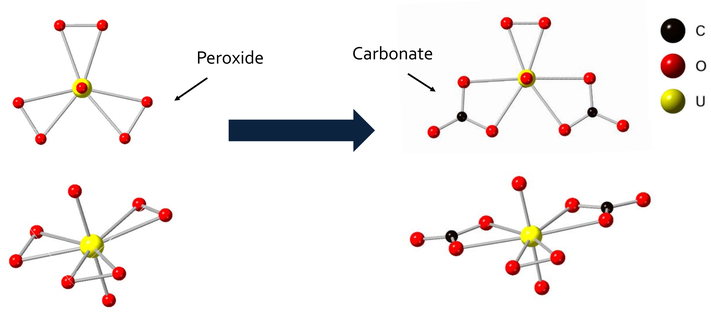
- **Mechanism of Reaction**
  - Utilize Raman spectroscopy and powder X-ray diffraction to analyze process over spectrum of humidity to determine whether atmospheric water assists in conversion
  - Determine if products other than the dicarbonate, monoperoxide monomer form at higher humidity
- **Cation Effects**
  - Determine how the starting cation affects carbonation using K^+, Na^+, and Li^+ uranyl triperoxide monomers

EXPERIMENTAL SETUP



RESULTS

MONOMER CONVERSION



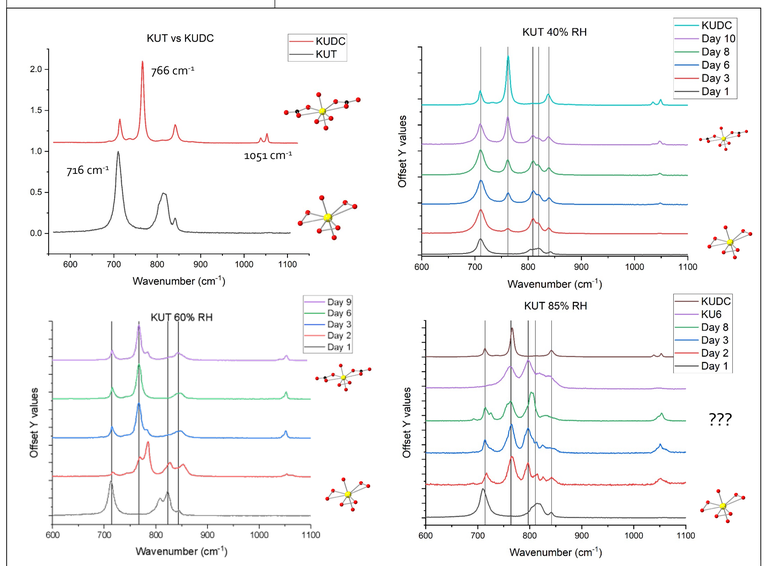
Potassium Uranium Triperoxide Monomer (KUT)

$K_4[UO_2(O_2)_3]$

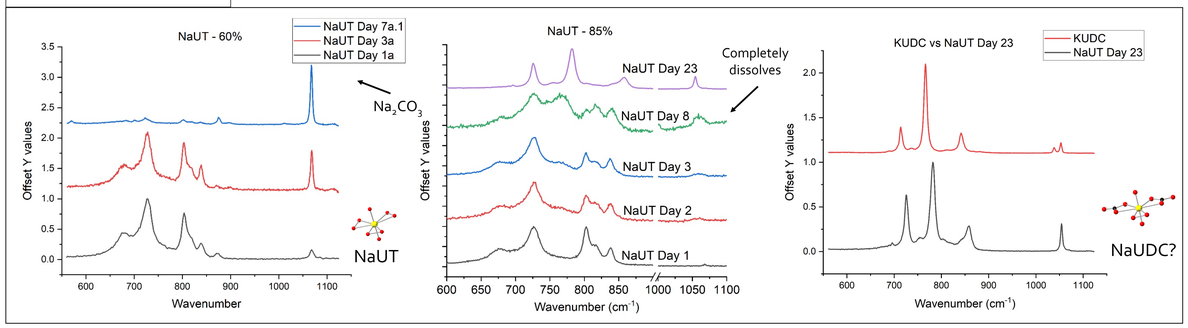
Potassium Uranium Dicarbonate Monoperoxide Monomer (KUDC)

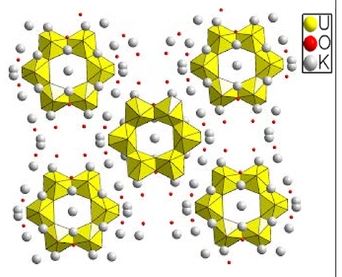
$K_4[UO_2(CO_3)_2O_2]$

HUMIDITY EFFECTS



CATION EFFECTS





$K_{12}[UO_2(O_2)_2]_6$ (KU6)

FUTURE WORK

- **Synthesize Unreported Compounds**
  - Some compounds already have Raman data, such as Potassium Uranyl Tricarbonate (KUTC)
  - Others, not so much. Difficult to acquire crystal structures at high humidity since crystals tends to dissolve then precipitate as a powder
- **Use Powder X-ray Diffraction**
  - Can help with above issue by giving insight to crystal structure of powder compounds, instead of single crystal
  - Also, there is the potential to determine reaction rate with CO_2 since PXRD can analyze bulk properties unlike Raman which only analyzes the surface.

REFERENCES

1. Dembowski, M.; Bernales, V.; Qiu, J.; Hickam, S.; Gaspar, G.; Gagliardi, L.; Burns, P. Computationally-Guided Assignment of Unexpected Signals in the Raman Spectra of Uranyl Triperoxide Complexes. *Inorg. Chem.* **2017**, *56* (3), 1574–1580. https://doi.org/10.1021/acs.inorgchem.6b02666.
2. Kravchuk, D. V.; Forbes, T. Z. Thermodynamics and Chemical Behavior of Uranyl Superoxide at Elevated Temperatures. *ACS Mater. Au* **2022**, *2* (1), 33–44. https://doi.org/10.1021/acsmaterialsau.1c00033.
3. Goff, G. S.; Brodnax, L. F.; Cisneros, M. R.; Peper, S. M.; Field, S. E.; Scott, B. L.; Runde, W. H. First Identification and Thermodynamic Characterization of the Ternary U(VI) Species, UO2(O2)(CO3)24−, in UO2−H2O2−K2CO3 Solutions. *Inorg. Chem.* **2008**, *47* (6), 1984–1990. https://doi.org/10.1021/ic701775g.

ACKNOWLEDGEMENTS

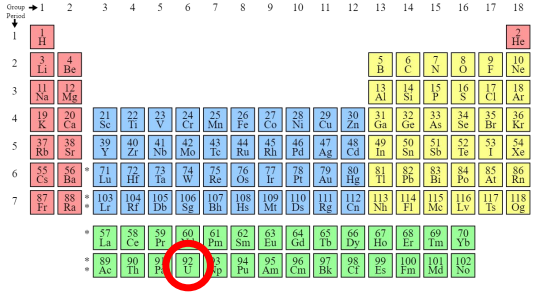
- Dr. Peter Burns and the Actinide Super Group
- PhD Candidate Daniel E. Felton
- Dr. John Loring – Pacific Northwest Laboratory
- Dr. Mateusz Dembowski
- ND Energy Vincent P. Slatt Fellowship for funding this research

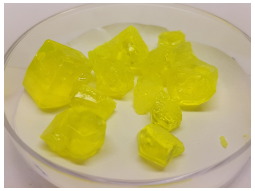
Uranium Crystal CO_2 Adsorption

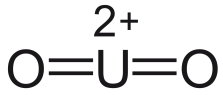
By Nick Poole

Background

Background







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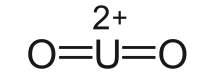

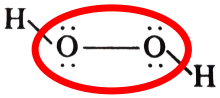

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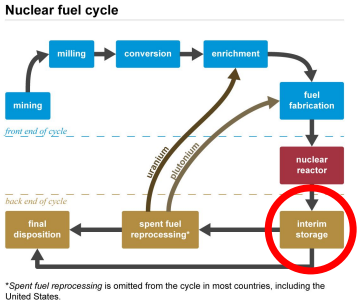

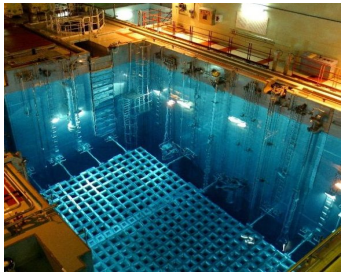

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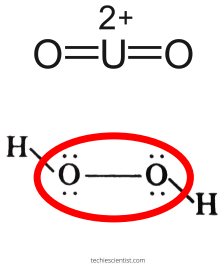
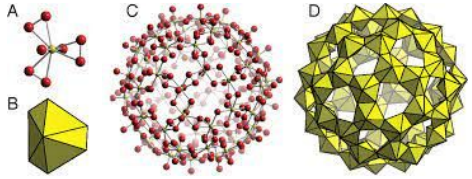
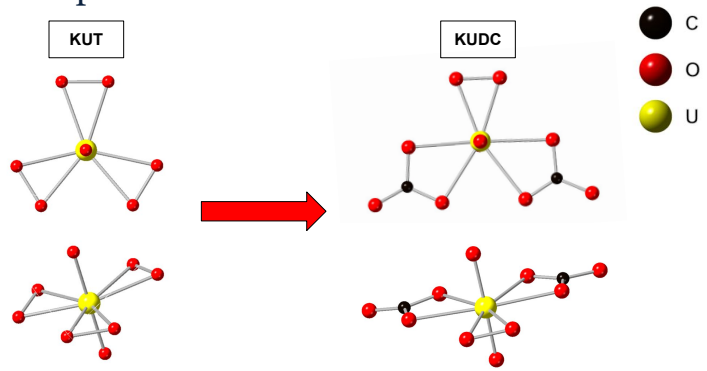




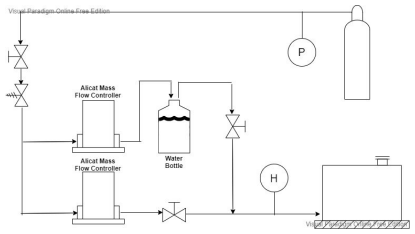
Goals of Experiment



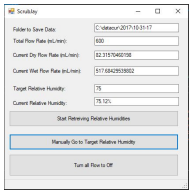
Goals of Experiment

- Examine process at variety of humidities
  - Water involved in conversion?
  - Unexpected materials form?
- Examine process for a variety of starting materials
  - Potassium (K)
  - Calcium (Ca)
  - Lithium (Li)
  - Sodium (Na)

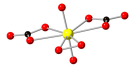
Experimental Set-up

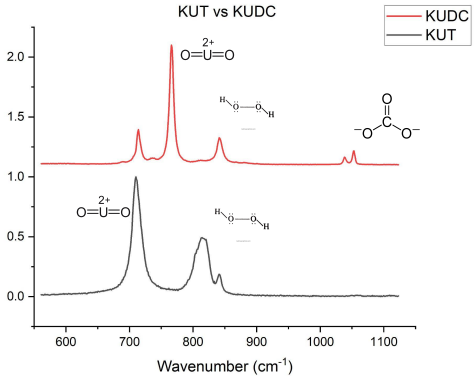


System Schematic

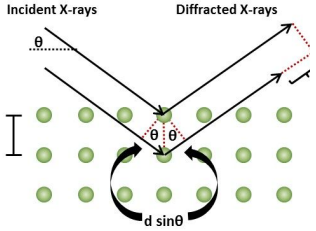


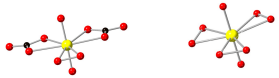
Experimental Setup - Raman Spectroscopy

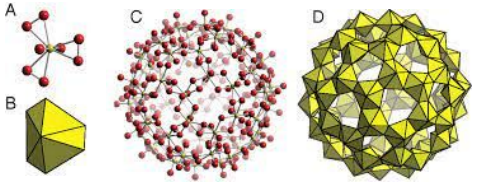




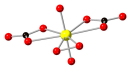
Experimental Setup - Xray Diffraction



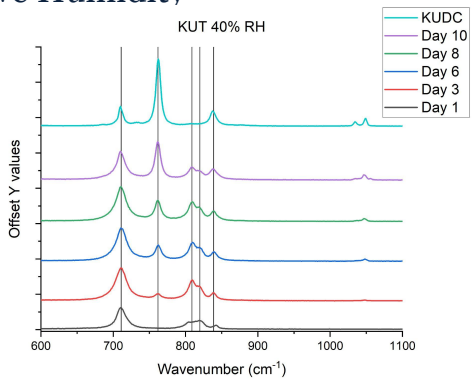




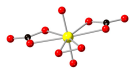
40% Relative Humidity



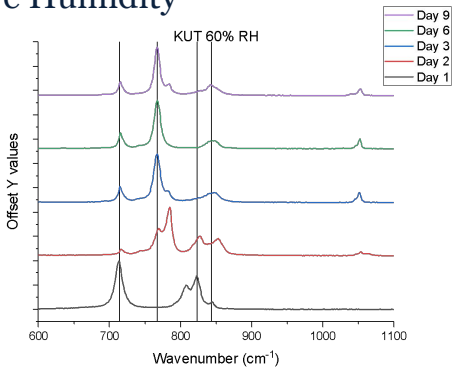
(Day 11)



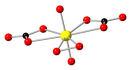
60% Relative Humidity



(Day 3-6)



85% Relative Humidity



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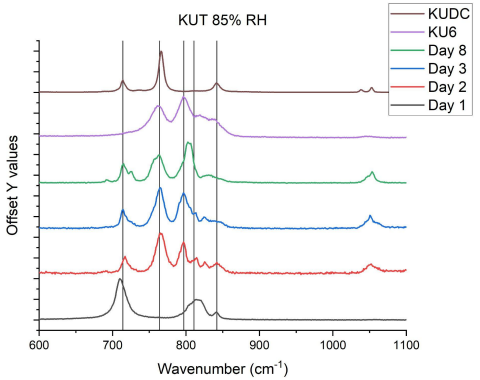
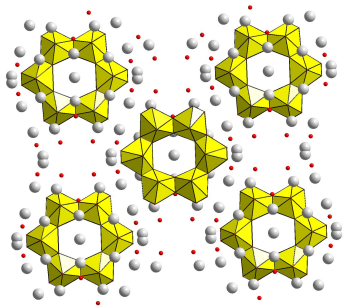
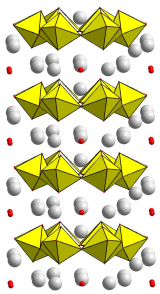
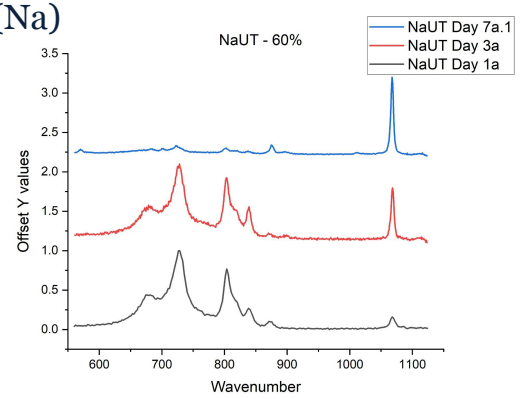


KU_6 Structure





Sodium (Na)



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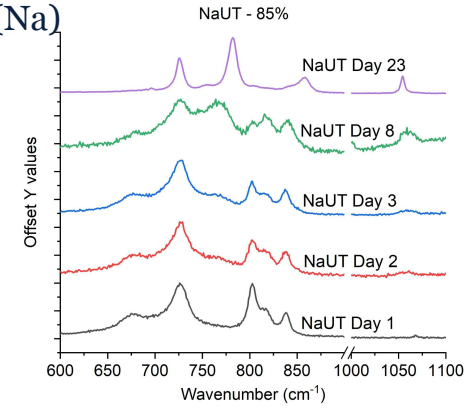
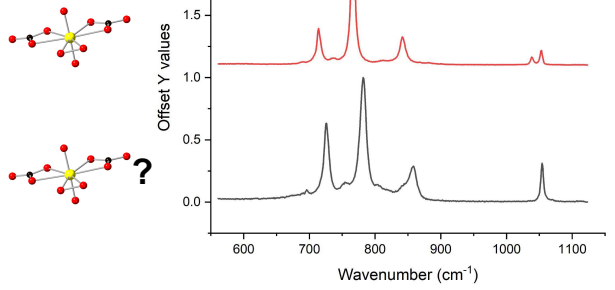


Sodium (Na)



Future Work

- Synthesize Uranyl Mono, Di, and Tricarbonate compounds
  - Characterize with Raman to determine conversion products by matching peaks
- Utilize Powder Xray Diffraction to determine structures of amorphous compounds and maybe also reaction rate of CO_2 adsorption

Thank you for listening!

Questions?