# Speciation of Uranyl Compound at Different pH and Its Precipitation Characteristics in Nitric Acid

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**Abstract. Uranyl is one of the most common chemical compounds that can be found in the waste of nuclear plants. As such, understanding the speciation of uranyl is important to ensure that the best waste treatment option is taken to purify the uranyl inside the waste, whether it is through flocculation, evaporation, or other waste treatment option. As most uranyl waste is either acidic or basic, different pH levels would be the basis of measurement for the speciation analysis of uranyl. Neutralizing the pH of the solution turns out to be the best method to separate uranyl compounds.**

Keywords: Speciation; pH; Uranyl; Solubility; Nitric Acid

## 1. INTRODUCTION

Uranyl ($UO_2^{2+}$) is a cation formed from the highest oxidation state of uranium (+6) bonded with 2 oxygen ligands. The chemical structure of uranyl can be found in the figure below.

Figure 1. Uranyl ion structure

Understanding how uranyl forms in different conditions will be very useful for many researchers. As one of the main substances in the waste created from nuclear fuel production, determining which waste processing system would be the best choice to use relies on knowing the element's physical and chemical properties. With those properties changing depending on the forms of the substances that exist in the system, knowing and understanding the speciation of uranyl is very important.

## 2. SPECIATION

Speciation can be defined as the study of how a chemical substance can exist in different forms in a particular system. This study is important because some compounds in certain forms can be highly toxic to others (Templeton, et al., 2000).

The term "speciation" is commonly utilized to describe the process of identifying chemical species and assessing their distribution. It is also used often to signify that a particular method provides more detailed insights into the elemental form compared to commonly used techniques. To avoid confusion, it is advisable to use the term "speciation analysis" when referring to the analytical activity of identifying and measuring these different chemical species (Templeton, et al., 2000).

There are 4 types of speciation:

1. Acid-Base Speciation: In an aqueous solution, acids can donate protons ($H^+$ ions), and bases can accept protons. The speciation of acids and bases depends on the pH of the solution.
2. Metal Complex Speciation: Transition metal ions can form complexes with ligands, which are molecules or ions that donate electron pairs to the metal ion. The speciation of metal complexes depends on the nature of the ligands and their coordination chemistry. Different ligands can result in various complex geometries and stability constants.

3. Redox Speciation: Redox reactions involve the transfer of electrons between species. Speciation in redox reactions is determined by the oxidation states of the elements involved.
4. Solubility Speciation: The solubility of compounds can vary depending on the conditions. Speciation in solubility equilibria involves the formation of different species based on the concentration and pH of the solution.

When doing speciation analysis, treatment of the sample is important to avoid errors and bias. The most challenging aspect of sample treatment is maintaining the original composition of the sample (Quiroz, 2021). When dealing with aqueous samples, the presence of oxygen from the surrounding air can alter the redox state of the species (Quiroz, 2021). Additionally, a rise in pH due to the loss of dissolved carbon dioxide can result in the formation of metal hydroxo complexes and even lead to the precipitation of metal oxide-hydroxides (Quiroz, 2021).

## 3. URANYL SPECIATION

At different pH levels, uranyl can form various compounds due to the hydrolysis of uranyl ions. The graphic shown in Figure 2 represents the speciation of uranyl in nitric acid solution

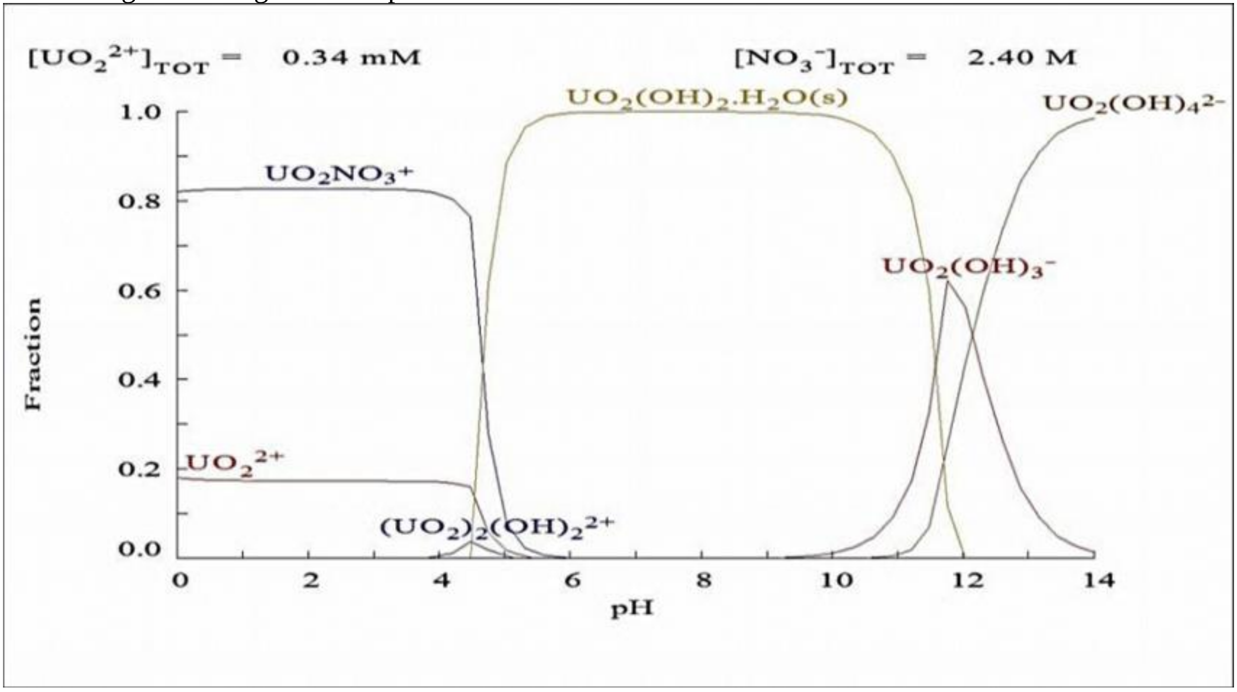

Figure 2. Predicted aqueous speciation of U (VI) as a function of pH in 2.4 M HNO3 (pH of 0.38) using Hydra-Medusa program (source: (Hussein, Youssef, Taha, & El-Maadawy, 2017)

When the pH is below 4.5, uranyl mostly exists in the form of $UO_2NO_3^+$ ions, though some will not react and stay in the form of free $UO_2^{2+}$ ions. Once the pH is increased, hydroxide ions will start to react with uranyl, forming uranyl hydroxide cations $(UO_2)_2(OH)_2^{2+}$) though their numbers are very little (below 1%) due to the low presence of hydroxide ions in acidic condition

Further increasing the pH above 4.5 will create more uranyl hydroxide, but this time, they will be in the form of hydrate crystals complex compound ($UO_2(OH)_2.H_2O$). This can be explained by the increasing presence of hydroxide ions that have bypassed the nitrate ions ($NO_3^-$), which makes the uranyl that once bonded with nitrate ions instead bonds with hydroxide.

When the pH is increased further above 10, most uranyl will take another hydroxide ions that are now extremely abundant forming uranyl hydroxide, this time as anions instead of cations in the form of $UO_2(OH)_3^-$ (bonded with 3 hydroxides) or even $UO_2(OH)_4^{2-}$ (bonded with 4 hydroxides) at stronger base.

## 4. PRECIPITATION CHARACTERISTIC

Precipitation refers to the formation of a solid substance from a solution during a chemical reaction which occurs when certain ions in a solution combine to form an insoluble compound, which separates from the solution as a solid.

One of the most important things to consider for compounds to precipitate is their solubility. According to the solubility rule, salts containing nitrate ions ($NO3^-$) are generally soluble (Mursa &

Busch, 2019). Therefore, no precipitation would occur when the pH level is less than 4.5.

In basic conditions, with a pH level above 10, uranyl has bonded with too much hydroxide. Even if according to the solubility rule, most hydroxide salts are only slightly soluble (Mursa & Busch, 2019), they immediately dissolve in the solution. This is further enforced by the fact that they form as anions.

Between the pH level of 6 and 9, most of the uranyl hydroxide crystallizes and traps a water molecule, forming a crystallized hydrate complex compound.

## 5. CRYSTALLIZATION

Crystallization is a scientific phenomenon where the mass transfer of a solute from solution to solid. In chemistry, crystallization is one of many ways to separate a mixture, in which the solute is dissolved into a solvent and heated before it is cooled slowly until a crystal is formed (Nichols, LibreTexts Chemistry, 2022).

The crystallization process is divided into 4 steps:

1. The formation of supersaturated solution: This solution can be created by adding more solute than solvent, which means the solute concentration must be way higher than the solvent concentration inside the solution.
2. The formation of a nucleus (nucleation): This is the step in which molecules, ions, and atoms started to gather and create cores (nuclei), which will act as the place where the crystal growth step would occur (Nugroho, 2022)
3. Crystal growth: The nucleus that was formed from the previous step would collide with other nuclei, which will combine and create a much bigger crystal that will grow. This step can be sped up by mixing the solution.
4. Recrystallization: This is an optional step that can be done to purify the crystals that were formed from the last step. Since the purpose of this experiment is to only crystallize the wastes, this step is skipped.

When doing crystallization, some things need to be considered to ensure the yield from this process is maximized. First is the compatibility between solute and solvent. Solute must not dissolve in the solvent at room temperature (298 K), but must dissolve when heated. The solvent must also not be poisonous, expensive, or react with the solute. A low boiling point is also good for solvents (less than 3763 K) (Nichols, Crystallization, 2022). Another thing that needs to be considered is the cooling time of crystallization. This part affects the quality and purity grade of the crystals. To get high-purity crystals, the cooling process must be done slowly. If the cooling process is done too fast, impurities will be crystallized together with the solute, which will decrease the purity grade of the crystals. Lastly, the concentration of solute in regards to the solvent will also affect the quality and number of the crystal’s yield. Too much solvent will lower the yield and quality of the crystals.

In crystallization, the most important thing that determines whether or not crystallization can happen is the solubility product constant ($K_{sp}$). Crystallization can only occur if the concentration of the solute exceeds the constant (Clark & Bonicamp, 2000). $K_{sp}$ can change based on the 2 major factors, which are temperature and pH (Euler, Kirschenbaum, & Ruekberg, 2000). If the temperature is lowered, or the value of pH got closer to 7, $K_{sp}$ value will decrease, which enabled the solute to exceed $K_{sp}$ value and for the crystallization to occur. The formula to calculate Ksp can be seen below:

$$K_{sp} = [A^{+}]^{a}[B^{-}]^{b}$$

Equation 1. Solubility product constant equation (source: (Euler, Kirschenbaum, & Ruekberg, 2000))

where $K_{sp}$ is the solubility product constant, $[A^+]$ is the cation in an aqueous solution in mol/L, $[B^-]$ is the anion in an aqueous solution in mol/L, and both a and b is the constant of [A] and [B] respectively. An easier method to determine if crystallization would occur is by looking at the solubility data of the substance, which could be obtained from experimentation or already existing data. The criteria for crystallization to happen is the same as $K_{sp}$; if the concentration of the substance is higher than in the solubility data, crystallization will happen and the amount of crystal would be the difference between the concentration and solubility data value.

## 6. SUPPORTING LITERATURE

Based on other journals and research, the writer felt confident that the crystallization of PCP wastes is possible. As there were no works that involve the crystallization process of PCP waste, the author took inspiration from other forms of the crystallization process in nuclear waste. Some of the work that the writer took note of is about the recovery of uranium through crystallization (Baron, et al., 2019). In their work, the writer hopes that by crystallizing the Uranium and separating them, the rest of the waste can be processed or at least can be safely modified to achieve the needed criteria to be processed. Although using crystallization to recover Uranium is strictly prohibited by the Indonesian government, using it to separate Uranium is still a possibility.

From the journal about uranium purification using a Fast Breeder Reactor (FBR), a crystallization process is used to crystallize uranyl nitrate hydrate through New Extraction System for TRU Recovery (NEXT) process (Takeuchi, et al., 2015). Below is the diagram of the NEXT process and the picture of the crystallized uranyl nitrate hydrate.

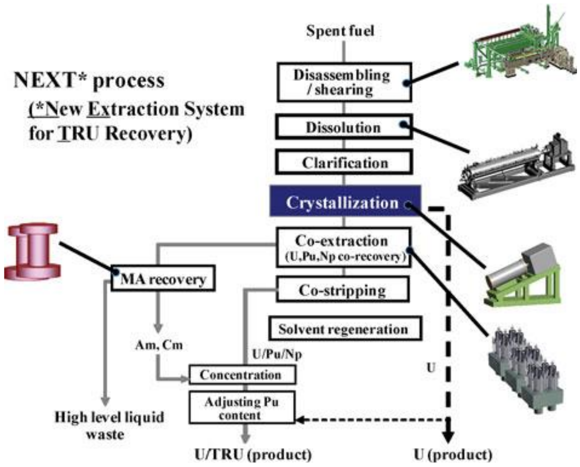

Figure 3. NEXT process structure (source: (Takeuchi, et al., 2015))

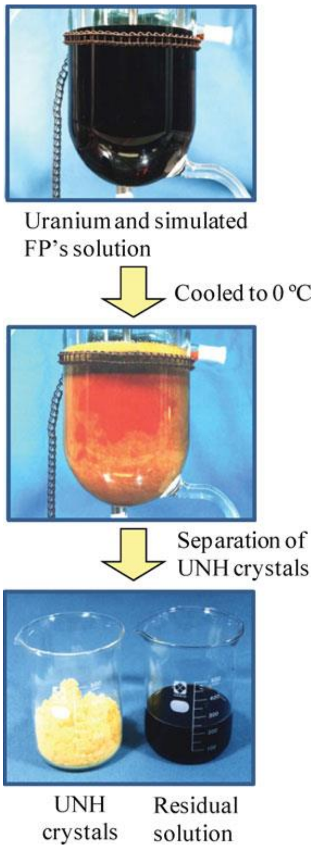

Figure 4. Uranyl Nitrate Hydrate crystallization state (source: (Takeuchi, et al., 2015))

As can be seen from the pictures above, it is possible to crystallize uranyl nitrate, which is a substance that is largely found in the sludge waste of the PCP process. Therefore, the writer is convinced that crystallizing PCP waste is possible.

Another application of crystallization in the nuclear industry can be seen in the crystallization of uranyl nitrate hydrate (UNH) (Kikuchi, 2020). Toshiaki analyzed the possibility of using a crystallization process to recycle nuclear fuel like uranium and plutonium. The crystallization process would be done after the impurities inside the spent nuclear fuel are separated and the solvent is extracted. Once the crystallization process is done, the crystal would be filtered and the mother liquor would be recrystallized.

Another study with uranyl speciation was done in high temperatures and pressure. This research looked at how uranyl behaves when it is exposed to high temperatures (up to 100°C) and pressures (up to 40 MPa) by using time-resolved laser-induced fluorescence spectroscopy. When the temperature is increased, the emission intensities and lifetime of uranyl hydrolysis species decreased significantly, which suggests that temperature affects uranyl speciation that leads to changes of uranyl species' luminescence properties. However, pressure changes did not cause significant changes in the emission spectra and lifetimes of uranyl species (Kirishima, Kimura, Tochiyama, & Yoshida, 2004).

When uranyl is mixed in different solutions, such as carbonate, it will form and bind with different elements, mostly the conjugate acid or base of their solution (Krestou & Panias, 2004). In the case of water, acidic water has more thermodynamic inconsistencies than neutral and alkaline water (Mühr-Ebert, Wagner, & Walther, 2019).

## 7. CONCLUSION

From the speciation of uranyl at different pH values in nitric acid solution, the writer concludes that neutralizing the pH between 6 and 9 is the best precipitation region as almost all uranyl crystallizes into uranyl hydroxide hydrate ($UO_2(OH)_2.H_2O$). Therefore, to crystallize uranyl nitrate, the best way is to increase the pH to between 6 and 9.

## References

Baron, P., Cornet, S. M., Collins, E. D., DeAngelis, G., Cul, G. D., Fedorov, Y., . . . Taylor, R. (2019, November). A Review of Separation Processes Proposed for Advanced Fuel Cycles Based on Technology Readiness Level Assessments. 54. Retrieved May 7, 2023

Clark, R. W., & Bonicamp, J. M. (2000). Solubility and Solubility Products (about J.Chem. Educ. 1998, 75, 1179-1181 and J.Chem. Educ. 1998, 75, 1182-1185). *Journal of Chemical Education*.

Euler, W. B., Kirschenbaum, L. J., & Ruekberg, B. (2000). Determination of Ksp, ΔG0, ΔH0, and ΔS0. *Journal of Chemical Education*.

Hussein, A. E., Youssef, W. M., Taha, M., & El-Maadawy, M. M. (2017). Uranium Adsorption from Aqueous Nitric Acid Solution by Solvent Impregnated Polypropylene. *The Egyptian Society of Nuclear Sciences and Application*.

Kikuchi, T. (2020). Technology Options For Future Recycling. *Nuclear Fuel Cycle Center*, 6.

Kirishima, A., Kimura, T., Tochiyama, O., & Yoshida, Z. (2004). Speciation Study on Uranium(VI) Hydrolysis At High Temperatures and Pressures. *Journal of Alloys and Compounds*.

Krestou, A., & Panias, D. (2004). Uranium (VI) Speciation Diagrams in the UO22+/CO32-/H2O System at 25°C. *The European Journal of Mineral Processing and Environmental Protection*.

Mühr-Ebert, E. L., Wagner, F., & Walther, C. (2019). Speciation of Uranium: Compilation of A Thermodynamic Database and Its Experimental Evaluation Using Different Analytical Techniques. *Applied Geochemistry*.

Mursa, A., & Busch, K. W. (2019, January 27). *Solubility Rules*. Retrieved from LibreTexts Chemistry: https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Equilibria/Solubilty/Solubility_Rules

Nichols, L. (2022, April 8). *Crystallization*. Retrieved November 14, 2022, from LibreTexts Chemistry: https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Organic_Chemistry_Lab_Techniques_(Nichols)/03%3A_Crystallization

Nichols, L. (2022, April 8). *LibreTexts Chemistry*. Retrieved November 14, 2022, from LibreTexts Chemistry: https://chem.libretexts.org/Bookshelves/Organic_Chemistry/Organic_Chemistry_Lab_Techniques_(Nichols)/03%3A_Crystallization

Nugroho, C. (2022). *Kristalisasi*. Retrieved from Academia: https://www.academia.edu/29494556/KRISTALISASI_docx#:~:text=Berdasarkan%20prosesnya%2C%20kristalisasi%20dapat%20dibagi,)%20Sublimasi%204)%20Kristalisasi%20larutan.

Quiroz, W. (2021). Speciation Analysis in Chemistry. *Lecture Text*.

Takeuchi, M., Yano, K., Shibata, A., Sanbonmatsu, Y., Nakamura, K., Chikazawa, T., & Hirasawa, I. (2015). Purification of uranium products in crystallization system for nuclear fuel reprocessing. *Journal of Nuclear Science and Technology*, 9.

Templeton, D. M., Ariese, F., Rita, C., Danielsson, L.-G., Muntau, H., Van Leuween, H. P., & Łobiński, R. (2000). Guidelines for terms related to chemical speciation and fractionation of elements. Definitions, structural aspects, and methodological approaches (IUPAC reccomendations 2000). *Pure Appl. Chem.*, 1453-1470.