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Background of Uranium Chemistry

1.1 Introduction of Uranium in Nuclear Industry

1.1.1 Importance of Uranium Resource in Nuclear Industry

Uranium is the basic material in the nuclear industry and is widely used in nuclear power generation, nuclear weapon manufacturing, and medical health fields [1–3]. As global climate change becomes a hot topic in the international community, the world's major carbon-emitting countries have proposed emission reduction plans and advocated the development of clean and low-carbon energy to address the pressure of energy conservation and emission reduction. Nuclear power, as an environmentally friendly, safe, and efficient source of energy, plays a significant role in improving climate change [4]. According to the International Atomic Energy Agency (IAEA, as of December 2023), 31 countries are operating nuclear reactors, with 418 reactors and a global operational power capacity of 387 GW [5]. The total reported production amounted to 2552.07 TWh, marking an increase of 2.6% compared to 2022. In 2023, the leading nations in nuclear power generation are the United States, China, and France. The United States possesses the largest nuclear fleet in the world, accounting for 31% of the total nuclear power generation with an output of 779.2 TWh. China followed with its nuclear power generation constituting 16% (406.5 TWh) of the global total. France produced 323.8 TWh, representing 13% of the worldwide. In 2023, the global nuclear reactors under construction totaled 59, with an operational power capacity of 61.1 GW. Currently, the construction of nuclear power reactors worldwide exhibits a rapid growth trend.

Uranium resources are fundamental fuel for nuclear power generation [6–8]. The development of the nuclear power industry directly influences the demand for uranium resources. In 2021, the global uranium production reached 43,731 t, meeting only 74% of the global demand for nuclear reactors [5]. This suggests that the current global uranium production is still short of fulfilling the demand for uranium, with approximately 30% of the requisite supply being met by secondary uranium resources (uranium that has been previously utilized in nuclear reactors and subsequently recovered and processed for potential reuse). In 2035, the total capacity of operational nuclear power reactors worldwide is projected

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to reach 683 GW, corresponding uranium demand of 104,740 t. The relationship between uranium resources and uranium demand is characterized by a mutual dependency, where an increase in uranium demand leads to a corresponding rise in uranium production. Moreover, most of the uranium-consuming nations do not produce uranium, whereas uranium-producing nations do not consume uranium. In light of the growing demand for resources in the global nuclear power reactor, ensuring a stable supply of uranium resources has emerged as an issue that requires urgent resolution.

1.1.2 Uranium Cycle in Nuclear Industry

The uranium cycle in the nuclear industry is a complex industrial process that includes uranium mining, purification, enrichment, chemical conversion and fuel fabrication, reactor application, and reprocessing [9–11]. The cycle commences with uranium extraction from underground mines, involving drilling and geological surveys to locate and extract raw uranium ore. Subsequently, the uranium ore undergoes crushing and chemical purification to extract uranium. After purification, uranium must be enriched to increase the proportion of ^{235}U [12]. Uranium enrichment typically involves converting the uranium into gaseous UF_6 and employing techniques such as centrifugation or diffusion to enhance the concentration of ^{235}U, which is necessary for fabricating fuel elements for reactors [13]. The enriched uranium is further processed into fuel rods for nuclear reactors in the conversion facility. The fuel rods are installed into nuclear reactors, facilitating the controlled fission of ^{235}U releasing thermal energy, which is then converted to generate electricity. The used fuel rods which are known as spent fuel require proper handling. Spent fuel can be reprocessed to extract the unreacted uranium and the produced plutonium [14]. The reprocessed uranium and plutonium obtained from the spent fuel can be used again as fuel in fuel fabrication [15, 16]. Alternatively, the spent fuel may also be securely packaged and stored until its radioactivity diminishes to a lower level before final disposal. Every step in the uranium cycle must strictly follow the international nuclear safety and environment protection standards to ensure the safety of the public. With the advancement of nuclear industry technology, the uranium cycle technology is gradually being optimized to achieve more efficient utilization of nuclear energy.

1.2 Coordination and Species of Uranium

1.2.1 General Chemical Properties of Uranium

Uranium (U), as one of the heaviest elements in nature, possesses a series of unique chemical properties that make it important in nuclear industry. Uranium has an atomic number of 92 and belongs to the actinide group of elements in the periodic table. The electron configuration of uranium is $[Rn]5f^3 6d^1 7s^2$, which endows uranium with distinctive chemical behaviors. Uranium has multiple oxidation states, such as U(III), U(IV), U(V), and U(VI) [17, 18]. In both natural environments and nuclear industry, the common oxidation states for uranium are U(IV) and U(VI).

U(VI) exists in uranium ore as the uranyl ion (UO_2^{2+}). In addition, UO_3 and U_3O_8 are also common oxides in uranium, with the latter frequently found in uranium ores [19]. Uranium is relatively stable in air, but finely powdered uranium can easily autoignite and form uranium oxide. When heated, uranium can directly react with nonmetallic elements such as oxygen, fluorine, chloride, and sulfur to form corresponding compounds. This reactivity implies that uranium can exhibit diverse chemical properties in redox reactions. Uranium is soluble in HNO_3, forming $UO_2(NO_3)_2$; it can also dissolve in HCl, forming UCl_4. In the presence of oxidizing agents such as H_2O_2, HNO_3, and $HClO_4$, uranium can react with dilute H_2SO_4 to produce UO_2SO_4 [20]. Uranium does not directly react with alkaline solutions but can react with H_2O_2 and Na_2O_2 solutions to form soluble uranate salt.

The propensity of uranium to undergo hydrolysis in an aqueous solution is pronounced, especially in its higher oxidation state, resulting in the formation of stable hydroxides. This characteristic is crucial for understanding and controlling the handling of uranium in the nuclear fuel cycle. Uranium can also form various complexes involving numerous ligands, such as carbonate, phosphate, and organic acids [21, 22]. The formation of these complexes directly impacts the extraction, purification, and waste treatment of uranium.

The radioactivity of uranium is one of its most notable characteristics, which allows for a wide range of applications in medicine, nuclear power industry, and weapon manufacturing. For instance, radioactive isotopes of uranium can serve as tracers to study geological processes and environmental changes [23, 24]. The chemical properties of uranium isotopes, especially ^{235}U and ^{238}U during nuclear fission, make uranium a significant aspect of nuclear technology. In a nuclear reactor, ^{235}U can undergo fission reactions by capturing thermal neutrons, thereby releasing a large amount of energy for electricity generation. ^{238}U can undergo a series of transformation processes to become fissionable ^{239}Pu [25]. These transformation processes make ^{239}Pu an important nuclear fuel, particularly in regenerative nuclear energy and nuclear weapons.

In summary, the chemical properties of uranium are complex and diverse, and its behavior in nuclear industry requires precise control and monitoring. Through research into the chemical properties of uranium, scientists and engineers can better manage nuclear resources, ensuring the safety and sustainable development of nuclear industry.

1.2.2 Basic Uranium Species in the Solution-Uranyl and Uranyl Compound

To release the uranium species in the uranium-containing wastewater or seawater, the chemical valence state of uranium is introduced. Uranium exists in compounds with four primary valence states: hexavalent (VI) uranium, pentavalent (V) uranium, tetravalent (IV) uranium, and trivalent (III) uranium, among which U(VI) and U(VI) exhibit the most stable valence states [26, 27]. In aqueous solution systems, the most common oxidation state of uranium is uranyl ion (UO_2^{2+}). In addition, U(VI) possesses a small ionic radius of 1.05×10^{-8} cm and is insoluble in solution, which typically exists in the form of UO_2 or U_3O_8.

Under the nuclear fuel cycle, uranium fluorides such as UF_4 and UF_6 play a significant role in the uranium conversion process. U_3O_8 is first reduced to UO_2, which subsequently reacts with HF to form UF_4. After that, UF_4 reacts with gaseous F_2 to form UF_6. In addition, UF_4 can react with water to form uranyl fluoride and its hydrated forms. Initially, the primary product of this reaction is UO_2F_2. As time progresses, various uranium compounds such as U_3O_8, UO_2, and UO_3 are also formed alongside UO_2F_2. UF_6 is a volatile compound at relatively low temperatures (about 56 °C) and is crucial to the enrichment process in nuclear enrichment technologies such as gas diffusion and centrifugation. The majority of commercially operational nuclear power reactors require uranium enriched in ^{235}U as fuel, which necessitates the enrichment of UF_6.

Uranium species are influenced by variations in pH value and the presence of ligands in aqueous solution [27, 28]. The UO_2^{2+} is known to form stable complexes with CO_3^{2-}, SO_4^{2-}, OH^-, and Cl^-. In the alkaline solution, uranium can form soluble carbonate complexes, such as $UO_2(CO_3)_3^{4-}$. Under acidic conditions, uranium is more likely to form complexes with ions like chloride and sulfate. For instance, in the presence of sulfate, uranium can form $UO_2SO_4^{2-}$ and $[(UO_2(SO_4)_2)]^{2-}$, which are significant in the context of uranium leaching and transport in acidic environments. Uranium can also form hydroxyl complexes, such as UO_2OH^+ and $UO_2(OH)_2$. In addition to these inorganic complexes, uranium can also form organic complexes with naturally occurring organic ligands.

The formation of these various complexes has implications for the extraction, processing, and environmental impact of uranium in the context of nuclear fuel cycles and waste management. Understanding these complex reactions is crucial for predicting the behavior of uranium in nuclear industry.

1.2.3 Valence Transformation of Uranium

The valence transformation of uranium plays a significant role in uranium extraction. The transformation is commonly accompanied by redox reactions between U(IV), U(V), and U(VI), as shown in Figure 1.1 [29]. U(I) is typically stabilized in specific coordination environments. For instance, tetramethyl uranium is unstable due to the undercoordinated uranium center, while the use of benzyl ligands can enhance the stability of uranium compounds through a multidentate coordination mode. U(II) is relatively rare in nature, but it can be obtained under laboratory conditions through chemical reductions. U(III) is a relatively common oxidation state of uranium and is capable of utilizing its 5f orbitals for coordination with corresponding ligands. U(IV) is the stable oxidation state of uranium in virtually all solvent media and ligand environments. U(V) is a relatively stable oxidation state, which undergoes disproportionation under certain conditions. For instance, U(V) may disproportionate to U(IV) and uranium U(VI). U(VI), commonly known as uranyl UO_2^{2+}, is considered the most stable oxidation state of uranium and is a primary target for redox extraction in both natural environments and nuclear wastewater treatment.

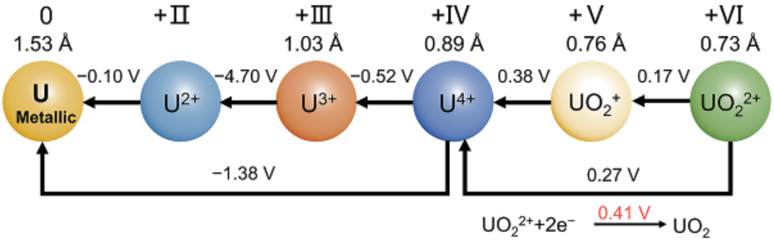

Figure 1.1 The valence state transformation of uranium.

Currently, uranium reduction involves three mechanisms concerning the specific electron transfer process of uranium. The initial mechanism involves a one-electron reduction process, where U(VI) is first transformed to U(V) through the absorption of a single photogenerated electron, followed by the additional reduction of U(V) to U(IV) from another photogenerated electron. The other approach is the two-electron mechanism, where U(VI) can directly reduce from two photogenerated electrons [30]. In addition, the third mechanism is that in acidic conditions, H^+ participates in the two-electron reduction to accelerate the reduction of U(VI) [31].

Parallel to photoreduction, the electrochemical approach can reduce U(VI) by applying current on the electrode [32]. The electrochemical reduction typically involves the reduction of U(VI) to U(V). The electrochemical reduction occurs at the electrode–electrolyte interface, where U(VI) is first adsorbed on the electrode surface and then reduced through a series of electron transfer steps. These steps are facilitated by the electric field, which lowers the activation energy required for the reduction, thus enhancing the kinetics and efficiency of extraction. The formation of uranium during electrolysis often leads to the precipitation of uranium oxides or hydroxides on the electrode surface, which can be further analyzed or collected for subsequent processing.

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