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Original Article

Study of the Changes in Composition of Ammonium Diuranate with Progress of Precipitation, and Study of the Properties of Ammonium Diuranate and its Subsequent Products Produced from both Uranyl Nitrate and Uranyl Fluoride Solutions

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ABSTRACT

Uranium metal used for fabrication of fuel for research reactors in India is generally produced by magnesio-thermic reduction of UF_4. Performance of magnesio-thermic reaction and recovery and quality of uranium largely depends on properties of UF_4. As ammonium diuranate (ADU) is first product in powder form in the process flow-sheet, properties of UF_4 depend on properties of ADU. ADU is generally produced from uranyl nitrate solution (UNS) for natural uranium metal production and from uranyl fluoride solution (UFS) for low enriched uranium metal production. In present paper, ADU has been produced via both the routes. Variation of uranium recovery and crystal structure and composition of ADU with progress in precipitation reaction has been studied with special attention on first appearance of the precipitate Further, ADU produced by two routes have been calcined to UO_3, then reduced to UO_2 and hydroflorinated to UF_4. Effect of two different process routes of ADU precipitation on the characteristics of ADU, UO_3, UO_2 and UF_4 were studied here.

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1. Introduction

The role of research reactors for the development of a nuclear program of any country is well established [1–3]. Research reactors are utilized to produce radioisotopes and offer irradiation facilities for testing various nuclear fuel and structural materials [4,5]. Radioisotopes such as Co-60, Cs-137, and I-131 are used in the fields of medicine, industries, agriculture, and food processing [6]. Apart from these, research reactors are also used for neutron beam research activity, testing neutron detectors, testing materials for mew power plant, training of manpower, etc. With a rapid expansion of the nuclear program in India, more research reactors are needed for nuclear technology as they contribute to the creation of essential infrastructure for research and for building capabilities. Metallic uranium of very high purity has been used for the production of research reactor fuel. Uranium production processes are categorized into four groups as follows: (1) reduction of uranium halides with metals, (2) reduction of uranium oxides with metal and carbon, (3) electrolytic reduction, and (4) disproportionation or thermal decomposition of uranium halides [7]. Reduction of uranium tetrafluoride with calcium or magnesium is one of the main industrial methods for producing pure uranium ingot. Ammonium diuranate (ADU) is the first intermediate product in solid powder form in the flow sheet of uranium metal ingot production [8]. ADU is generally produced from uranyl nitrate for natural uranium fuel production and from uranyl fluoride for low enriched uranium fuel production. In both the production processes, uranyl solution (either nitrate or fluoride) reacts with ammonia (either gaseous or aqueous form) and precipitation occurs when the concentration of the product (ADU) exceeds its solubility.

$$UO_2\,(NO_3)_2 + NH_3 + H_2O \rightarrow (NH_4)_2U_2O_7\ (ADU)\downarrow + NH_4NO_3 + H_2O \quad (1)$$

$$UO_2F_2 + NH_3 + H_2O \rightarrow (NH_4)_2U_2O_7\ (ADU)\downarrow + NH_4F + H_2O \quad (2)$$

This process is called reactive precipitation or crystallization. Reaction, nucleation, growth, agglomeration, and breakage are the kinetics of reactive precipitation [9,10]. As the formula suggests, the ratio of NH_3:U should be 1; however, several authors [11–18] reported variable NH_3:U ratios, varying from 0.15 to 0.6 depending on the production procedure. However, practically no systematic study was carried out to observe how the composition and structure of ammonium uranate change during the course of precipitation. ADU is further calcined to UO_3. The UO_3 is then reduced to UO_2, followed by hydrofluorination of UO_2 to UF_4. Uranium metal ingot is produced by magnesio-thermic reduction (MTR) of UF_4. The performance of MTR reaction and recovery of uranium largely depend on the properties of UF_4 [19–21]. UF_4 normally contains a small amount of uranyl fluoride (UO_2F_2), known as a water-soluble content; unconverted uranium oxides; moisture, and a small amount of free acid (HF). UO_2F_2 in UF_4 plays a major role in the reduction reaction. UO_2F_2, when heated in the presence of moisture, hydrolyzes to UO_3 and HF. UO_3 remains unreduced during the MTR, and as a result, the bomb yield decreases. HF reacts with magnesium and forms a refractory MgF_2 film on magnesium, which hinders the vaporization of magnesium chips and the triggering of the reaction is delayed. Hydrogen generated by this side reaction reacts with UO_2F_2, producing harmful HF again. The unconverted uranium oxide present in the green salt is a mixture of all the unhydrofluorinated oxides. These oxides neither get reduced during the course of the reaction nor get dissolved in the slag, and as a result, reduce the fluidity of the slag and the separation of metal and slag. The tap density of UF_4 is also important for the performance of MTR operation [5,21]. In the present study, ADU has been produced by reactions of gaseous ammonia with both uranyl nitrate and uranyl fluoride. The progress of ADU precipitation has been observed very closely, with special attention on the first appearance of the precipitate for both nitrate and fluoride routes. Changes of recovery and composition with pH and time have also been observed during the course of precipitation. ADU produced by both the routes have been calcined to UO_3, further reduced to UO_2, and hydrofluorinated to UF_4 under similar conditions. Both chemical and physical properties of the products have been analyzed carefully to understand how the properties of UF_4 are inherited from its precursors.

2. Materials and methods

ADU precipitation reaction was carried out in a 3 L agitated glass reactor (10 of Fig. 1) of 0.150 m diameter. The reactor was fitted with four equally spaced 15-mm-wide baffles. A

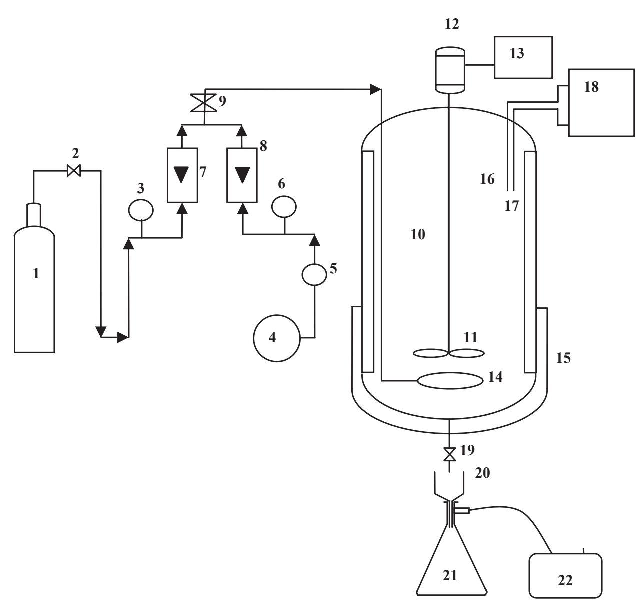

Fig. 1 – Schematic diagram of ADU precipitation system. The numbers in the figure represent the following: 1, ammonia gas cylinder; 2, pressure reducing valve; 3, pressure gauge; 4, air compressor; 5, pressure regulator; 6, pressure gauge; 7, NH_3 rotameter; 8, air rotameter; 9, nonreturn valve; 10, glass reactor; 11, impeller; 12, motor; 13, variable frequency drive; 14, sparger; 15, muffle heater; 16, pH electrode; 17, PT 100 RTD; 18, pH meter; 19, bottom valve; 20, Buchner funnel; 21, conical flask; and 22, vacuum pump.

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