

Chemical process for recycling of uranium metal chips generated during fuel fabrication of metallic fuel at Fuel Fabrication Facility

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Abstract:

During the fabrication of metallic fuel used for Research Reactor by machining, a large portion of uranium metal ingot got rejected as impure uranium metal chips. The long term storage of uranium metal chips under water leads to the risk of fire hazards due to hydrogen generation and accidental safety hazards because of possible leakage of radioactivity from the storage site. To mitigate risk of fire and accidental leakage of radioactive materials, a chemical process has been developed to oxidase uranium metal chips in sodium hypochlorite solution to hydrated uranyl hydroxide without the risk of hydrogen generation. Various parameters like effect of uranium metal chips to hypochlorite ratio, time and temperature has been evaluated to get optimum process parameter. It is observed that for complete dissolution of uranium metal chips 1g: 15 mL (metal: (10%) hypochlorite) is sufficient for a time period of 30 hours at room temperature. With increase in temperature at 40°C, the dissolution time is reduced to 10-12 hours. The dissolution process has been scaled up to 4 kg batch size and the uranyl hydroxide has been collected using centrifuge with a speed of 2200-2700 rpm. The material produced was dried and dissolved in nitric acid for further purification to nuclear grade ammonium di uranate for reactor fuel application.

Keywords: Uranium, Metal chips, Sodium hypochlorite, Hydrogen, Recycling

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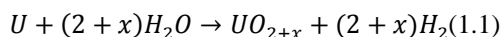
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I. Introduction

Following the discovery of nuclear fission in 1938 by Meitner, Han, Strassmann and Fischer a new era is initiated for possibility of utilization of uranium as nuclear fuel [1, 2]. The first nuclear reactor Experimental Breeder Reactor-I called EBR-1 was built at Idaho's vast desert landscape in the USA where a liquid metal like sodium – or the sodium-potassium alloy used as coolant for better heat transfer than light-water reactors[3]. Further, a large number of nuclear reactors based on enriched uranium as well as natural uranium have been constructed and operated worldwide between 1960 and 1980 for research as well as nuclear power generation[4-10]. Currently, 454 nuclear power reactors producing more than 10% of world's electricity are in operation[11]. In India, twenty two nuclear power reactors are in operation with a total installation capacity of 6780 MW of electricity, major of them are pressurized heavy water reactor (PHWR)[12]. Natural uranium di oxide is used as nuclear fuel for pressurized heavy water power reactor [13, 14]. For fast reactor mixed oxide (MOX) is being as nuclear fuel [14]. India has few research reactors in operational like Dhruva and APSARA II at Bhabha Atomic Research Centre, Mumbai, Kalpakkam Mini Reactor (KAMINI) and fast breeder test reactor (FBTR) at Kalpakkam, IGCAR[15]. Dhruva, a 100MW PHWR reactor based on metallic uranium (natural) rod as nuclear fuel along with aluminum as clade materials and heavy water as moderator as well as coolant. The operation of research reactor, Dhruva is important from the view point of research and training purpose. It is also utilized for the production of radioisotopes for medical application, materials testing using neutron beams, neutron activation analysis etc.

Uranium Extraction Division (UED) of BARC produces in excess of 30 tons of Metallic uranium per year to meet the fuel requirement of Dhruva Reactor. The uranium metal ingots produced then undergoes a series of processes which include machining, vacuum induction melting and a series of thermo-mechanical processes in Atomic Fuels Division (AFD) before the final fabrication of Fuel Assemblies for Dhruva is completed. The machining processes generate a significant quantity of Uranium metal wastes especially in the form of metal turnings, fines, MgF₂ slag discs etc. The uranium metal wastes which are broadly termed as 'U-metal Scraps' or chips, account to approximately 50% of the initial uranium input. Metallic uranium is pyrophoric in nature which burn at air at 241 °C. In open air at room temperature it will rapidly form a layer of uranium oxide, UO_{2+x} due to exposure in oxygen for longer periods [16]. Further exposure to air will leads to the formation of U₃O₈ and UO₃ at the surface of metallic uranium which would increase the air born activities at

the storage site. Currently, the uranium metal chips are stored under water for oxidation and further recycling to nuclear grade ammonium di uranate by Indian Rare Earth Limited (IREL), India. During under water storage, there is a big safety concern on fire hazard due to production of hydrogen and leakage of radioactivity in accidental condition. The metallic uranium readily reacts with water to form uranium oxide along with hydrogen as a reaction product according to the following equation:



Depending upon the chemical environments like temperature (>250°C), value of x may vary from 0 to 0.18 [17-

22]. With rise in temperature of the system between 250 -275 °C there is a formation of U₃O₈ with the x value of 0.67. Further, under water conversion of uranium metal chips to uranium oxides take long time, almost one year which impose shortage of storage space and long time to recycle the materials. A number of alternate process are reported on chemical conversion of uranium metal chips to other compounds mainly for disposal purpose [23-29]. The most popular process is the chemical oxidation of metal chips to uranium oxide using oxygen as oxidant [16]. The main drawback of the air oxidation is risk of air born activity and uncontrolled chemical reaction. Several wet chemical oxidation routes exists for uranium dissolution as metallic uranium is highly reactive with several oxidizing agents and acids [28-29]. Literature shows the use of acids, a mixture of acids and combination of acids with oxidizing agents for the milder dissolution of metallic uranium [23-29]. The prime consideration in the selection of process has been elimination of hydrogen generation, effluent generation and reactivity of reaction. Los Alamos National Laboratory (LANL) has developed a sodium hypochlorite (NaOCl) based chemical process for conversion of depleted uranium metal to UO₂ for disposal to the environment [30]. The uranium metal dissolved in sodium hypochlorite at ambient temperature to U(VI) compound and reduced to UO₂ using sodium thiosulphate. LANL had a geographical disadvantage in terms of effluent handling as the facility was set up in the land locked state of New Mexico in United States. LANL process scale up was dropped mainly because of liquid effluent generation related disposal issue and high capital required. As in the case of UED, a close proximity to sea mitigates the effluent discharge limitation as the major effluent generated in the process in NaCl and Na₂SO₄. As far as the initial capital requirement in concerned, the as the input material is recycled uranium chips that goes back into the process instead of being disposed (as in case of LANL), thus, the process has a financial advantage due to its end use applicability to justify the initial capital cost. Apart from the capital cost upfront, the reagent consumption cost is minimal as NaOCl (used as household bleach) is a cheap reagent.

In the present work, we have demonstrated the safe dissolution of uranium metal chips in sodium hypochlorite solution without hydrogen generation at laboratory scale (5 g) as well as at bench scale (4 Kg). The uranium metal chips dissolved in sodium hypochlorite solution and immediately precipitated as uranyl hydroxide. Various parameters including dissolution time, solid to liquid ratio etc has been optimized. The intermediate product has been characterized as uranyl hydroxide using XRD technique. The intermediate product (uranyl hydroxide) was further processed to produce nuclear grade ammonium di uranate for nuclear grade uranium metal production which will be used a reactor fuel in research reactor, Dhruva, BARC, Mumbai. A detail on effluent generation and waste management strategy has been discussed with respect to current process.

II. Experimental

2.1 Reagents and chemicals

Sodium hypochlorite (NaOCl) (10% w/v supplied by local supplier, Mumbai, India), Tri butyl Phosphate (TBP) (Heavy Water Board, India, 97% pure), and *n*-dodecane (supplied by LobaChemie Pvt Ltd, Mumbai, India) were used without further purification. All other reagents used were of A.R grade unless stated otherwise. Stock solutions of TBP and its mixture were prepared by diluting with *n*-dodecane. Natural uranium metal chips for this study were collected from Uranium Extraction Division (UED), Bhabha Atomic Research Centre. This source was selected as the same grade uranium was supplied to fuel fabrication facility for further processing. The uranium metal chips of size 4-10 cm were stored under water medium before study.

2.2 Instruments

Total X-ray florescence Spectrometer (TXRF, Model XT 2000, G.N.R. Italy, accuracy ±5%), has been utilized for measurement of uranium concentration in effluents. Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, Model Ultima-Expert, Horiba Jobin Yvon SAS, France, accuracy ±2-5%) were used to determine the trace concentrations of uranium and other trace metal ions in different uranium samples and final products during these studies. The crystal structures of intermediate products was evaluated using INL (Model No: EQUINOX-3000) make X-ray diffractometer. The high concentrations of uranium in aqueous and organic

solutions were determined by Davis and Gray method [29]. The free acidity was determined by titrimetry. The concentration of sodium hypochlorite was determined by volumetric titration method using sodium thiosulphate as titrant and starch/iodine mixture as indicator. A thermo-Orion make pH meter containing Ross make glass electrode was used to determine pH of various solutions. Laser Diffraction Particle Size Analyzer from CILAS (Model No. CILAS 1064 Liquid) was used to evaluate the average particle size of various samples.

2.3 Experimental Procedure

The uranium metal chips of size 4-10 cm were stored under water medium before study. A commercially available sodium hypochlorite ~ 10% has been used to study the dissolution behavior of uranium metal chips under various experimental conditions. Initial experiments were carried out using 5 g metal chips under different amount of sodium hypochlorite. The reaction was carried out in a glass beaker at room temperature and continued for longer period till the full dissolution of the metal chips. Further based on experimental data, a 0.5, 1, 2 Kg as well as 4 Kg dissolution batch was decided to carry out the experiment. The experiment was carried out in a tank with water jacket for cooling and stirrer for stirring the whole system of liquid and solid. The intermediate product after dissolution of metallic uranium has been collected using 1L centrifuge with the rotation of 2200-2700 rpm. The crude intermediate product, uranyl hydroxide was dried and dissolved in 8 M HNO₃ to prepare uranyl nitrate solution which was used as feed solution for counter current extraction and purification of crude uranium intermediate product. The ten stages of counter current liquid-liquid extraction were performed using 30 % (v/v) TBP/dodecane mixture in acrylic make mixer settler unit with a mixing capacity of 50 mL at organic to aqueous phase ratio of 1: 1. The stripping of uranium from organic phase was carried out via counter current liquid-liquid extraction mode using demineralized (D.M) water of pH 2 on acrylic made 10 stage mixer settler unit. Finally, the precipitation of uranium as ADU from aqueous stripped solution was performed using ammonia + air mixture at 60 °C temperature. All the experimental results are reported within ± 5% error.

III. RESULTS AND DISCUSSIONS

3.1. Dissolution studies of uranium metal chips

In a beaker when uranium metal chips was stirred with Sodium Hypochlorite solution (NaOCl), the color of the metal chips was changed from black to yellow-orange and temperature was increased from 25 °C to 55 °C. After a certain period (4 h) the temperature start falling and final temperature of the mixed solution become 30 °C. **Figure 1** shows the change of color of the solution and metal chips mixture at different times.

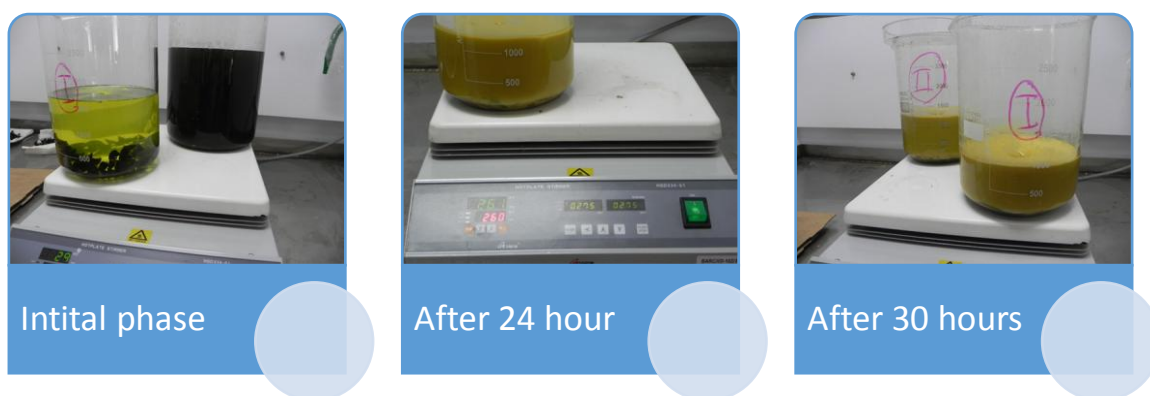


Figure 1: Change of color of the NaOCl solution and metal chips mixture at different times

Variation of uranium metal chip: Hypochlorite ratio was carried out to obtain optimum process condition for complete dissolution of metal chips in reasonable time. **Table 1** shows the dissolution of metal chips at different volume of Hypochlorite solution at ambient condition.

Table 1: Dissolution of metal chips at different volume of Hypochlorite solution at ambient condition

Sr. No	U metal, g	Mixing time, hours	Volume of NaOCl, mL	% Undissolved
1	5	30	47 (minimum)	16.4
2	5	30	52 (10% excess)	8.18
3	5	30	57 (20% excess)	5.86
4	5	30	62 (30% excess)	2.89
5	5	30	67 (40% excess)	0
6	5	30	72 (50% excess)	0

It is observed that for complete dissolution of 5 g uranium metal chips, 67 mL hypochlorite solution is required for a period of 30 hours dissolution time without any temperature regulation. For further study an optimum solid to liquid ratio of 1 g U metal: 15 mL of 10% NaOCl was decided. Literatures data available on dissolution of uranium metal by sodium hypochlorite solution indicated that with controlled temperature at 40°C the dissolution time was drastically reduced to 8-10 hours [25, 30, 32]. Further increase in temperature beyond 40 °C, the degradation of NaOCl will leads to the decrease of the overall efficiency of the dissolution process. Hence 40°C is selected as optimum for safe and complete dissolution of uranium metal chips at reasonable time (10 h). Based on literature data further study was conducted at constant temperature 40 ±2 °C with an optimized solid to liquid ratio of 1 g U metal: 15 mL of 10% NaOCl with different batch sizes ranging from 5 g to 4000 g. **Table 2 shows** the results of metallic uranium chips dissolution at different batch sizes at constant temperature 40 ±2 °C. With increase in batch size from 5 g to 4 Kg there is a complete conversion of uranium metal in to yellow color precipitate and hence the dissolution efficiency of uranium was 100%. The analysis of supernatant solution for uranium content using TXRF technique indicate that at every batch the uranium concentration was less than 1ppm.

Table 2: Dissolution of uranium metal chips at different batch size at constant temperature, T: 40 ±2 °C

Exp. No	U metal, g	Time, h	Volume of NaOCl, mL	% undissolved U metal	[U], ppm in supernatant solution
1	5	10	75	0	<1
2	500	10	750	0	<1
3	1000	10	1500	0	<1
4	2000	10	3000	0	<1
5	4000	10	6000	0	<1

Further, to evaluate the repeatability of the chemical process, at bench scale, a 4Kg batch size was decided and total 10 experiments were carried out to convert 40 Kg metallic uranium chips in to yellow color product. **Figure 2** shows the pictures of detailed experimental set up for scaling up of dissolution batch size up to 4 Kg.



Figure 2: Experimental set up for dissolution of uranium metal chips using sodium hypochlorite solution, Batch Size: 4 Kg.

The yellow product collected was washed with distilled water and dried at oven at 120°C and send for further characterization. X ray diffraction (XRD) technique was used to evaluate the chemical composition of the yellow product. **Figure 3** shows the XRD profile of the final product. The peaks at 2θ: 38.88, 45.57 and 56.59 is matching with uranyl hydroxide (UO₂(OH)₂). The particle size analysis of the yellow product was investigated using laser diffraction particle size analyser and its average particle size was ~10 μm. The collection of uranyl hydroxide was carried out using centrifuge of 1 L capacity at 2500-2700 rpm and the supernatant solution was stored for further treatment.

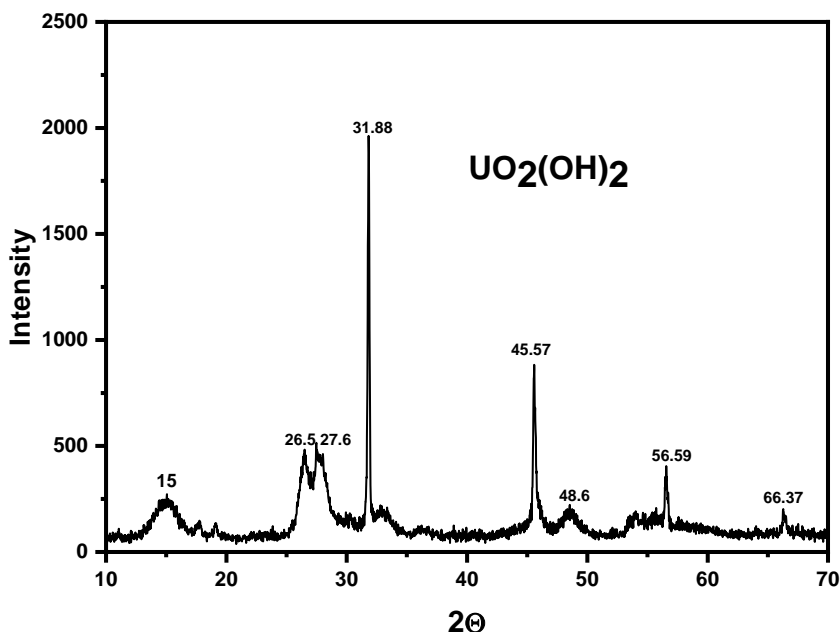
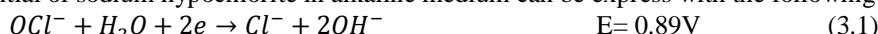


Figure 3: XRD of U metal dissolution product (uranyl hydroxyl, UO₂(OH)₂) using NaOCl solution

3.2. Chemistry of metallic uranium dissolution in NaOCl medium

The electrode potential diagram of U(0)/U(VI) system in 1M HClO₄ is given in **Figure 4**. Similarly the standard electrode potential of sodium hypochlorite in alkaline medium can be express with the following equation:



The electrode potential of Hypochlorite system is 0.89V which is much higher than the U(0)/U(VI) and hence the sodium hypochlorite acts as strong oxidant which convert all U(0) to U(VI) i.e. metallic uranium to uranyl hydroxide. Uranium metal chips containing UO₂ or hydrated UO₂ will not be stable in hypochlorite media. In alkaline media, the electrode potential of U(IV)–U(VI) system is 0.69 V which is much lower than sodium hypochlorite system (0.89V) and hence all the UO₂ present in metallic uranium will oxidise to uranyl hydroxide [33-36].

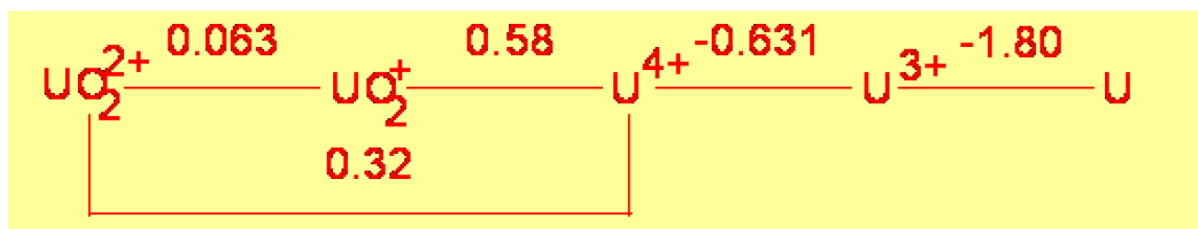
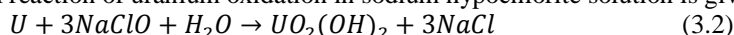
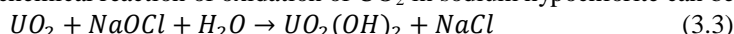


Figure 4: Electrochemical potential of uranium in different oxidation state at 1M HClO₄ solution

The overall chemical reaction of uranium oxidation in sodium hypochlorite solution is given below:



Similarly the overall chemical reaction of oxidation of UO₂ in sodium hypochlorite can be express as [36]:



Assuming uniform linear oxidation at all metal surface, with increase in hydroxide growth there is a decrease in oxidation of metallic uranium as the rate of reaction is caused by thermal diffusion or charged particle migration

and inversely proportional to the oxide layer thickness. The rate of dissolution is dominated by migration of anionic species like OH⁻, O²⁻ OCl⁻ or a combination from hydroxide layer to metal surface and hence a diffusion controlled chemical reaction was observed. During the gradual increase in thickness of hydroxide layer on uranium metal surface because of corrosion, elastic strain is gradually formed due to difference in density between metal (19.1 g/cm³) and oxide (10.97g/cm³) which leads to the formation of more porous and delaminated layer at the metal-hydroxide interface. Phenomena like active creaking and spallation often increase the rate of reaction for a short period of time as after creaking a fresh metal surface is exposed to the reactive species (OH⁻, OCl⁻, O²⁻) for further progress of corrosion reaction. Formation of hydroxide layer at metal surface will diminish the rate of dissolution reaction. The cyclic process is repeated till the reaction is completed.

3.3. Filtration and Uranium Cake recovery

The Uranyl hydroxide cake formed is sticky in nature and is recovered using a centrifuge. The filtrate contains residual un-reacted NaOCl, NaCl and NaOH. The solution approximately has a pH of 9-11.

3.4. Uranium Cake processing

The wet containing some amount of residual chlorine is re-dissolved in nitric acid followed by Solvent extraction using TBP in a non-metallic mixer settler unit. Rest of the process remains in-line with the existing process for uranium purification and recovery.

3.5. Waste Generation and Treatment

Approximately 15 L of liquid effluent is generated per kg of U metal chips processed. The effluent mainly contains residual NaOCl, NaCl and NaOH. The effluent is first neutralized from pH 9 to pH 7 by the addition of small amounts of H₂SO₄. This is followed by addition of small amounts of sodium thiosulphate as reducing agent for residual hypochlorite. This can be followed by direct sea disposal

3.6. Associated Reactions

3.6.1. Scrubbing of Chlorine Gas

On rare occasions chlorine gas may be liberated due to complex side reactions. NaOH lye scrubbing will be used for the removal of Chlorine gas generated.



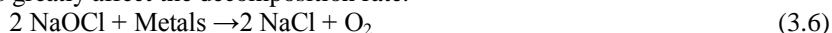
3.6.2. Spontaneous Decomposition of NaOCl (During Storage)

The primary pathway of NaOCl decomposition lead to the formation of sodium chlorate salt. Which if present in higher concentration can lead to precipitation. Reaction is pH, temperature and concentration dependent.



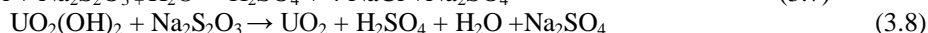
3.6.3. Decomposition of NaOCl during Reaction with Uranium

The primary pathway for NaOCl decomposition during reaction with uranium is by the formation of oxygen. Transition metals greatly affect the decomposition rate.



3.6.4. Residual hypochlorite Neutralization

Hypochlorite can be neutralized by a variety of oxidizing or reducing agents. The most preferred reaction for the process is using sodium thiosulphate. Excess thiosulphate will reduced some amount of uranyl hydroxide also.



3.7. Purification of the uranyl hydroxide to nuclear grade ammonium di uranate

The 5 kg of uranyl hydroxide dried in the furnace at 250 °C was dissolved in nitric acid solution to make feed solution having uranium concentration of 120 g/L and free acidity of 2.1. A 10 stage mixer settler was utilized to conduct counter current extraction using 30 % TBP with aqueous to organic phase ratio of 1:1. **Table 3** shows the counter current extraction data of each stages.

Table 3: Counter current extraction of uranium from nitric acid medium using 30% TBP-dodecane; [U]: 120 g/L; F.A: 2.1 M HNO₃, O/A: 1:1

Stages	[U] _{Org.} g/L	[U] _{Aqr.} g/L
1	110.52 (Loaded Org)	108.92
2	107.58	108
3	106.99	102
4	105.81	88.85
5	95.82	41.79
6	61.14	8.21
7	3.06	0.59
8	0.71	0.027
9	0.41	0.018
10	0.28	0.012 (Raffinate)

Feed	120 (FA: 2.1)	
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It is observed that after 8 stages complete extraction of uranium from aqueous phase to organic phase is achieved. The uranium concentration in organic phase after 10 stages of extraction is 110 g/L and uranium concentration and raffinate end after 10 stages is 0.012 g/L. Similarly the stripping of uranium from loaded organic phase was carried out using 10 stage mixer settler system with demineralized water of phase ratio aqueous: organic of 1:1. **Table 4** shows the stage wise concentration profile of uranium in lean solvent and aqueous phase.

Table 4: Counter current stripping of uranium from uranium loaded 30% TBP-dodecane using DM water at pH~2; O/A: 1:1

Stages	[U] _{org} , g/L	[U] _{Aq} , g/L
1	61.73	69.76 (UNPS)
2	32.92	42.47
3	12.35	23.75
4	4.41	8.34
5	0.29	1.72
6	0.65	0.55
7	0.53	0.26
8	0.47	0.25
9	0.47	0.21
10	0.41 (LS)	0.14

After 10 stages of counter current stripping the uranium concentration in lean solvent become 0.4g/L and concentration of the aqueous phase become ~61 g/L. The uranium from stripped solution was precipitated as ammonium di uranate using gaseous ammonia at 60°C. The analysis of ADUC qualifies the nuclear grade purity (**Table 5**). **Figure 5** shows the whole process for conversion of metallic uranium to nuclear grade ammonium di uranate.

Table 5: Analysis impurities of ammonium diuranate (ADU) cake produced after purification of uranyl hydroxide using liquid-liquid extraction followed by precipitation with gaseous ammonia

Elements	Concentration, ppm
Fe	23
Al	<1
Cr	<1
Mg	40
Ni	<1
B	<0.12
Cd	<0.12
Co	<1.2
Ce	<0.2
Sm	<0.1
Gd	<0.04
Dy	<0.1
Er	<0.1
Eu	<0.04
Y	<0.1
Yb	<0.1



Figure 5: a) Metallic uranium chips

b) Dissolution of U chips in NaOCl



c) Uranyl hydroxide (UO₂(OH)₂)

d) Nuclear grade ammonium di uranate (ADU)

3.8. Effluent Data Generation on Batch Experiments (Bench Scale)

10 Nos of Batch experiments consisting of 4 Kg batches of standardized dissolution process parameters such as reaction temperature at ~ 40°C and optimum Uranium metal to hypochlorite ratio [1 :15, 10% (w/v)] sodium hypochlorite were carried out for the following purpose:

- i. Estimation & variation of residual sodium hypochlorite content in the Effluent
- ii. Estimation & variation of residual chlorine content in the filtered uranyl hydroxide cake
- iii. Estimation & variation of Activity levels in the Effluent solution

The data obtained and the method used is listed below:

a) Residual Sodium Hypochlorite in Effluent

For every batch of experiment, the residual NaOCl has been determined using titration technique and results are given in Table 6. It is observed that for every batch of dissolution of metallic uranium chips in sodium hypochlorite solution the residual NaOCl contains in effluent is very low (> 0.1%) which is below safe discharge limit.

Table 6: Residual Sodium Hypochlorite in Effluent

Sl. No.	Batch No.	Aliquot (mL)	Na ₂ S ₂ O ₃ (N)	Na ₂ S ₂ O ₃ (mL)	NaOCl (N)	NaOCl, % (w/v)
1	1	10	0.10095	2.3	0.02322	0.086
2	2	10	0.10095	1.23	0.01242	0.046
3	3	10	0.10095	0.48	0.00485	0.018
4	4	10	0.10095	2.85	0.02877	0.107
5	5	10	0.10095	0.3	0.00303	0.011
6	6	10	0.10095	0.5	0.00505	0.019
7	7	10	0.10095	0.48	0.00485	0.018

8	8	10	0.10095	0.65	0.00656	0.024
9	9	10	0.10095	0.35	0.00353	0.013
10	10	10	0.10095	0.28	0.00283	0.011

Method used:

Classical Iodometric titration using acetic acid and sodium thiosulphate. Sodium hypochlorite being an oxidizing agent reacts with acetic acid in the presence of potassium iodide to release Iodine as per the equation given below:



Equivalent moles of Iodine release is titrated against Sodium thiosulphate as reducing agent in the presence of Starch Indicator equation (3.10)



b) Residual Chlorine Content in Uranyl Hydroxide Cake

Residual chlorine content of the obtain uranyl hydroxide cake is carried out using classical gravimetric method using silver nitrate as precipitating agent. The amount of silver chloride precipitated directly equates to the amount of chlorine present in the cake. A total of 6 batches of uranyl nitrate cake were analyzed after the filtration and drying, after the wet chemical oxidation process. The result of which are tabulated in the **table 7** below.

Table 7: Residual Chlorine Content in Uranyl Hydroxide Cake

Sl. No.	Sample Wt. (gm)	Makeup Volume (mL)	Aliquot (mL)	5% AgNO ₃ (mL)	AgCl (gm)	Total Cl (%)
1	5	100	10	10	0.1535	7.594
2	5	100	10	10	0.1485	7.346
3	5	100	10	7	0.1544	7.638
4	5	100	10	7	0.1516	7.500
5	5	100	10	5	0.1485	7.346
6	5	100	10	5	0.1497	7.406

Note: Residual NaOCl was also analyzed in the dried UO₂(OH)₂ cake, the results returned an expected BDL value. But as the results don't have any analytical significance the results weren't tabulated.

c) Activity in NaOCl Effluent solution

The effluent generated from the dissolution batches were analyzed for alpha and beta activity before confirming to disposal regulations. Activity levels in the effluent were below detectable limit in all the 10 batches analyzed (**Table 8**). This implicates that there is no solubility of uranium hydroxide in the alkaline effluent solution.

Table 8: Activity in NaOCl Effluent solutions

Batch No.	[U], ppm	α Activity (Bq/ml)	β Activity (Bq/ml)
1	1	BDL	BDL
2	0.05	BDL	BDL
3	0.50	BDL	BDL
4	0.20	BDL	BDL
5	0.53	BDL	BDL
6	0.51	BDL	BDL
7	0.38	BDL	BDL
8	0.23	BDL	BDL
9	0.16	BDL	BDL
10	0.20	BDL	BDL

3.9. Advantages of Uranium metal dissolution in NaOCl over storage under water

Storage under water	NaOCl dissolution process
Under water storage of uranium metal chips will produce hydrated UO ₂ along with hydrogen which catch fire. It is not safe on the view point of fire hazard.	NaOCl dissolution will produce uranyl hydroxide without any hydrogen generation and hence it is a safe chemical process
Under water reaction of uranium metal chips is very slow and it takes almost a year to convert all metallic uranium in to UO ₂ or mixed oxide for further processing.	The NaOCl dissolution of metallic uranium is fast enough (10-12 Hours) to recycle the waste uranium metallic chips to a usable products.
As conversion of metallic uranium chips takes almost one year, a large amount of storage space is required for storage of such	Since, the process is sufficiently fast, the metallic uranium chips could be recycled with a reasonable time and hence a very little

radioactive materials with fire as well as radioactive spillage safety.

storage space is required for storage of uranium metal chips.

IV. CONCLUSIONS

A hypochlorite based chemical dissolution process has been developed for safely dissolution of uranium metal chips at ambient temperature without any hydrogen generation. For 5 g sample complete dissolution of metal chips was observed with 67 mL 10% hypochlorite solution for a period of 30 hours. With increase in temperature at 40 °C the reaction time reduce to 10-12 hours. Variation of solid to liquid ratio and temperature indicate that for complete dissolution every 1 Kg of uranium chips 15 Liter of NaOCl (10% v/v) is required at 40 °C for a period of 10 hours. The metallic uranium dissolution in NaOCl solution would leads to the formation of uranyl hydroxide which was purified to nuclear grade ammonium di uranate cake by liquid-liquid extraction followed by precipitation with gaseous ammonia. The process can be utilized for recycling of uranium metal chips coming from uranium metal fabrication plant.

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