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Purification of Crude Sodium Di-Uranate from Tummalapalle Source, India to Nuclear Grade Ammonium Di-Uranate Using Sulphamic Acid Dissolution Route

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Abstract: Crude Sodium Di-Uranate (SDU) from the Tummalapalle mine in India contains 2-3% (w/w) silica, in addition to 5-7% (w/w) organic matter, including polyacrylamides and humic masses, with 2-5% Zirconium (Zr) (w/w) as major impurities. Hence, the direct conversion of SDU to Nuclear Grade (NG) Ammonium Di-Uranate Cake (ADUC) for fuel fabrication via the HNO_3-Tributyl Phosphate (TBP) extraction route is onerous due to silica gel creation. The third phase inception indicates the presence of excess Zr, and micro-emulsion formation confirms that organic matter introduces difficulties in the filtration, recovery, and purification stages. Various analytical techniques, such as X-Ray Diffraction Analysis (XRD), Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray Spectroscopy (EDS), Fourier Transform Infrared Spectroscopy (FTIR), and Inductively Coupled Optical Emission Spectrometry (ICP-OES), have been utilized to characterize the raw material (SDU), intermediate products (gel and residues), as well as the final product (NG-ADUC). In this research, an innovative, novel route for the dissolution of SDU employing sulphamic acid (25% w/v) to remove silica, organic matter, and Zr, followed by the conventional route to NG-ADU, eliminates the three major process difficulties, namely (i) gelation, (ii) third phase formation, and (iii) microemulsion formation. In addition, the sulphamic acid-extracted Uranium (U)-bearing stream ultimately achieves 99.5% overall U recovery and produces nuclear-grade U with desirable morphological characteristics.

Keywords**:** Uranium, Sodium Di-Uranate, sulphamic acid, gel, silica

1. Introduction

The success of the nuclear power programme of a country like India depends on its own resource of U.[1-3] In India, the main resources of U can broadly be divided into two categories: primary sources like U ore present in different geological basins (Singhbhum Shear zone, Cuddapha basin, Mahadek basin, Bhima basin, and Delhi Super-group of rocks) and secondary sources like Monazite sand and phosphate rock.[4-8] Recently India has discovered a large size of U mineralization in Vempalle dolostone at Tummalapalle, Cuddapa basin Andhra Pradesh (AP).[6,7,9-11] It is the largest U deposit in the country accounting for almost 52% of the total deposit (1, 44, 541 metric tonnes).[12] Tummalapalle reserve has a lean tenor concentration of 0.042% of U_3O_8 confined in the host rock of alkali (dolomite and calcite).[13] The major composition of the ore is carbonate (~80%), Quartz and feldspar clasts (~12.15%), cellophane (~3.9%),

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pyrites (~1.24%).[5, 13-16] Due to the presence of excess carbonate, carbonate leaching of U is the only preferable option for recovery of U from Tummalapalle ore.[17-18] A number of steps such as ore crushing, grinding, high pressure, and high temperature leaching followed by decantation and clarification are involved to produce pregnant liquor. Typical concentration of U impregnate liquor vary from 0.6-1.2 g/L.[19] The recovery of U from Tummalapalle ore is carried out using an alkaline leaching process where the ore is leached with a mixture of $Na_2CO_3/NaHCO_3$ in presence of air at 9 bar pressure and 130-140 °C in autoclave.[19,20] During alkali leaching of U ore, a large amount of silica as sodium silicate, humic acid, and fulvic acid are leached into the pregnant solution.[20] The chemical reactions involving the overall process from leaching to final product (SDU) preparation can be described with the following chemical reactions:[19,20]

$$UO_2 + \frac{1}{2}O_2 \rightarrow UO_3 \tag{1}$$

$$UO_3 + 3Na_2CO_3 + H_2O \rightarrow Na_4UO_2(CO_3)_3 + 2NaOH \tag{2}$$

$$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O \tag{3}$$

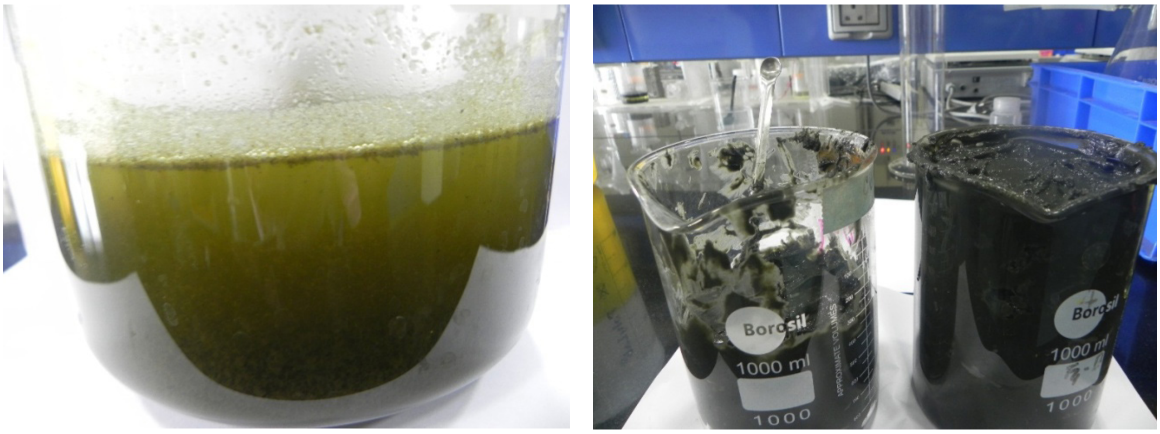
$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O \tag{4}$$

$$2Na_4UO_2(CO_3)_3 + 6NaOH \rightarrow Na_2U_2O_7 + 6Na_2CO_3 + 3H_2O \tag{5}$$

The pyrites and other sulphide minerals are also oxidized to sodium sulphate and solubilized in leach liquor during the alkali pressure leaching according to the following equations:

$$2FeS_2 + 7O_2 + 8Na_2CO_3 + 6H_2O \rightarrow 2Fe(OH)_2 + 4Na_2SO_4 + 8NaHCO_3 \tag{6}$$

Flocculants are added during two stages of crude SDU processing. Nonionic polyacrylamides are added during the pressure filtration stage just proceeding the alkaline leaching whereas Anionic flocculants Flomin 4995/Magnafloc 611 are essentially modified polyacrylamide/polyacrylic based flocculants are used during the precipitation stage of crude SDU production. The addition of polyacrylamides in clarifiers accelerates the solid-liquid separation by liberating U from the finely grounded ore. The solution containing fine suspended solids and clarifying agents are removed by a pre-coated Rotary Vacuum Drum Filter (RVDF). The pregnant liquor containing 0.6-1.2 g/L U is processed further to recover U. Finally, the U in leach liquor is precipitated with NaOH solution at atmospheric pressure and 50-60 °C as SDU. Magnesium and calcium silicates formed at a high concentration of NaOH (~25 g/L) are precipitated along with SDU as its solubility is limited at the highly alkaline solution. The precipitated SDU is later spray dried in air at 500 °C causing the partial thermal degradation of polyacrylamides and humic substances present in the final SDU ore concentrate. HNO_3-TBP route is a widely accepted process for purification of any crude U raw materials to nuclear grade U compounds.[8, 21-23] For counter-current extraction of U via the TBP-HNO_3 route, the crude U compounds must be completely dissolved in nitric acid medium. The dissolution of crude SDU, Tummalapalle source in nitric acid is incomplete with respect to recovery of U. The presence of silica/silicate leads to the formation of gel-like structures of silicones which prevent complete leaching and filtration of U.[24] The gel recovered after the dissolution of SDU in nitric acid medium contains ~7-8% (w/w) U which is difficult to recover and purify. Further, the presence of Zr in percentage level creates a third phase formation whereas the presence of acid-soluble fulvic acid, degraded humic acid, and degradation products of polyacrylamides and humic mass create microemulsion formation at the aqueous-organic interface during countercurrent extraction of U via HNO_3-TBP-dodecane route using mixer settler setup.[25,26] The presence of a trace amount of Dibutyl Phosphate (DBP) in TBP leads to the formation of white precipitate in presence of Zr.[27] On the other hand, air drying of SDU ore concentrate leads to the formation of low molecular weight degraded organic substrates that later dissolve in nitric acid or oxidizes to form carboxylic acid moieties causing emulsion formation in the mixer settler system.[25] Figure 1 shows the 1.5 L of gel recovered during the dissolution of 5 kg SDU in nitric acid medium. Similarly, Figure 2 shows the microemulsion formation at the organic-aqueous interface during counter-current extraction. Dissolution of SDU in other acidic mediums like sulphuric acid, hydrochloric acid does not solve the problem of gel, the third phase, and microemulsion formation. This clearly indicates that there is a need for a new process development for purification of crude SDU obtained from carbonate leach solution of Tummalapalle source, India.



(a) During dissolution of SDU

(b) Gel obtain after decantation of uranium

Figure 1. Gel formation during dissolution of SDU in nitric acid medium

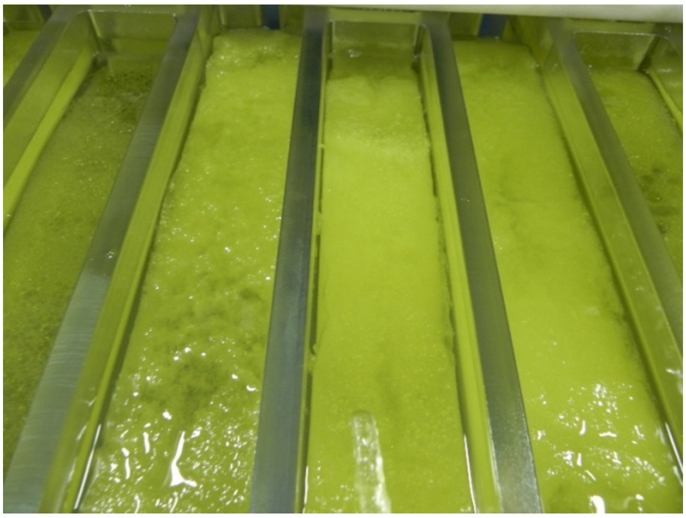


Figure 2. Permanent emulsions formed at interface of mixer settler during solvent extraction of SDU dissolved in nitric acid medium

The main aim of this study is to develop a purification process of crude SDU of Tummalapalle specific source to nuclear grade ADUC without any gel as well as third phase formation. As those phenomena create technical difficulty during the purification of crude SDU via the HNO_3-TBP-dodecane solvent extraction route.

In the present work, sulphamic acid dissolution is used as an intermediate step for the reduction in Zr carryover with simultaneous prevention of gelation caused due to silicates present in crude SDU. This is followed by purification to nuclear grade Ammonium Di-Urinate (ADU) through conventional solvent extraction route using TBP-n-dodecane as extractant.[28]

2. Experimental

2.1 *Reagents and chemicals*

TBP (Heavy Water Board, India, 97% pure), Sulphamic acid (95% pure, supplied by S D Fine Chem Ltd., Mumbai, India), and n-dodecane (supplied by Loba Chemie Pvt Ltd., Mumbai, India) were used without further purification. All other reagents used were of Analytical Reagent (AR) grade unless stated otherwise. Stock solutions of TBP and its mixture were prepared by diluting with n-dodecane. Crude SDU from the Tummalapalle source was collected from Uranium Corporation of India Limited (UCIL) the purity of which is given in Table 1.

Table 1. composition of SDU

Element/Compound	% Mass
$Na_2U_2O_7$	79.9 ± 1.5#
$ZrO(CO_3)_2$	4.41 ± 0.05#
Na_2CO_3	5.4 ± 0.05*
Mg as silicate	2.2 ± 0.02*
SiO_2 as Silicate	3.1 ± 0.03*
Polyacrylamide and humic mass	5.1 ± 0.05$
Trace element	0.12 ± 0.006*

Determined by EDXRF
* Determined by ICP-OES
$ Determined by loss of ignition
CO_3^{2-} Determined by potentiometric method

2.2 *Instruments*

UV-1800 (Shimazu, Japan) (accuracy ± 2%), Energy-Dispersive X-Ray Fluorescence (EDXRF), Model No. EX-6600SDD (Xenemetrix Ltd., Israel, accuracy ± 2%) was used to determine U concentration and Zr concentration in various samples. Thermo Fischer Scientific make Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) machines (accuracy ± 2-5%) were used to determine the trace concentrations of U and other trace metal ions in different U samples during these studies. The crystal structures of SDU were evaluated using INL (Model No: EQUINOX-3000) to make X-Ray diffractometer. The Bruker, Germany make FTIR, Model V-70 with ATR system was used to collect the FTIR spectra of various samples. Scanning Electron Microscope (Quanta 200) with EDS detector has been utilized for surface analysis of U samples. The high concentrations of U in organic solutions were determined by Davis and Gray method.[29] The free acidity was determined by titrimetry. A thermo-Orion make pH meter containing Ross make glass electrode was used to determine the 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 30% (v/v) TBP was prepared by dissolving 30 mL TBP in dodecane solution and the volume of the solution was make up to 100 mL. The crude SDU is dissolved in Sulphamic acid solution (25% w/v) at room temperature under vigorous stirring and the dissolution was completed within one hour. The slurry containing U was filtered with the Buckner funnel. The concentration of Crud Uranyl Nitrate (CUN) was 100 g/L, at pH 1.5. The resultant uranyl sulphamate solution was precipitated as ADU using an air-ammonia mixture. The crude ADUC was calcined at 800 °C to remove fulvic acid and other dissolved organic compounds. The calcined ADU, i.e. crude U_3O_8 was dissolved in 8 M HNO_3 to prepare uranyl nitrate solution which was used as feed solution for counter-current extraction and purification of U. 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 2 : 1. Similarly, ten stages of counter-current liquid-liquid scrubbing of U from the organic phase were carried out with the help of 0.5 M HNO_3 solution at a phase ratio of organic: aqueous 10 : 1. The stripping of U from the 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 U as ADU from an aqueous stripped solution was performed using ammonia + air mixture at 60 °C temperature. All the experimental results are reported within ± 5% error.

3. Results and discussions

3.1 *Characterization of crude Sodium Di-Uranate*

The characterization of SDU, Tummalapalle, UCIL, India, was carried out using various instrumental analysis like XRD, SEM with EDS, FTIR, ICP-OES, etc. The crystal structure and identity of the materials as SDU was confirmed from XRD analysis (Figure 3). The intense peaks at 2θ: 15, 26.67, 28, and 33° is matching with the $Na_2U_2O_7$ compound (JCPDS file No. 00-043-0347).[30] The SDU crystal is monoclinic in nature with the Space group of C2/m (12) and unit cell parameters of a = 12.796000 Å, b = 7.822000 Å, c = 6.896000 Å, β = 111.419998°. The total cell unit volume is 642.549988 $Å^3$.

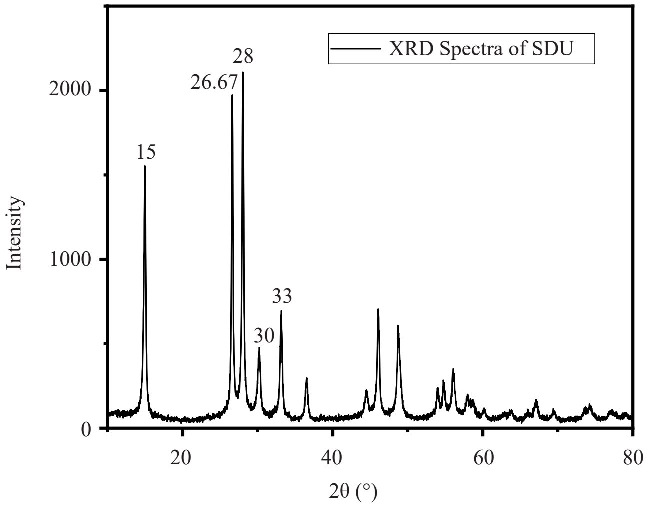


Figure 3. X-Ray Diffraction Spectra of SDU collected from Tummalapalle, UCIL, India

The surface properties and surface structure of the SDU were evaluated using Scanning Electron Microscopic (SEM) analysis. Figure 4 is the SEM images of SDU under different magnifications. A close look of the SEM image reveals the non-uniform particle size distribution of SDU and each particle is a collection of the number of small particles. The large grain is a porous and cloud-like structure with average grains size of 16 µm. The elemental analysis of the samples was carried out in the small region of the SEM images with the help of Energy Dispersive X-Ray analysis (Figure 5).

The major elements present in the samples are Uranium (U), Nitrogen (N), Oxygen (O), Sodium (Na), Zirconium (Zr), Silicon (Si). The several peaks of gold (Au) in EDS spectra are due to the sample preparation step where the gold coating is used to prepare the sample specimen for SEM analysis. Further, Quantitative analysis of Zr and Si are carried out in EDXRF and ICP-OES. Table 1 shows the various chemical compound present in crude SDU collected from Tummalapalle, UCIL, India. The presence of various functional groups in SDU was evaluated using FTIR analysis (Figure 6).

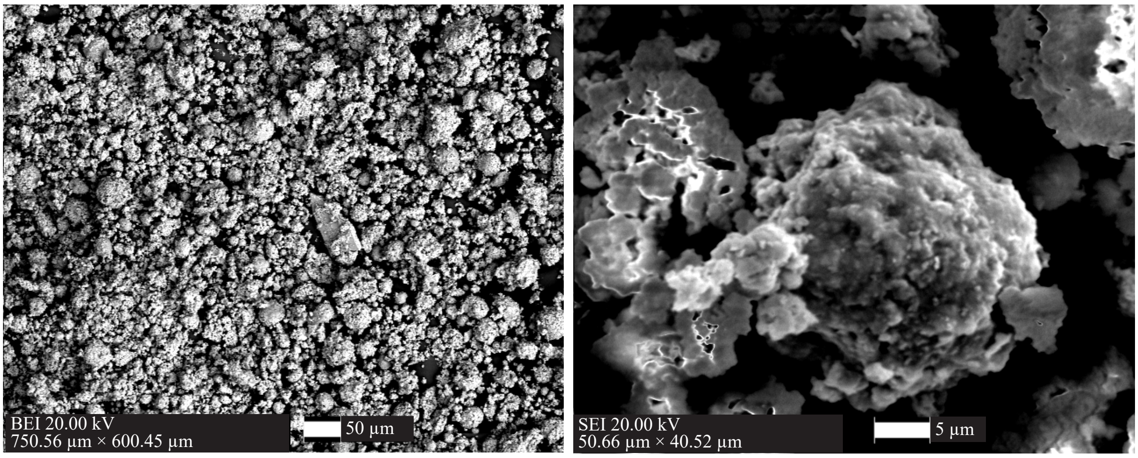


Figure 4. Scanning Electron Microscopic (SEM) images of SDU collected from Tummalapalle, UCIL, India at different magnification

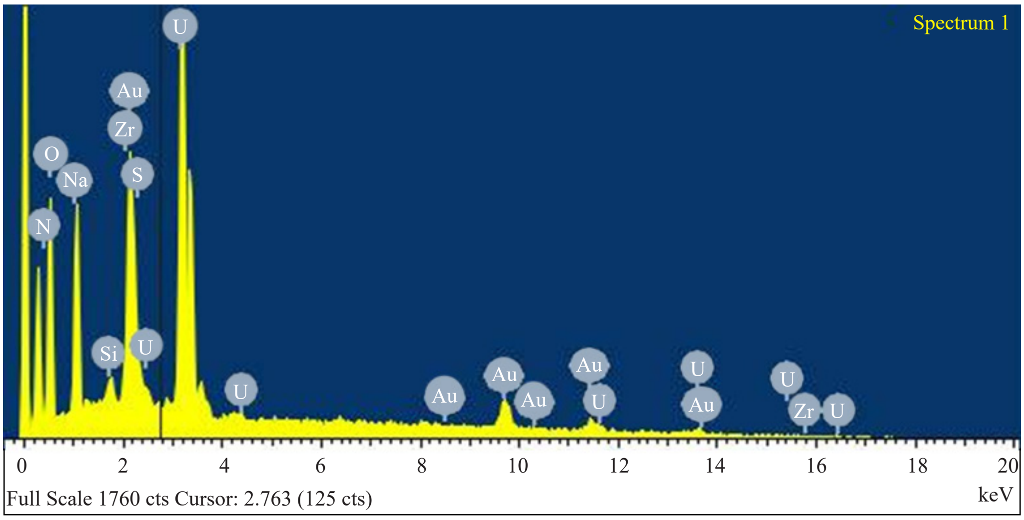


Figure 5. Elemental analysis of SDU collected from Tummalapalle, UCIL, India using EDS analysis

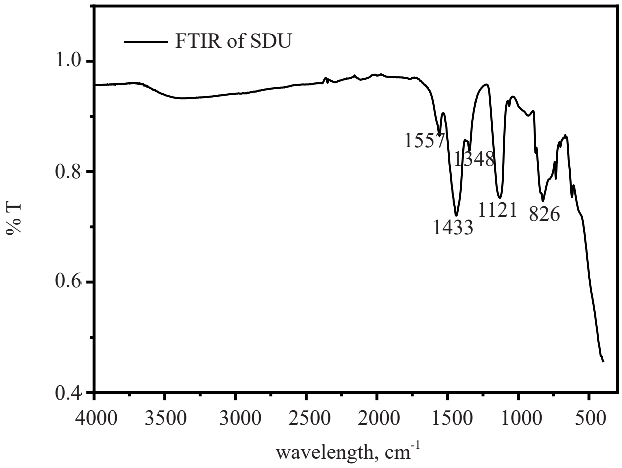


Figure 6. FTIR Spectra of SDU collected from Tummalapalle, UCIL, India

The peaks at 1557 (w) cm^{-1}, 1433 (s) cm^{-1}, 1348 (w) cm^{-1}, and 1121 (s) cm^{-1} are due to presence of C-O (bending), C=O (Carbonate/organic carbonyl), \$ NH_2 and C-O (Carbonate/organic carbonyl) functional group. The strong absorption at the 826 cm^{-1} regions indicates the characteristic SDU present in the sample.[31]

3.2 *Selection of acids*

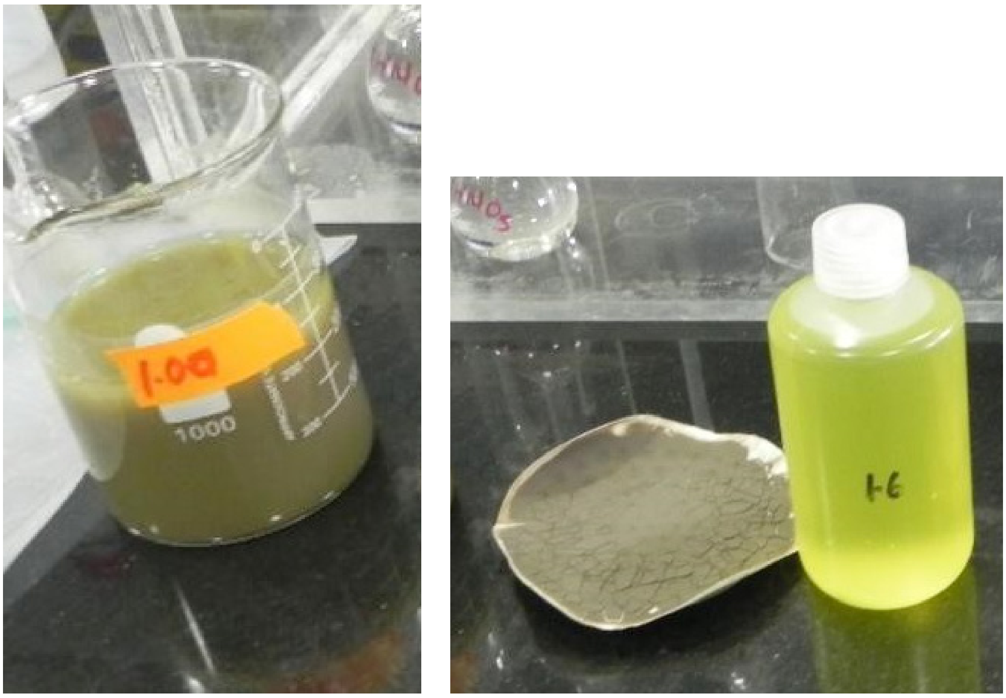
The dissolution of crude SDU was carried out in different acidic solutions like HNO_3 (8 M) H_2SO_4 (4 M) and Sulphamic acid (25%). The dissolution of SDU in those acids except Sulphamic acid formed a hydrogel (Figure 7).

(a) A partially filterable gel obtained after of SDU in sulphuric acid

(b) Gel obtained after dissolution of SDU in dissolution nitric acid through decantation

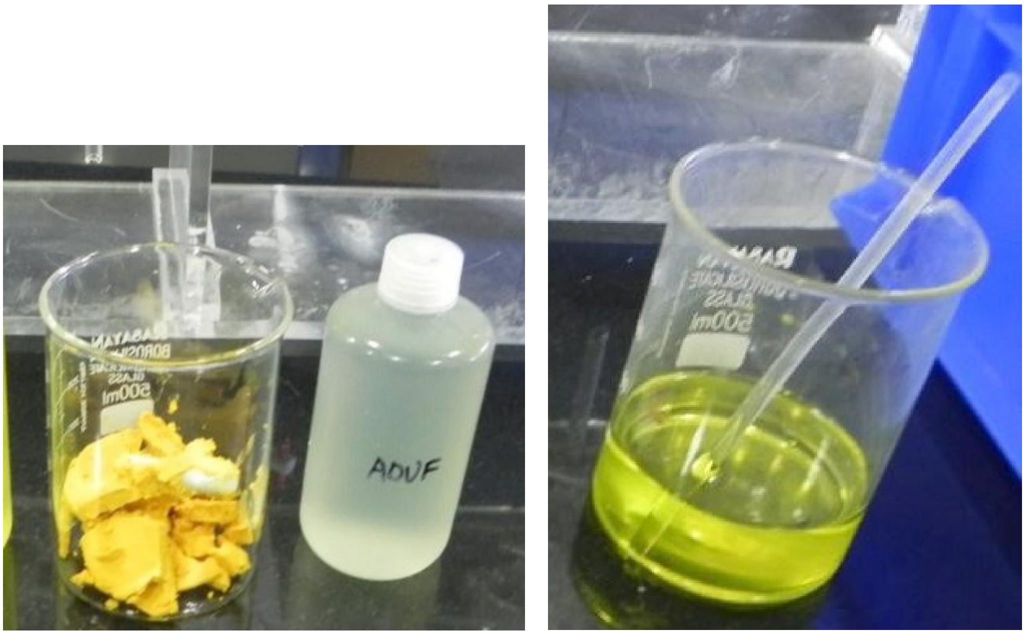
Figure 7. Gel formation during dissolution of crude SDU in different acids

The filtration of gel using a conventional filter like vacuum filter is not possible and the gel in presence of Zr, humic acid, and fulvic acid create third phase and micro-emulsion during solvent extraction of U using 30% (v/v) TBP-dodecane in counter-current mode. On the other hand, the gel contains 10-15% (w/w) U along with an excess amount of water which is difficult to recover. The crude SDU contains ~3.24% (w/w) sodium silicate which gets hydrolyzed in presence of acid and water and gets converted into a gel called silicones.[32,33] Similarly, the polyacrylamide, humic acid present in crude SDU, may also contribute to the gel formation as they have a strong affinity towards water. The FTIR analysis, as well as Scanning Electron Microscopic (SEM) analysis along with EDS analysis of gel, indicate the presence of a large amount of silicate, iron, Zr, and U (ESI-1). The analysis of the U and Zr ratio in gel samples was carried out using the EDXRF technique. The results indicate that in SDU powder only a small amount of Zr is present whereas in gel almost 45-55% Zr with respect to U is present (ESI-1). Further FTIR data of gel indicates the presence of silica (ESI-1). The gel contains mainly silica, Zr, and U along a large amount of water in nitric acid medium. With the increase in pH of the solution containing silica from 0-9, there is a decrease in gel formation at pH 1-3 with a minimum value at pH ~2 which is the isoelectric point of silica with maximum gel lag time.[32] Further increase in pH again leads to the formation of the gel. The dissolution of SDU containing silica in HNO_3, H_2SO_4 leads to the formation of gel as the pH of the resulting solution is less than 1. On the other side, the dissolution of SDU in Sulphamic acid leads to the selective dissolution of U leaving silica, polyacrylamide, humic acid, and Zr in residue and there is no gel formation because the pH of the resulting solution is 1.7, which is close to the isoelectric point of silica (Figure 8a, b, c & d).



(a) SDU in sulphamic acid solution

(b) Residue and uranyl sulphamate solution



(c) Ammonium Di-Uranate and filtrate

(d) Uranyl nitrate solution after dissolution of Ammonium Di-Uranate in HNO_3

Figure 8. Different stages of SDU processing in sulphamic acid solution

The polyacrylamides in the presence of a strong acidic medium undergo hydrolysis forming a cross-linked globular polyamine structure and polyacrylic acid, which in turn absorbs dissolved U and Zr nitrates to contribute to the retention of metals in the gel. Experimental results show that during the dissolution of 5 Kg SDU in 8 M, 8 L HNO_3 medium, there is a 2.4 Kg gel generation which occupied a volume of 1.5 L (Table 2).

Table 2. Dissolution of 5 Kg SDU in 8 M, 8 L nitric acid solution

Parameters	Value
Gel volume occupied in solution	4 L (50%, v/v)
Gel volume after compression using decantation at 700 G	1.5 L (18.75%)
Weight of gel	2.4 Kg
U content in gel	14.66 (w/v) %
U content in gel after 1st wash	6.35 (w/v) %
U content in gel after 2nd wash	2.41 (w/v) %

Being a weak acid Sulphamic acid prevents polymerization of silica in solution which prevents gel formation. Similarly, the presence of-NH_2 group in Sulphamic acid may prevent water uptake in polyacrylamides as-NH_2 group is more basic than water. The dissolution of SDU in Sulphamic acid leads to the formation of slurry that can be filtered easily through a vacuum filter with a clear-cut solid-liquid separation (Figure 9). The U recovery using Sulphamic acid is 99.5% (w/w) in the dissolution stage. Hence, for further study, we have used Sulphamic acid to dissolved U from crude SDU.

Figure 9. Silica/silicate, Zr and Polyacrylamides separated from crude SDU dissolved in sulphamic acid

3.3 *Optimization of dissolution parameters*

The Sulphamic acid can selectively leach U from SDU leaving all the polyacrylamide and partially leaving transition elements like vanadium, Zr, etc. in the residue. 25 g SDU containing initial 2.2% (w/w) of Zr and ~10% (w/w) of polyacrylamide as major impurities was dissolved in 25% (w/v) Sulphamic acid at various SDU/Sulphamic acid weight ratio at room temperature with vigorous stirring. The solution is filtered with 22-micron filter paper and residue is analyzed for % weight. The dissolution of SDU in Sulphamic acid does not show any gel formation. Table 3 shows the results of the leaching of U from solid SDU in 25% (w/v) sulphamic acid solution at room temperature. With an increase in SDU/sulphamic acid (w/w) ratio there is an increase in U leaching from the solid SDU and it becomes optimum at 0.8-1 where almost 90-99.5% (w/w) U gets leached from SDU. Similarly, with the increase in SDU/

Sulphamic acid ratio, there is a decrease in the weight of residue (undissolved SDU) and it becomes constant at 1-1.4 which accounts for the mass of Zr and polyacrylamide. The decrease in residue with a further increase in weight ratio is due to excess dissolution of polyacrylamide in Sulphamic acid medium. For, further study, a ratio of 1 is taken as the optimum ratio for maximum leaching of U from SDU.

Table 3. Leaching of U from crude SDU using different concentration of Sulphamic acid

Sr. No	SDU/Sulphamic acid ratio	% U leaching (w/w)	Zr/U ratio (w/w)	Residue (g)	% Na_2SiO_3 in residue (w/w)
1	0.2 ± 0.002	0.1 ± 0.001	0.18 ± 0.002	22.30 ± 0.112	3.09 ± 0.062
2	0.4 ± 0.004	0.35 ± 0.0035	0.36 ± 0.003	20.6 ± 0.101	3.08 ± 0.062
3	0.6 ± 0.006	6.6 ± 0.0066	0.38 ± 0.004	7.80 ± 0.039	2.75 ± 0.055
4	0.8 ± 0.008	90 ± 0.009	0.5 ± 0.005	2.86 ± 0.0143	2.24 ± 0.045
5	1 ± 0.001	99.5 ± 0.01	0.51 ± 0.005	2.31 ± 0.012	1.34 ± 0.027
6	1.2 ± 0.0012	99.8 ± 0.01	0.65 ± 0.006	2.03 ± 0.010	1.26 ± 0.025
7	1.4 ± 0.0014	99.9 ± 0.01	0.81 ± 0.008	2 ± 0.010	1.23 ± 0.025
8	1.6 ± 0.0016	99.9 ± 0.01	0.89 ± 0.009	1.54 ± 0.008	1.23 ± 0.025

It is interesting to note that with an increase to weight ratio from 0.2 to 1.6 there is an increase in Zr leaching from SDU to U solution from 0.18% to 0.89% (w/w) by weight while at a 0.8-1 (w/w) ratio is becomes constant to 0.5% (w/w). A similar leaching experiment is carried out with SDU containing a high % of Zr (5% w/w) and results show that the sulphamic acid can reduce the Zr leaching to a 0.5 at weight ratio of 1 (Table 4). The constant value of Zr in leach solution (0.5) may be the solubility limit of Zr in Sulphamic acid medium at that particular concentration.

Table 4. Leaching of Zr from crude SDU containing different amount of Zr

Sr. No	Initial Zr/U (w/w) ratio in SDU	Zr/U (w/w) in leach solution
1	1.1 ± 0.011	0.5 ± 0.005
2	2.2 ± 0.022	0.5 ± 0.005
3	5.1 ± 0.051	0.51 ± 0.005

3.4 *Precipitation of Uranium from Sulphamic acid medium*

The precipitation of U from Sulphamic acid medium is carried out using various chemical reagents like NaOH, KOH, H_2O_2, and gaseous ammonia. With NaOH, KOH, and gaseous ammonia the U is precipitated as SDU, KDU, and ADU quantitatively leaving < 10 ppm U in the filtrate (Table 5).

The average particle size of the precipitate is in the range of 15-20 microns. The precipitation of U from Sulphamic acid leach solution using H_2O_2 at a pH range of 3-4 is incomplete. The incomplete precipitation of U in the H_2O_2 medium may be due to the more complexing ability of Sulphamic acid with U as compared to other acidic mediums. Further, dissolved organic or fulvic acid may play a crucial role in the incomplete precipitation of U by polymerization and complexation of organic compounds with U. However, gaseous ammonia is chosen as a precipitating agent because the ammonium salt of U, humic acid, and fulvic acid are easily converted to other products at low temperature as compared to other forms of salts like Na or K salts.[34]

Table 5. Precipitation of U from Sulphamic acid medium using different chemical agents

Chemical agent for U precipitation	U concentration in filtrate
KOH	< 10 ± 0.5 ppm
NaOH	< 10 ± 0.5 ppm
Ammonia-air	< 10 ± 0.5 ppm
H_2O_2	2 ± 0.02 g/L

3.5 *Removal of humic acid and fulvic acid*

Literature survey indicates that humic acid and fulvic acids are classes of organic polyaromatic compounds which are soluble in alkaline medium. They are associated with U (mainly in carbonate ore) in the earth's crust.[35] During leaching of U using carbonate solution, the leaching of humic acid and fulvic acid is possible in leached solution, and precipitation of humic acid and fulvic acid along with U precipitation from leached solution using NaOH leads to the formation of crude SDU containing sodium humate and fulvate.[35] Currently, there is no method available for the removal of humic acid and fulvic acid from U-containing SDU or ADU. The removal of humic acid and fulvic acid from crude ADU was carried out by calcining crude ADU at 700-800 °C. Literature data shows that > 80% humic acid and fulvic acid can be removed by heating at 800 °C.[34]

3.6 *Dissolution of crude Uranium oxide*

The calcination of crude ADU at 800 °C leads to the formation of U oxide called crude U_3O_8 and the dissolution of crude U_3O_8 was carried out in 8 M HNO_3 to obtained crude uranyl nitrate solution. The humic masses, fulvic acids, and other dissolved organic compounds (coming from the degradation of polyacrylamides) during calcination are converted to acid-insoluble organic nitrates (red mass in Figure 10 after dissolution in nitric acid) which is filtered through a vacuum filter.

Figure 10. Acid insoluble obtained after dissolution of U_3O_8 (obtained by calcination of Ammonium Di-Uranate) in nitric acid medium

The red mass obtained is vacuum dried at 100 °C and qualitative analysis was carried out to identify the nature of the functional group present using FTIR as we expect it is a mixture of organic compound coming from humic acid and fulvic acid. Figure 11 showed the FTIR spectra of red mass recorded from 4000-500 cm^{-1}.

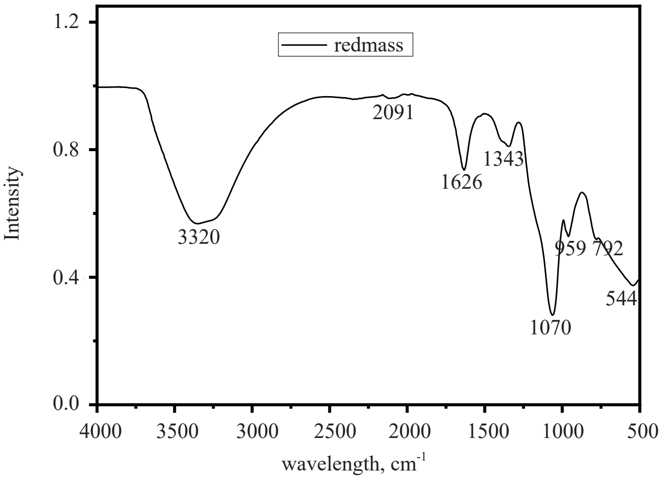


Figure 11. FTIR Spectra of red mass obtained after dissolution of crude U oxide (obtained from calcination of Ammonium Di-Uranate) in nitric acid

The intense and broad peak at 3320 cm^{-1} is due to the presence of the O-H group where at sharp peaks at 1626 cm^{-1}, 1343 cm^{-1}, and 1070 cm^{-1} are confirmed the presence of NH_2, C=O, \$ NH_2, and C-O or C-N aliphatic bonds in the organic compounds. The crude uranyl nitrate solution after filtration is used as a feed solution for counter-current extraction of U using 30% TBP in 10 stages mixer settler unit.

3.7 *Countercurrent extraction of Uranium using 30% TBP-dodecane mixture*

For counter-current extraction of U using 30% TBP-dodecane medium, it is important to generate a Mc-Cabe-Thiele diagram of U extraction under similar conditions. For plant scale implementation of the process, we have to construct a Mc-Cabe-Thiele diagram at the different nitric acid concentrations as the free acidity of uranyl nitrate feed solution may vary from batch to batch in plant scale. The Mc-Cabe-Thiele diagrams were generated by the extraction of various concentrations of U solution in fixed nitric acid concentration. The feed solutions for the generation of the Mc-Cabe-Thiele diagram at fixed acidity were prepared by dissolution of nuclear grade pure U_3O_8 in nitric acid medium. Figure 12 shows the Mc-Cabe-Thiele diagram of extraction of U at the various nitric acid concentrations (1.1 M, 2.1 M, and 3.1 M).

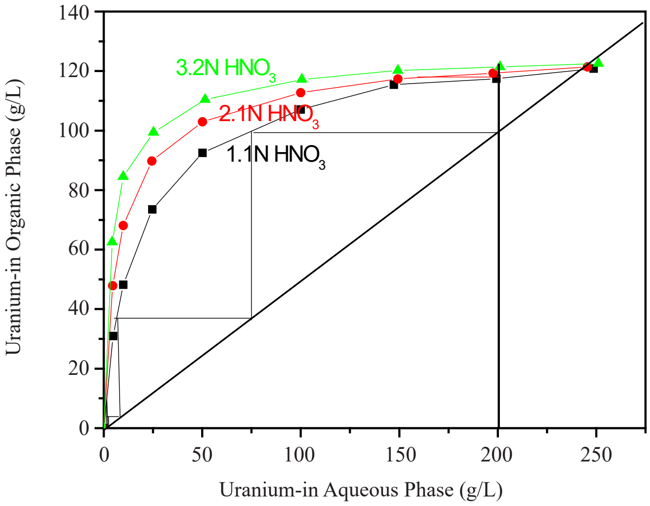


Figure 12. Mc-Cabe-Thiele diagram of extraction of U from nitric acid medium using 30% TBP-dodecane mixture

Theoretically, for a feed concentration of 200 g/L U and at organic: aqueous 2 : 1 ratio a total 3 number of stages were needed for complete extraction of U from the aqueous phase. Practically, counter current extraction of U using 210 g/L U and 2.1 Free Acidities (FA) were conducted in a 10 stages acrylic make mixer settler system. With the increase in the number of stages, there is a steady decrease in U concentration in the aqueous phase and an increase in the organic phase (Table 6). Experimental data indicates that only 3 stages are required to recover all U from the aqueous phase to the organic phase leaving all the impurities in the raffinate under the above condition which is confirmed with the theoretical calculation of a number of stages from the Mc-Cabe-Thiele diagrams. The U concentration in raffinate becomes constant (< 0.01 g/L) at the 6th stage. On the other side, the maximum concentration of U in the organic phase can reach up to 120 g/L, which is the saturation level of 30% TBP-dodecane mixture.

Table 6. Counter current extraction of U from nitric acid medium using 30% TBP-dodecane; [U]: 210 g/L; FA: 2.1 M HNO_3, O/A: 2 : 1; T: 25 °C, P: 1atm

Stages	$[U]_{Org}$	$[U]_{Aq}$
1	120.55 ± 1.205 (Loaded Org)	32 ± 0.32
2	64.86 ± 0.649	12 ± 0.12
3	12.85 ± 0.128	0.75 ± 0.075
4	3 ± 0.03	0.13 ± 0.013
5	0.72 ± 0.007	0.04 ± 0.004
6	0.24 ± 0.002	< 0.01 ± 0.001
7	0.18 ± 0.002	< 0.01 ± 0.001
8	0.18 ± 0.002	< 0.01 ± 0.001
9	0.18 ± 0.002	< 0.01 ± 0.001
10	0.18 ± 0.002	< 0.01 ± 0.001 (Raffinate)
Feed	210 ± 2.1 (FA: 2.1)	

3.8 *Scrubbing of organic phase using 0.5 M nitric acid*

Table 7. Counter current scrubbing of impurities from U loaded 30% TBP-dodecane phase using 0.5 M HNO_3, O/A: 10 : 1; T: 25 °C, P: 1atm

Stages	$[U]_{Org}$	$[U]_{Aq}$
1	120.89 ± 1.209	140.85 ± 1.485
2	116.39 ± 1.164	140.89 ± 1.408
3	115.20 ± 1.152	139.62 ± 1.396
4	112.82 ± 1.128	137.19 ± 1.372
5	110.34 ± 1.103	136.81 ± 1.368
6	109.85 ± 1.098	132.63 ± 1.326
7	110.82 ± 1.108	127.35 ± 1.274
8	110.45 ± 1.104	119.93 ± 1.199
9	105.70 ± 1.057	115.63 ± 1.156
10	95.60 ± 0.956	113.66 ± 1.137

The scrubbing of U from U loaded in 30% TBP-dodecane mixture was carried out at 10 : 1 Organic: aqueous (Org: Aq) phase ratio to scrub all unwanted impurities in 10 stages mixer settler system leaving most of the U in the organic phase. With the increase in the number of stages, there is a decrease in U concentration in the organic phase and it became 95.6 g/L at the 10th stage, while with the increase in the number of stages there is an increase in U concentration in the aqueous phase from 113 to 140 g/L (Table 7).

3.9 *Counter current stripping of Uranium from the organic phase*

Mc-Cabe-Thiele diagram on counter current stripping of U from loaded organic (30% TBP-dodecane) using distilled water was available in the literature[23] where organic: aqueous phase ratio was kept constant at 1 : 1. The literature data indicates that a six (6) number of stages are sufficient to strip all U from 30% TBP-dodecane mixture containing 100 g/L U in the organic phase at room temperature. Based on literature data, a 10 stages counter current stripping of U was carried out to strip U from the loaded organic phase at a phase ratio of organic: aqueous, 1 : 1 at room temperature with the initial concentration of U at 95.6 g/L. Instead of pure distilled water, we have to use distilled water at pH 2 to prevent emulsion formation during stripping. With the increase in the number of stages, there is an increase in U concentration in the aqueous phase and a decrease in the organic phase. The present study indicates that 9 stages of counter-current stripping are required to strip all U in the aqueous phase if we use distilled water at pH 2 (Table 8). The difference in the theoretical stages and experimental stages is due to the use of distilled water at pH 2, which is less efficient than distilled water.

Table 8. Counter current stripping of U from U loaded 30% TBP-dodecane using DM water at pH ~2; O/A: 1 : 1; T: 25 °C, P: 1atm

Stages	$[U]_{Org}$	$[U]_{Aq}$
1	81.95 ± 0.819	93.8 ± 0.938 (UNPS)
2	68.29 ± 0.683	76.81 ± 0.768
3	57.60 ± 0.576	63.12 ± 0.631
4	48.50 ± 0.485	52.74 ± 0.527
5	39.15 ± 0.391	42.39 ± 0.424
6	23.37 ± 0.234	33.18 ± 0.332
7	9.50 ± 0.095	20.62 ± 0.206
8	2.64 ± 0.0264	10.12 ± 0.101
9	0.96 ± 0.01	4.73 ± 0.047
10	0.54 ± 0.005 (LS)	1.83 ± 0.018

3.10 *Nuclear grade ADUC preparation*

The stripping of U from the 30% TBP-dodecane phase generates a nuclear grade pure uranyl nitrate solution called UNPS which contains ~60-65 g/L U. The recovery of U from the UNPS solution was carried out by precipitation method using gaseous ammonia. The precipitation of U was performed at 60 °C using an air-ammonia mixture in a SS 304 L make reactor vessel under a stirring condition (Figure 13).

The flow rate of air: ammonia was kept constant at 10 : 1. The pH of the solution was monitor from time to time and at pH 8 the flow of the air ammonia mixture was stopped. The reaction mixture was left under a stirring condition for 1 hour and Ammonium Di-Urinate (ADU) was the filter through a filtration unit under vacuum using a 5-micron pore size filter cloth (Figure 14).

Figure 13. Precipitation of U from stripped solution after purification through HNO_3-TBP route as ADUC using air-ammonia mixture

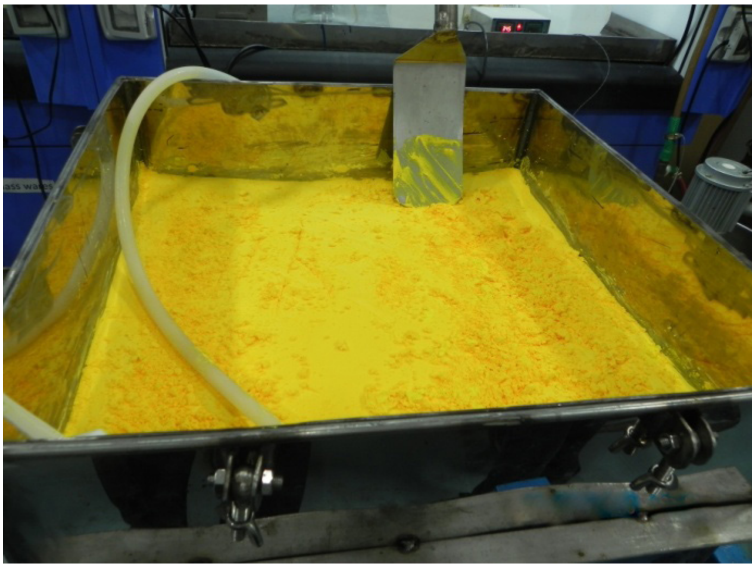


Figure 14. Filtration of nuclear grade ADUC using pan filter under vacuum

The U concentration in the filtrate was < 10 ppm. The distribution of particle size of dried ADU powder was measured using a laser diffraction particle size analyzer and the average particle size was calculated as ~21 microns. The chemical analysis of impurities present in ADU was measured using the ICP-OES technique and analytical data indicate that the ADU satisfies the quality control criteria of nuclear grade (Table 9).

Table 9. Analysis of ADUC prepared from crude SDU

Elements	Concentration, ppm
Fe	5 ± 0.25
Al	< 1 ± 0.05
Cr	< 1 ± 0.05
Mg	< 1 ± 0.05
Ni	< 1 ± 0.05
B	< 0.12 ± 0.006
Cd	< 0.12 ± 0.006
Co	< 1.2 ± 0.06
Ce	< 0.2 ± 0.01
Sm	< 0.1 ± 0.006
Gd	< 0.04 ± 0.002
Dy	< 0.1 ± 0.005
Er	< 0.1 ± 0.005
Eu	< 0.04 ± 0.002
Y	< 0.1 ± 0.005
Yb	< 0.1 ± 0.005

3.11 *Preparation of process flow-sheet*

Based on optimized experimental conditions a process flow-sheet for preparation of nuclear grade ADUC from crude SDU, Tummalapalle source has been prepared (Figure 15). The crude SDU containing polyacrylamides, fulvic acid, and other metallic impurities were dissolved in a 1 : 1 (w/w) ratio of 25% Sulphamic acid solution at room temperature. U from leach solution is recovered as crude ADU using air-ammonia mixture and crude ADU is calcined at 700-800 °C to obtain crude U_3O_8. In the next step, U_3O_8 is dissolved in 6-8 M nitric acid to obtain the crude Uranyl Nitrate Solution (UNS). The UNS is a filter to remove acid-insoluble organic matter and U, free acidity is adjusted to prepared feed solution. The counter-current solvent extraction of the feed solution was carried out using 30% TBP-dodecane. Similarly, scrubbing and stripping of U were carried out using 0.5 M nitric acid and distilled water at pH 2. Finally, the U from strip solution was precipitated as nuclear grade ADU using air-ammonia mixture at 60 °C. The effluent ammonium salt of Sulphamic acid will go for regeneration and recycling in the 1st dissolution step.

4. Conclusions

The crude SDU, Tummalapalle source, India, contains 3-4% silica, 5-7% polyacrylamides, 2-5% Zr, humic acid, and fulvic acid as major impurities. The dissolution of crude SDU in nitric acid, as well as sulphuric acid, leads to the formation of gel which creates a problem for further processing like solid-liquid separation using established filtration techniques. The dissolved organic like humic acid, fulvic acid, or degraded polymers form microemulsion during countercurrent extraction of U from the nitric acid medium using 30% TBP-dodecane in mixer settler unit. The presence of excess Zr leads to the formation of the third phase during countercurrent extraction of U. A sulphamic acid dissolution process followed by precipitation and HNO_3-TBP purification process has been developed for purification of crude SDU to nuclear grade ADUC without gel, the third phase, and microemulsion during the processing of SDU. The ADUC prepared using this process meets the nuclear grade purity.

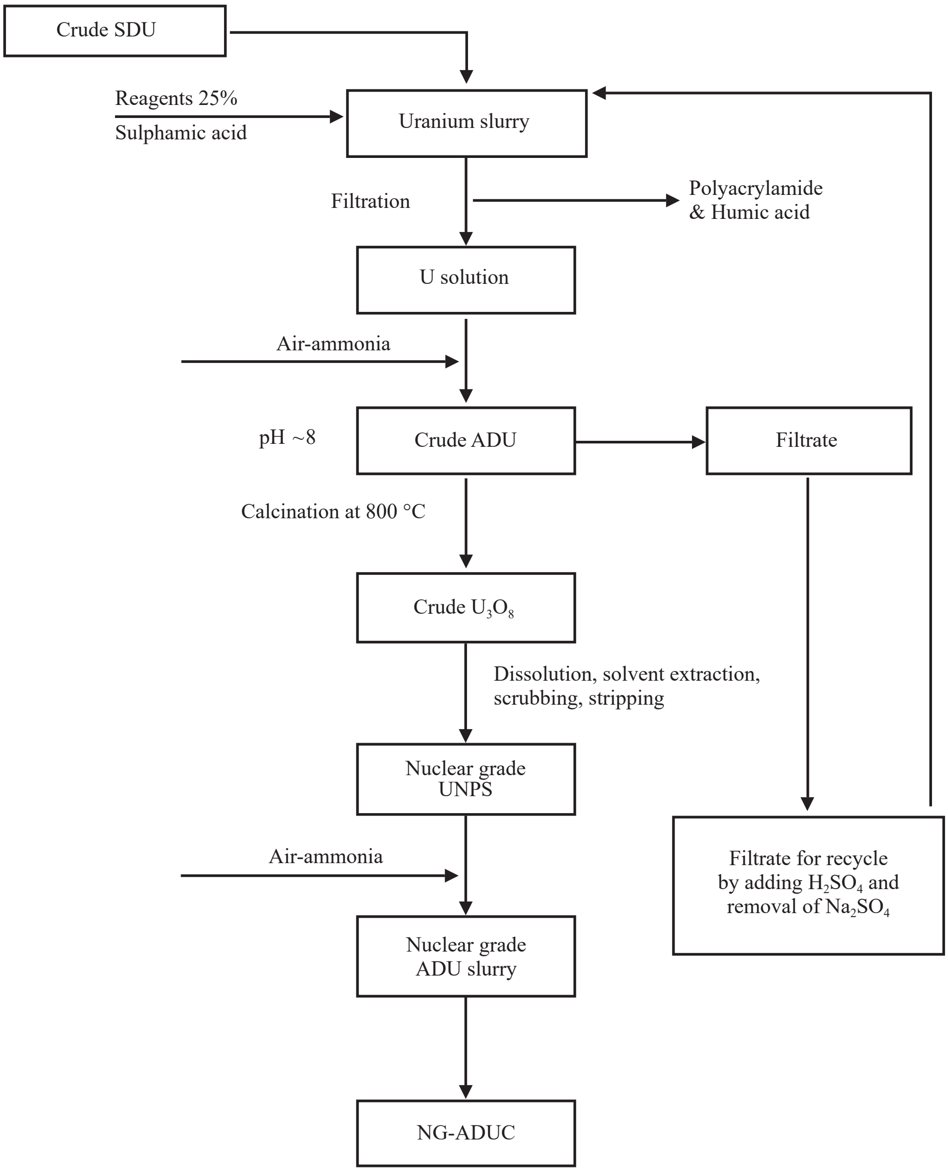


Figure 15. Process flow-sheet for preparation of nuclear grade ADUC from crude SDU, Tummalapalle source, India

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Conflict of interest

The authors declare that they have no competing interest.

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