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Recycling of chemicals from alkaline waste generated during preparation of UO_3 microspheres by sol–gel process

Ashok Kumar, T.V. Vittal Rao, S.K. Mukerjee *, V.N. Vaidya

Fuel Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

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Abstract

Internal gelation process, one of the sol–gel processes for nuclear fuel fabrication, offers many advantages over conventional powder pellet route. However, one of the limitation of the process is generation of large volume of alkaline liquid waste containing hexamethylenetetramine, urea, ammonium nitrate, ammonium hydroxide etc. Presence of ammonium nitrate with hexamethylenetetramine and urea presents a fire hazard which prevents direct disposal of the waste as well as its recycle by evaporation. The paper describes the studies carried out to suitably process the waste. Nitrate was removed from the waste by passing through Dowex 1 × 4 anion exchange resin in OH^- form. 1.0 M NaOH was used to regenerate the resin. The nitrate-free waste was further treated to recover and recycle hexamethylenetetramine, urea and ammonium hydroxide for preparation of UO_3 microspheres. The quality of the microspheres obtained was satisfactory. An optimized flow sheet for processing of the waste solution has been suggested.

PACS: 81.20.Fw; 28.41.Bm; 28.41.Kw; 82.39.Wj

1. Introduction

Sol–gel process offers an alternative route for fuel fabrication. The preparation of UO_2 microspheres by sol–gel process has many advantages over the conventional powder pellet route. One of the sol–gel method viz, Internal Gelation Process, originally developed at the KEMA labs [1] has since been incorporated with various modifications in a number of places throughout the world [2,3]. The process also has been developed at Bhabha Atomic Research Centre (BARC), Mumbai [4] and large quantities of UO_2 fuel prepared.

Fig. 1 gives flow sheet for the preparation of UO_2 pellets by internal gelation process. The process involves preparation of feed broth by mixing cooled acid-deficient uranyl nitrate solution (ADUN) with cooled equimolar mixture of hexamethylenetetramine (HMTA) and urea. The feed broth is dispersed as droplets through a capillary into a gelation column containing hot silicone oil. The gel spheres formed are separated from oil and are first washed with carbon tetrachloride to remove adhering silicone oil followed by ammonium hydroxide to remove ammonium nitrate as well as unreacted

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* Corresponding author. Tel.: +91 22 25594578; fax: +91 22 25505345.
E-mail address: smukerji@magnum.barc.ernet.in (S.K. Mukerjee).

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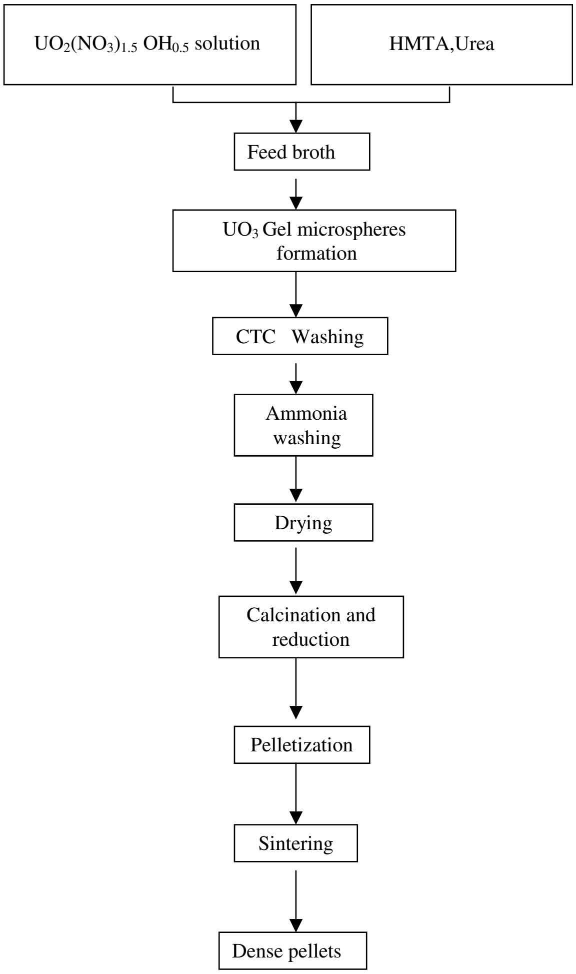


Fig. 1. Flow sheet for the preparation of UO_2 pellets via internal gelation process.

HMTA and urea. Washing with ammonia is essential to prevent cracking of gel spheres during drying step. To ensure survival of the gel spheres, NH_4NO_3 content in the gel has to be decreased by a factor of 1000 [5]. Since NH_4NO_3 is the slowest diffusing species, this is the primary waste generating step.

Preparation of each kg of UO_2 microspheres generates approximately 15 liters of ammonia washing effluent (waste) containing HMTA (0.2 M), urea (0.2 M), NH_4NO_3 (0.3 M) and NH_4OH (3 M). Although lot of work has been carried out towards production aspects of gel microspheres, not much has been done towards proper management of the waste. HMTA and nitrate together are known to form an explosive mixture. Therefore, from safety point of view, neither the waste can be disposed off directly nor can be concentrated by direct evaporation and stored.

Also the fact that only a small percentage of HMTA and urea is utilised during gelation and major part finds its way in the waste stream along with other chemicals, any process leading to safe recycling of the waste is worth considering [6]. In this context, present study was undertaken to suitably process and recycle the waste. Dowex 1×4 resin in combination with NaOH as eluant was used to separate nitrate. However the elution rate was found to decrease as the elution process progressed, and needed a very large volume of eluant for complete regeneration of resin to its original capacity. To overcome this, modifications were incorporated in the loading and elution cycles which lead to better efficiency of the separation of nitrate from the waste limiting the volume of the eluant needed and thus avoiding the generation of large volumes of nitrate bearing secondary waste. The nitrate-free solution so accumulated was distilled at low pressure to recover ammonia. HMTA and urea were concentrated as per requirement of the feed broth. Recovered HMTA and urea were then used for the preparation of UO_3 microspheres.

2. Experimental

2.1. Chemicals

Waste generated during preparation of UO_3 microspheres was used. All other chemicals used were of AR grade.

2.2. Determination of nitrate

Determination of nitrate was carried out spectrophotometrically using Cary-500-SCAN-UV–VIS–NIR spectrophotometer. Absorbance at 302 nm was recorded [7,8]. Other species present in the waste e.g. ammonium hydroxide, HMTA and urea were found to have no effect on absorbance value of nitrate.

2.3. Determination of uranium

Uranium was determined spectrophotometrically using arsenazo (III) as the colour forming agent. Absorbance at 655 nm was recorded [9] using the spectrophotometer mentioned above.

2.4. Thermo-gravimetric studies

SETARAM TG–DTA 92-18 thermal analyzer was used. TG/DTA curves were recorded for pure urea, HMTA, NH_4NO_3, mixture of urea and NH_4NO_3, mixture of HMTA and NH_4NO_3 and actual waste both before and after separation of nitrate. All the experiments were carried out in argon atmosphere at a constant heating rate of 10 K/min. About 1–10 mg of sample was used for each experiment.

2.5. Separation and recovery of waste constituents

2.5.1. Conditioning of Dowex 1 × 4 resin

Since the chloride form of the resin added chloride impurity to the separated HMTA and urea, the resin was converted to hydroxide form using 1.0 M NaOH solution till resin was free of chlorine as confirmed by silver nitrate test. Resin was thoroughly washed with distilled water to remove excess sodium hydroxide.

2.5.2. Separation of nitrate

Experiments were conducted both under batch equilibration conditions as well as through the column.

2.5.2.1. Batch experiments. For batch equilibration studies, 40 g of the resin in OH^- form was taken in a beaker and waste solution was added gradually, taking 20 ml at a time. After every addition of the waste, nitrate content of the supernatant was determined spectrophotometrically at different time intervals. Once nitrate content remained constant (which reached in less than 5 min) with respect to time (equilibrium concentration of nitrate), the next lot of the waste was added. From mass balance, amount of nitrate on the resin was determined. The resin was washed thoroughly with water and then stripped using 1.0 M NaOH taking 20 ml each time. After every addition of NaOH the nitrate content of the supernatant was determined spectrophotometrically at different intervals. Once nitrate content remained constant with time (equilibrium concentration of nitrate), the next lot of NaOH was added. It was observed that the equilibrium concentration of nitrate was reached after 20 min indicating that the resin could take up nitrate quite fast whereas the elution was rather sluggish. This fact was considered in choosing optimum flow rates during column experiments.

2.5.2.2. Column experiments. For column experiments, Dowex 1 × 4 resin (100 g when dry), initially converted to OH^- form as described above, was taken in a glass column (3.0 cm ID). The waste solution was passed through the column at various flow rates. When aim of the experiment was to determine capacity of the resin, waste solution was passed till 100% breakthrough of nitrate was achieved. Later, during separation of nitrate from the other constituents of the waste solution, to avoid contamination of HMTA and urea with nitrate, only that much waste was passed through the column which can be completely made nitrate free (no breakthrough of nitrate). In each case, effluent was assayed for nitrate content spectrophotometrically.

The column was washed with distilled water till effluent was neutral as confirmed by both pH and conductivity measurements. To regenerate the resin sodium hydroxide of different concentration was passed at various flow rates. As described in detail in discussion section, it was not possible to regenerate the resin completely due to slower kinetics of elution even at the optimum condition e.g. higher concentration of sodium hydroxide at slower flow rate. To overcome this modified cycles of loading and elution was employed.

2.5.2.3. Modified cycles for separation of nitrate. In the modified cycles, resin saturated with nitrate was regenerated partially e.g. elution was discontinued once saturation of the resin with respect to nitrate came down to about 60%. This was done to utilise faster kinetics of elution. Accordingly the loading segment of the separation cycle involved saturating the resin with nitrate from about 60% to 95%. Utilising the above mentioned modified cycles bulk of nitrate-free waste was collected for further processing.

2.5.3. Recovery of NH_4OH from the nitrate-free waste solution

The waste solution was distilled at reduced pressure and the NH_3 vapor was collected after passing through ice-cold water trap. By regulating the pressure, temperature was not allowed to exceed 60 °C. Solution left in the distillation flask contained HMTA and urea only. Recovered ammonia was determined by titrating it against standard nitric acid.

2.5.4. Determination of HMTA and urea

The solution left after recovery of ammonia was assayed for its HMTA and urea content.

(I) Determination of HMTA
Content of HMTA and ammonia (if any) was

determined by carrying out pH titration (Toshniwal model CL-54, pH meter) against 0.056 M standard HNO_3. Earlier, taking standard solutions it was observed that urea does not interfere with estimation of ammonia and HMTA. A typical curve depicting variation of pH with amount of standard nitric added is given in Fig. 2. The first and second point of inflexion represents neutralization of ammonium hydroxide and HMTA respectively.

(II) Determination of urea

For determination of urea a suitable aliquot of the sample (free from ammonia) was analysed for total nitrogen using Kjeldahl method [10]. By subtracting nitrogen contribution due to HMTA urea content was determined.

2.5.5. Preparation of UO_3 microspheres using recycled HMTA and urea

Recovered HMTA and urea solution was concentrated to required level. After concentration step HMTA and urea were mixed with ADUN in such a way that final feed composition was [U] = 1.25 M and [HMTA, urea]/[U] = 1.4. Using this feed solution, UO_3 microspheres were prepared by internal gelation process. The spheres were first washed with carbon tetrachloride to remove adhering silicone oil and then with 3 M ammonia solution to remove the reaction products and the unused HMTA and urea from the spheres. The wet microspheres were then dried in air oven at 100 °C for four hours to get dry UO_3 microspheres.

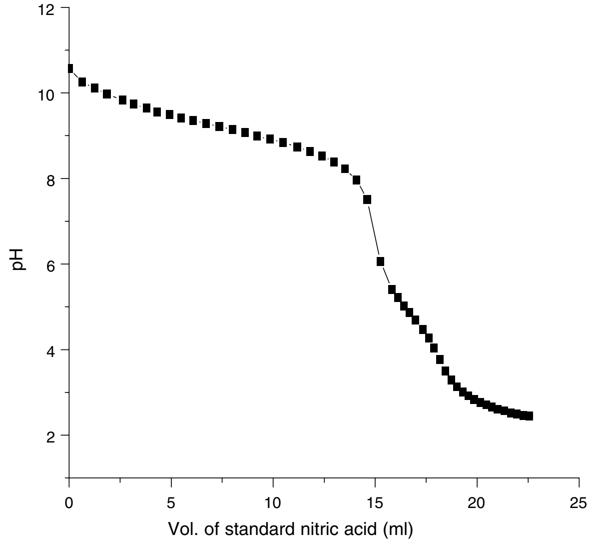


Fig. 2. Simultaneous pH titration of NH_4OH and HMTA vs. standard HNO_3.

3. Results and discussion

3.1. Thermo-gravimetric studies

To evaluate the explosive nature of ammonium nitrate, HMTA and urea mixture with respect to temperature, concentration and amount of the reactants, the thermo-gravimetric experiments were undertaken. TG/DTA curves for ammonium nitrate, HMTA and urea are given in Fig. 3, where it can be seen that decomposition of the each

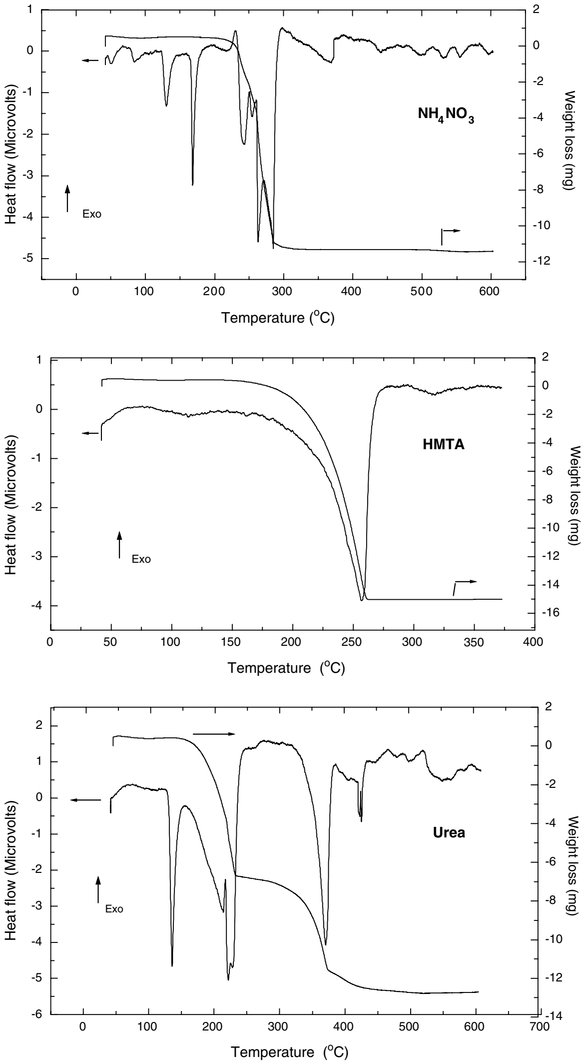


Fig. 3. TG/DTA curves for NH_4NO_3, HMTA and urea.

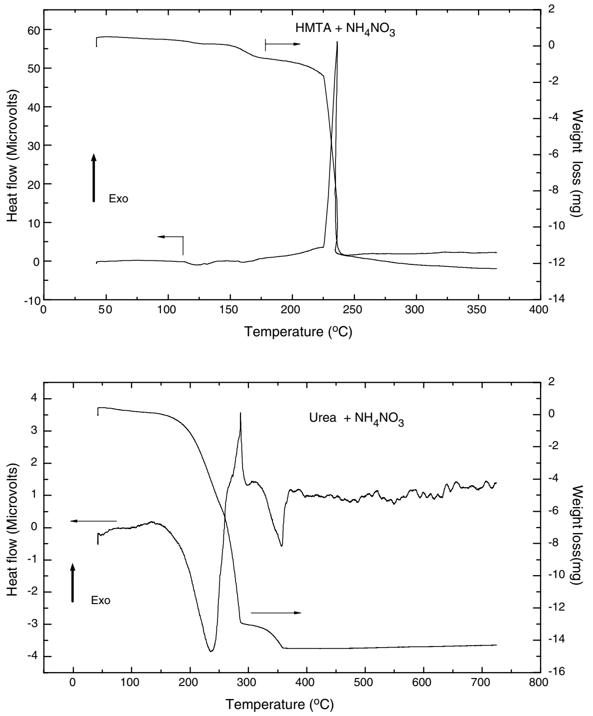


Fig. 4. TG/DTA curves for HMTA + NH_4NO_3 and urea + NH_4NO_3.

compound is accompanied by an endothermic peak, which meant that in isolation none of these three compounds presents any fire hazard. However, it can be clearly seen in Fig. 4 that in presence of ammonium nitrate both HMTA as well as urea react to give exothermic peaks, though heat output in the latter case is less. Fig. 4 suggests that since exothermic reaction between HMTA and ammonium nitrate does not start until 225 °C, it should be quite safe to concentrate the waste solution by evaporation. However any attempt to concentrate bulk of waste solution may present fire hazard due to two reasons. Firstly, temperature of initiation of the exothermic reaction depends on the amount of the reactant which could be much lower in the case of large volume of solution and secondly due to localized heating, exothermic reaction can get initiated in some part of the solution triggering the decomposition in the bulk.

3.2. Ion exchange studies

Using the data from the column experiments conducted at different flow rates during loading, a number of breakthrough curves were obtained. Fig. 5 shows that at flow rate of 1.0 bv/h (1bv = 200 ml) the resin could hold nitrate as much as 96% of the capacity before any breakthrough (average capacity of the resin, as obtained from the column experiments, was 2.76 meq/g at 100% breakthrough).

The difference in thermal behaviour of untreated waste as well as nitrate-free waste can be seen from TG/DTA patterns (Fig. 6). It can be seen that nitrate-free waste does not give any exothermic peak. Expected endothermic peaks in the nitrate-free waste (due to HMTA and urea) was not observed as amount of HMTA and urea was low

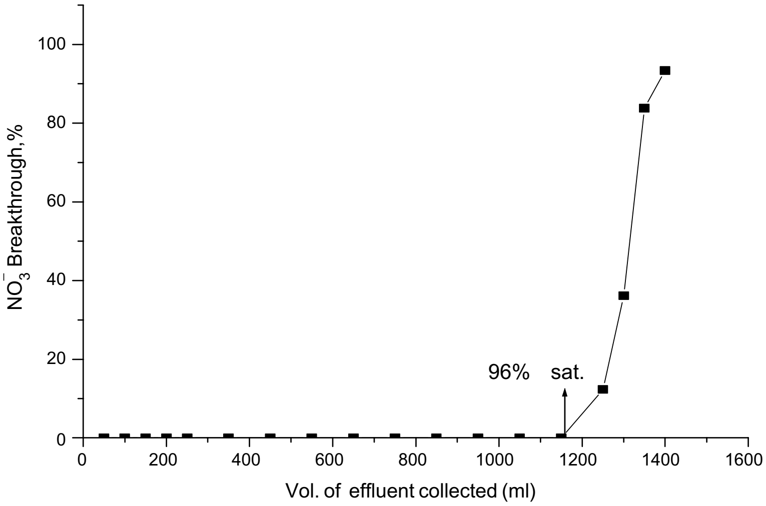


Fig. 5. Nitrate breakthrough curve for 100 g resin (when dry), flow rate = 1 bv (200 ml)/h.

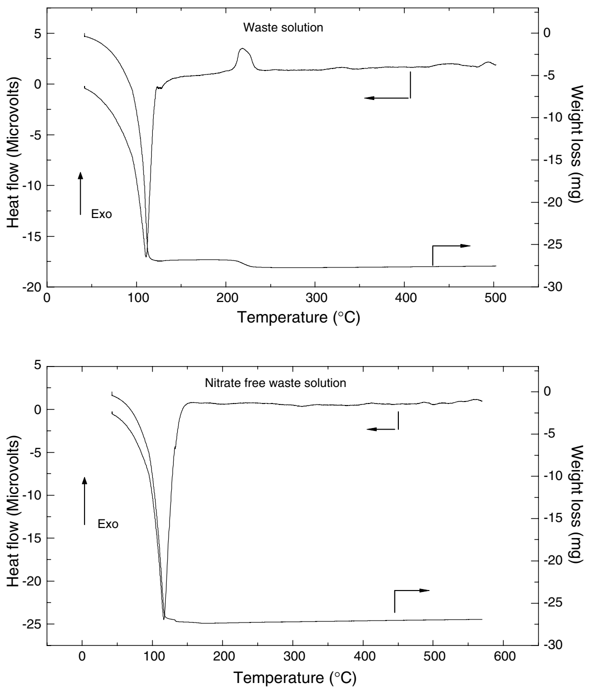


Fig. 6. TG/DTA curves for waste solution and nitrate-free waste solution.

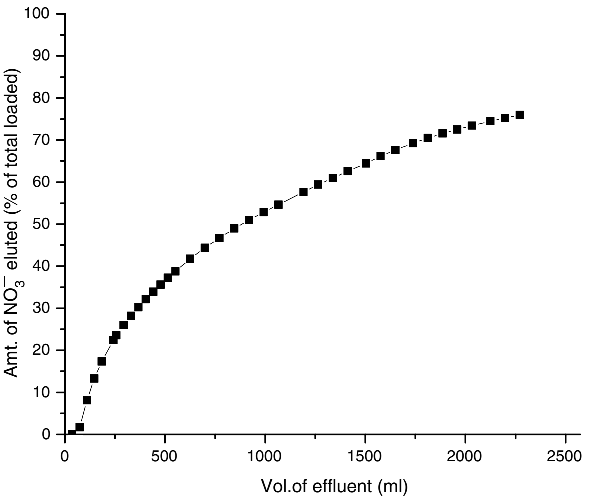


Fig. 7. Elution of NO_3^- by 1 M NaOH, flow rate = 0.75 bv (200 ml)/h.

(0.7 mg and 0.3 mg respectively). On the other hand, in case of untreated waste same amount of HMTA and urea reacted with ammonium nitrate (0.6 mg) to give a significant exothermic peak indicating higher yield of exothermic heat.

During elution of nitrate to regenerate the resin in the OH^- form, 0.5–1 M NaOH was passed at various flow rates. Use of still higher molarity of NaOH was unsuitable as it resulted in floating of resin bed. Even for a suitable concentration of NaOH and flow rate, nitrate eluted per ml decreased substantially as elution progresses. A typical elution curve using 1.0 M NaOH is given in Fig. 7. Similar curves were obtained for all molarity of NaOH used. It can be seen in the figure that first 30% of the nitrate could be eluted by passing about 360 ml of the eluant, whereas, next 30% required more than 900 ml of the eluant. This indicated that though, in principle, nitrate could be eluted out, it was practically impossible to regenerate the resin completely. Also any effort put towards greater extent of regeneration would only generate huge volume of secondary waste requiring more time and chemicals, thus making the process inefficient.

One of the factors responsible for slower kinetics of elution of nitrate could be about 25% shrinkage of the resin upon conversion from hydroxide to nitrate form and resultant swelling during conversion from nitrate to hydroxide form. Nitrate to hydroxide conversion initiates at the outer surface of the resin bead and subsequently propagates towards the core. The slower kinetics of conversion is presumably due to decrease in porosity upon conversion to swelled hydroxide form, which shields the unconverted resin (in nitrate form) from hydroxide ion. In other words, diffusion of hydroxide ions across the swollen outer layer of hydroxide-resin is difficult. During the course of elution this hydroxide-resin layer grows and diffusion process gradually decreases.

To overcome requirement of large volumes of eluting agent during regeneration of the resin, the process parameters were suitably modified to improve the separation process with respect to time and volume of secondary waste. Modifications carried out can be explained in the following way.

Since breakthrough curves had shown that maintaining a flow rate of about 1 bv/h, nitrate starts breaking through only after 96% saturation, hence by restricting the loading of nitrate up to about 95% of the capacity, the accumulated effluent would be essentially nitrate free. Main concern was the slower kinetics towards the final stage of the elution. In the modified cycle, elution was discontinued at somewhat higher level of saturation (about 60% with regard to NO_3^-) so that smaller volume of eluant could elute more nitrate. It appeared that employing this partial elution, only the outer surface (or a thin layer at the most) of the resin bead was taking part in the ion exchange process. This led to faster elution as well as optimum use of the eluant. After partial elution the resin was washed thoroughly with de-mineralised water. This was done to prevent any possible sodium contamination of the nitrate-free waste accumulated through loading cycles. To check this, at the end of water washing, an aliquot was assayed for sodium by spectroscopy and found to be below the detectable limit (<1 μg/ml). Partial elution was followed by reloading by passing the waste feed. It was observed that even about 60% saturated resin (with nitrate) could take up further nitrate up to 95% saturation without any breakthrough. This feature was reproducible through number of loading and elution cycles.

Results on loading and elution cycles of nitrate from waste onto Dowex 1 × 4 resin are summarised in Table 1. As can be seen from the table, performance of the resin was consistent during the various cycles. The nitrate concentration in the actual waste was 0.255 M, therefore 400 ml waste passed through the column in each loading cycle could increase extent of saturation of the resin (100 g when dry) with regard to nitrate by 37% (from about 58% to 95%). During the elution cycle it was observed that 450 ml of 1.0 M NaOH was sufficient to partially elute nitrate held on the resin from about 95% to 58%. Due to effect of experimental conditions saturation varied from 56.6% to 95.7%. Slight change in the amount of nitrate eluted (89.2 mmol to 107.8 mmol) was either due to different extent of saturation of the resin at the start of particular elution cycle or due to slight variation in the flow rate during elution or both. However these two factors, e.g. extent of saturation after the loading cycle and amount of nitrate eluted in the elution cycle influence each other in such a way that the extent of saturation at the end of elution in a particular experimental cycle (last column in the Table 1) remained comparatively close. This ensured that the nitrate supplied during the loading cycle never exceeds the requirement for 96% saturation and effluent remained nitrate free.

Nitrate-free waste solution was collected and analysed to determine concentration of ammonium hydroxide, HMTA and urea. The solution was then distilled at low pressure to recover ammonia by passing the vapours through ice-cold water. Recovered ammonia solution was estimated by titrating against standard nitric acid. It was found that about 70% ammonia could be recovered. Solution left in the distillation flask was pH titrated against standard nitric acid to determine HMTA. The pH titration curve also indicated that no ammonia was left with HMTA and urea. Total nitrogen was determined from which urea content could be obtained by subtracting nitrogen contributed by HMTA. Ammonia-free HMTA and urea solution was further concentrated at reduced pressure to required level of the feed needed for preparation of UO_3 microspheres.

To prepare UO_3 microspheres, internal gelation process was used, the feed composition chosen was, $[U] = 1.25$ M and $[HMTA,urea]/[U] = 1.4$. The characteristics of the UO_3 microspheres were satisfactory both during washing (by 3 M NH_4OH) and after drying. The dried microspheres were examined under microscope and found to be crack-free. Photograph of the dried microspheres is given in Fig. 8. Uranium content of the washing effluent was determined spectrophotometrically using Arsenazo (III) and found to be about 5 mg/l, which is not higher than usually obtained in the regular batches using fresh HMTA and urea.

3.3. An optimized flow sheet

Fig. 9 summarises the whole recycle process in the form of a flow sheet. The amount of chemicals appearing in the flow sheet are normalized for 1 L

Table 1
Summary of loading and elution cycles for nitrate waste on Dowex 1 × 4 resin

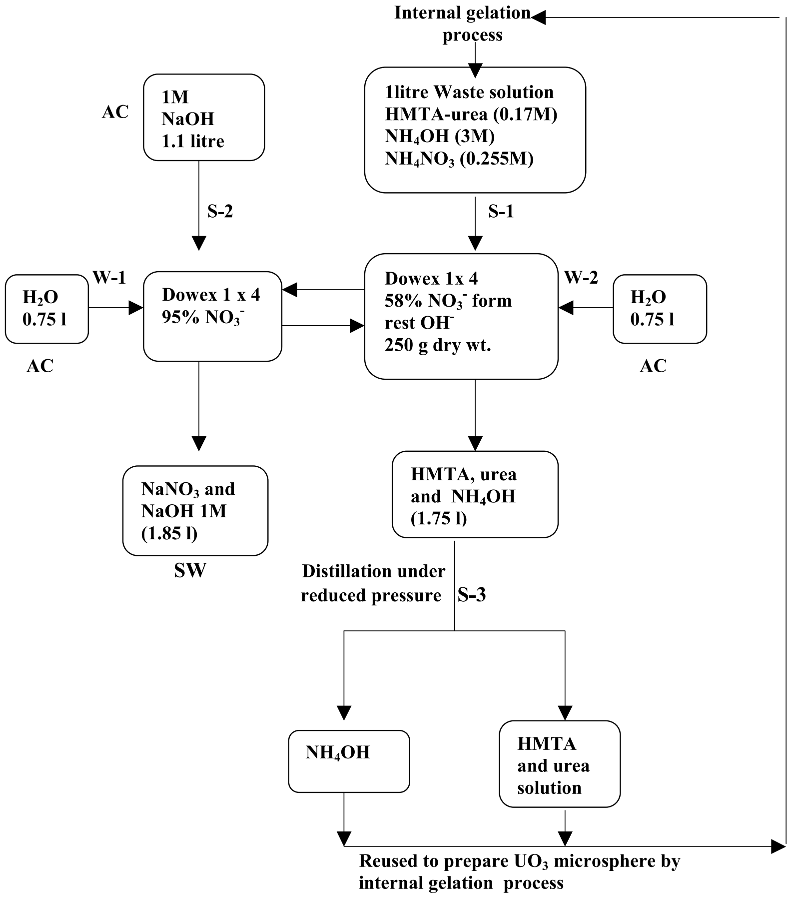
Experimental cycle	Initial nitrate in the resin (mmol)	Additional nitrate loaded (mmol)	Total nitrate loaded		Nitrate eluted (mmol)	Nitrate left in the resin after elution	
			mmol	% of sat. value		mmol	% of sat. value
1	149.2	101.9	251.1	91.1	89.2	161.9	58.7
2	161.9	101.9	263.8	95.7	105.5	158.3	57.4
3	158.3	101.9	260.2	94.4	98.4	161.8	58.7
4	161.8	101.9	263.7	95.7	107.8	156.0	56.6

Fig. 8. Dry UO_3 microsphere.

of the waste solution. Flow sheets starts with execution of the step-1 (S-1), where 1 L of the waste solution of the possible composition, ammonium nitrate (0.255 M), HMTA (0.17 M), urea (0.17 M) and ammonium hydroxide (3 M) is passed through a column containing 250 g of Dowex 1 × 4 resin, about 58% in nitrate form (rest in OH^- form). At the start of each loading cycle (S-1) resin is about 58% in nitrate form rather than 100% in OH^- form since, as discussed earlier, in each cycle after elution (at the end of step S-2 of the flow sheet) the resin is left partially saturated with nitrate to utilise better kinetics of the elution. Therefore amount of waste solution passed in the step-1 corresponds to that much amount which can saturate the resin with regard to nitrate from about 58% to 95%. In the present flow sheet, since the waste contains about 0.255 M of ammonium nitrate, 1 L of the waste solution was passed through the column to saturate 250 g of resin from 58% to 95% keeping in view the fact that capacity of resin is 2.76 meq of nitrate per gram of dry resin. After completion of step-1, the column is washed with water (step W-1) to avoid loss of HMTA and urea to the eluted fraction. It was observed that the passage of about 750 ml of water (1.5 bv) ensures complete washing. Completion of washing was confirmed by monitoring both conductivity and pH of the effluent. At the end of S-1 and W-1, about 1.75 L of solution containing HMTA, urea and ammonium hydroxide is accumulated and resin is saturated with nitrate from about 58% to 95%.

In the next step 95% saturated resin (with nitrate) is subjected to partial elution by passing 1.1 L of 1 M NaOH (step S-2). After step S-2, resin is thoroughly washed with 750 ml distilled water (W-2) to avoid sodium contamination in nitrate-free waste solution during following loading cycle (S-1). As shown in the flow sheet, after completion of S-2 and W-2 the resin is back to 58% saturation (of nitrate) level and ready for next cycle of S-1 step. Total amount of secondary waste (SW) generated by each cycle is 1.85 L containing $NaNO_3$ and NaOH. Additional chemicals (AC) used during each cycle of the process consists of 1.1 L of 1 M NaOH and 1.5 L of distilled water.

Nitrate-free waste accumulated through various cycles (each loading cycle yielding 1.75 L of nitrate-free waste containing HMTA and urea) is distilled at reduced pressure (S-3). Through this step ammonia is recovered and HMTA and urea are simultaneously concentrated as per requirement of the feed for preparation of UO_3 microspheres. Required amount of HMTA and urea is mixed with appropriate amount of ADUN solution and UO_3 microspheres are prepared following internal gelation process as outlined earlier in Fig. 1. Recovered ammonia also is reused for washing of the UO_3 microspheres during internal gelation process. Waste solution generated during ammonia washing



AC : Additional chemicals used

SW : Secondary waste generated while processing the waste solution

Fig. 9. Optimized flow sheet for reprocessing of the waste solution.

stage of the process is put back to the front end of the recycle flow sheet.

4. Conclusions

The present studies have illustrated the following:

1. The potential fire hazard associated with the waste was taken care by separation of nitrate from the waste.
2. Utilising a modified cycle of loading/elution it was possible to save time and reagents and restrict generation of large volume of secondary waste. A typical data shows that processing of 1 L of waste (containing 0.255 M nitrate) generates about 1.85 L of secondary waste containing about 1.0 M sodium hydroxide and 0.15 M sodium nitrate. However, the secondary waste so generated is completely free of any fire hazard.
3. Nitrate-free waste can be successfully processed to recover about 70% of ammonia and completely recycle HMTA and urea to prepare UO_3 microspheres without any compromise on the quality of the end product.

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