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NYLON DISSOLUTION

IN

NITRIC ACID SOLUTIONS

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H-Area Operations is planning to process Pu-contaminated uranium scrap in support of de-inventory efforts. Nylon bags will be used to hold materials to be dissolved in H-Canyon. In the present work, the solubility of the nylon material in HNO_3/0.025 M KF/2 $g \cdot L^{-1}$ B solutions, with nitric acid concentrations of 2.0, 2.5, and 3.0M, was investigated.

Based on this set of twelve nylon dissolutions, it is concluded that (when other variables are held constant):

- increased acid concentration results in increased dissolution rates;
- increased acid concentration results in a lower dissolution onset temperature;
- little, if any, H^+ is consumed during the depolymerization process; and
- 2.0 – 3.0 M HNO_3, with 0.025 M KF and 2 g/L B, is satisfactory for the dissolution of nylon bag materials to be used during H-Canyon processing.

Introduction

H-Area Operations is planning to process Pu-contaminated uranium scrap in support of de-inventory efforts. The Actinide Technology Section of Savannah River National Laboratory recently completed experiments in support of this activity.[1] During earlier work, a flowsheet was developed and the solubility of carbon steel and magnesium oxide (MgO) materials was investigated. Nylon bags will be used to contain materials being transferred to H-Canyon for dissolution. In the present work, the solubility of the nylon material in HNO_3/0.025 M KF/2 $g \cdot L^{-1}$ B solutions, with nitric acid concentrations of 2.0, 2.5, and 3.0 M, was investigated.

Experimental

The experiments were designed based on a set of earlier experiments by Pierce[1] involving the dissolution of carbon steel and MgO. During the present work, twelve experiments were performed. The experiments included dissolutions with nylon to solution volume ratios of 1000 g:7500 L, 1500 g:7500 L, 2000 g:7500 L, and 2500 g:7500 L at HNO_3 concentrations of 2.0, 2.5 and 3.0 M (with 0.025 M KF and 2 g/L B in the acid solution). Table 1 shows the actual solution concentrations and sample masses for the experiments performed.

Table 1. Nylon Dissolution Experimental Conditions

Experiment	$[HNO_3]_I$/M	$[KF]_I$/M	$[B]_I$/(g/L)	$Mass_{nylon}$/g
A-4	2.05	0.025	2	0.0102
A-1	2.05	0.025	2	0.0150
A-2	2.05	0.025	2	0.0202
A-3	2.05	0.025	2	0.0254
B-4	2.57	0.025	2	0.0104
B-1	2.57	0.025	2	0.0148
B-2	2.57	0.025	2	0.0206
B-3	2.57	0.025	2	0.0254
C-4	3.08	0.025	2	0.0109
C-1	3.08	0.025	2	0.0156
C-2	3.08	0.025	2	0.0200
C-3	3.08	0.025	2	0.0257

Table 1 legend: column 1 - experiment designation; column 2 - initial nitric acid concentration; column 3 - initial potassium fluoride concentration; column 4 - initial boron concentration (added as B_2O_3); column 5 - initial nylon mass.

The experiments were performed in a vessel with the following attributes:

- a relatively flat bottom which allowed even heating of the vessel;
- the o.d. about the same as a 100 mL beaker, but with the capability of containing ~200 mL solution, thus allowing adequate freeboard in the unlikely occurrence of a vigorous reaction of the acid solution and the nylon; and

- penetrations in the top of the vessel with the capability to be sealed in an airtight fashion to allow instrumenting of the vessel (with a type “K” thermocouple probe), introduction of the solution and nylon sample, and attachment of a water-cooled condenser (to ensure there was not significant volume loss during the boiling of the solutions).

The experimental protocol was as follows.

1. Solutions (500 mL each) of the appropriate [HNO_3], [KF], and [B] were mixed using deionized water, concentrated nitric acid (HNO_3), potassium fluoride (KF) and boron oxide (B_2O_3). The KF and B_2O_3 were weighed on an analytical balance; the volumes of deionized water and HNO_3 were measured using volumetric glassware.
2. The [H^+] in each mixed solution was determined by titration with 0.10 M NaOH, with phenolphthalein as an indicator, to one drop (or better) endpoints.
3. The reaction vessel was assembled and positioned on the hot plate.
4. 75.0 mL volume of the appropriate acidic solution was measured with volumetric glassware and delivered to the reaction vessel.
5. The nylon sample of known mass (weighed on an analytical balance) was added.
6. The hot plate was energized and the sample was stirred throughout the experiment.
7. The experimenter observed the reaction as the temperature increased (in an attempt to note significant events, such as the onset of dissolution, the temperature of dissolution onset, the physical appearance of the solution and nylon, the time and temperature at which dissolution was complete, the boiling temperature, the time at boiling, and/or any other observable behavior that seemed significant).
8. At the completion of the dissolution reaction, the dissolver solution was allowed to cool to room temperature.
9. The [H^+] of the room temperature solution was determined by titration with 0.10 M NaOH, with phenolphthalein as an indicator, to a one drop (or better) endpoint.
10. Some (not all) titration solutions were retained and observed over the period of several days in an effort to detect any post-dissolution precipitate formation.
11. All dissolver solutions were retained for observation for several days in an effort to detect any post-dissolution precipitate formation.

Results and Observations

The twelve experiments and associated titrations were performed over a one week period, during which time the ambient laboratory temperature appeared to undergo no unusual variations. The dissolutions were all similar in nature. The nylon sheet material tended to float on the surface of the acidic solution unless the solutions were stirred; therefore, the solutions were stirred at a rate fast enough to ensure the nylon was submerged in the solution. (The nylon bags in the plant dissolver are expected to be submerged during processing due to the weight of materials inside the bags).

The onset of dissolution was marked by the disintegration of the nylon sheet into small particles with the largest dimension on the order of a millimeter. As the dissolution proceeded, the particles became smaller and smaller until they were no longer visible. The solutions were checked for the presence of particles while the solutions were stirring and stagnant to ensure complete dissolution. The rate of temperature rise in each experiment was roughly equivalent. It generally took 10 to 20 minutes for the solutions to boil (except for those dissolutions in which the solids were completely consumed before the boiling temperature was attained).

The dissolution onset temperature clearly varies with the acid concentration (a higher the acid concentration corresponds to a lower the onset temperature). The lowest acid concentration dissolutions boiled for long periods of time, 118 to 157 minutes, before dissolution was complete. The intermediate acid concentration dissolutions boiled for much shorter periods, 20 to 35 minutes, before dissolution was complete. Complete dissolution of the nylon in the highest concentration solutions occurred before the solutions reached their boiling points. The initial and final $[H^+]$ were indistinguishable (within the experimental uncertainties of the titrations), showing only random variations.

The dissolver solutions were periodically inspected subsequent to the completion of the dissolutions to identify post-dissolution precipitate formation. In addition, five of the titrated aliquots were retained for further inspection. After 10 days of observation, none of the 12 product solutions or the five neutralized solutions has generated insoluble solids.

Discussion

The efficacy of dissolution of the nylon material is a function of both temperature and acid concentration. The onset of dissolution did not occur before 61^oC in any of the experiments, with the onset at the lowest temperatures being associated with the solutions with the highest nitric acid concentrations. Increases in the acid concentration from 2.05 to 2.57 to 3.08 M are accompanied by decreases in the dissolution onset temperatures in a nearly linear fashion.

After onset of dissolution, the time required to complete dissolution does not have a linear relationship to the acid concentration. Nylon dissolved in the 2.57 M HNO_3 solution three to five times faster than in the 2.05 M HNO_3 solution, while the nylon dissolved in the 3.08 M HNO_3 about ten times faster than in the 2.05 M HNO_3 solutions.

It is not clear why there is not an easily decipherable relationship between the mass of nylon dissolved and time necessary to dissolve the nylon. It is supposed that there is some inconsistency in the ability of the experimenters to detect the point at which no solid nylon remains in the mixture. Other contributors to the apparent time inconsistencies could be related to the uniformity of thickness of the nylon and the lack of uniformity in the perimeter of the nylon samples. In any event, these minor inconsistencies do not appear to cast doubt on the reliability of the results of the experiments with regard to the relationships between rate of dissolution and acid concentration.

The $[H^+]$ of each of the initial acid solutions and the dissolver solutions were determined by titration of aliquots of the respective solutions. The results show that any change in $[H^+]$ due to nylon dissolution is insignificant as compared to the uncertainties (about ± 2%) in the titration results, indicating the depolymerization reaction consumes little H^+.

Conclusions

Based on this set of twelve nylon dissolutions, it is concluded that (when other variables are held constant):

- increased acid concentration results in increased dissolution rates;
- increased acid concentration results in a lower dissolution onset temperature;
- little, if any, H^+ is consumed during the depolymerization process; and
- 2.0 – 3.0 M HNO_3, with 0.025 M KF and 2 g/L B, is satisfactory for the dissolution of nylon bag materials to be used during H-Canyon processing.

References

[1] R. A. Pierce, Carbon Steel and Magnesium Oxide Dissolution for H-Canyon Process Applications, WSRC-TR-2004-00035, Rev.0, January 2004.

Table 2. Experimental Results for 12 Nylon Dissolution Experiments

Expt.	**$[HNO_3]_I$/M**	**[KF]/M**	**[B]/(g/L)**	**$Mass_{nylon}$/g**	**V_{acid}/L**	**$T_{Diss.Init}/^oC$**	**$T_{Diss.F\ in.}/^oC$**	**bt_{dis}/min.**	**$[H^+]_F$/M**
A-4	2.05	0.025	2	0.0102	0.075	98	102	138	2.07
A-1	2.05	0.025	2	0.0150	0.075	98	102	118	2.10
A-2	2.05	0.025	2	0.0202	0.075	94	102	157	2.08
A-3	2.05	0.025	2	0.0254	0.075	93	102	153	2.07
B-4	2.57	0.025	2	0.0104	0.075	82	101	26	2.50
B-1	2.57	0.025	2	0.0148	0.075	78	101	35	2.50
B-2	2.57	0.025	2	0.0206	0.075	77	100	25	2.57
B-3	2.57	0.025	2	0.0254	0.075	78	102	20	2.53
C-4	3.08	0.025	2	0.0109	0.075	61	98	10(dnb)	3.08
C-1	3.08	0.025	2	0.0156	0.075	70	95	10(dnb)	3.08
C-2	3.08	0.025	2	0.0200	0.075	67	97	14(dnb)	3.05
C-3	3.08	0.025	2	0.0257	0.075	64	98	14(dnb)	3.05

Table 2 legend: (dnb): did not boil; column 1 - experiment designation; column 2 - initial nitric acid concentration, computed from titrations of the solutions; column 3 - initial potassium fluoride concentration, computed from the measured KF masses and solution volumes; column 4 - initial boron concentration (added as B_2O_3), computed from measured masses of B_2O_3 and solution volumes; column 5 - initial nylon mass; column 6 - volume of dissolving acid; column 7 - temperature at which dissolution of nylon was initially observed; column 8 - temperature at which nylon dissolution was complete; column 9 - time in which boiling took place (for dnb solution this is the length of time between onset and completion of dissolution); column 10 - final acid concentration.