REAGENTLESS CATALYTIC OXIDATION OF ORGANIC HYDRAZINE DERIVATIVES AND Pu (III) BY MEANS OF NITRIC ACID

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Abstract. *The recycling process of high-burnt irradiated nuclear fuels requires the organic reductant that is used during the previous stage to be deconstructed and Pu (III) to be oxidized to Pu (IV) before the extraction stage. Because of this, a reagentless method of oxidation using a carbon catalyst was proposed, and a search of different types of carbonic catalysts used in other scientific and technological areas was conducted. These experiments led to the choice of SKN carbon and optimal conditions for conducting reagentless catalytic oxidation of hydrazine derivatives and Pu (III) in nitric acid solutions.*

Key words: Extraction, affination, plutonium, reductants, oxidation, catalysis, activated carbon

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INTRODUCTION

Various reducing agents are used during extracted spent nuclear fuel recycling for plutonium and uranium separation. It should be noted that Pu (IV) is reduced to a trivalent state and it passes into the aqueous phase, and uranium remains in the extracting agent and proceeds to the next affination stage. For the realization of the second stage of the extracting purification, the plutonium must be transferred to an extractable form (Pu (IV)). This means that any extra reductant must be removed from the plutonium reextract. In the case of using organic hydrazine derivatives as plutonium stripping solutions [1], the most promising method is reagentless catalytic oxidation by means of nitric acid. Activated carbon [2] and noble metals (delivered via silica gel, alumogel, et al) [3] may be used as catalysts. The available variety of different carbon catalysts forces us to find the type most fitting to the criteria of physical durability, high reducing agent oxidation rate, resistance to nitric acid and density composition. The purpose of this research is finding the optimal type of carbon.

Complying with the works' purpose, the goals of this research are:

- Choosing the type of carbon sorbing agent, corresponding to all of the specifications for optimal oxidation
- Analyzing the oxidation process in static and dynamic conditions, depending on different parameters (temperature, nitric acid concentration, catalyst surface area)

- Specifying the oxidation process in plutonium test solutions in dynamic conditions with the selected carbon sorbing agent

- Narrowing down the optimal conditions for production use.

DIFORMYLHYDRAZINE DECOMPOSITION

Diformylhydrazine (DFH) synthesized in laboratory conditions using hydrazine hydrate and formic acid was used as an organic reducing agent [4].

The choice of carbon sorbent agent depended on the following specifications:

- At least 80% of the particles must be distributed in a size range of 0.5-2mm
- Density composition of 0.5–0.7g/cm³
- Resistance to nitric acid solutions
- Rub fastness of no more than 0.3% per minute

For this research, several types (listed below) were chosen:

1. SKN Carbon. Smooth spherical granules approx. 0.3-1.4mm in diameter. Most particles are distributed in a 0.4-1mm range.
2. SKNO Carbon. Smooth spherical granules approx. 0.3-1.4mm in diameter with most particles in a 0.4-0.6mm range.
3. OS-3 Carbon. Particles of random chip-like shape, 0.8-1.2mm in size.
4. VNIITU-1 Carbon. Smooth elliptical granules 0.5-1mm in size.

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Figure 1. Depicts the appearance of the carbons before conducting any experiments

The tests were conducted on solutions containing DFH and HNO_3 . Experiments using plutonium-containing test solutions were conducted after choosing a carbon type and specifying the conditions for dynamic oxidation. The search for optimal conditions was conducted in 2-5 mol/l HNO_3 , 1/10 – 1/40, 25 – 50 °C ranges of concentration, solid-to-liquid ratio and temperature respectively. All experiments were conducted in a temperature-controlled glass vessel of 25 ml volume. No forced stirring was administered, because the process passed with excessive gas evolution, which in turn stirred the solution naturally. Before each experiment a portion of the carbon was moistened for 10 minutes in a 5 mol/l nitric acid solution. This is necessary for activating the catalytic characteristics of the carbon. Solution samples were tested for DFH content by means of titration with sodium nitrite in a hydrochloric environment.

The experiments showed that, by increasing the nitric acid concentration and temperature, the DFH decomposition rate increases for all types of carbons, but at different rates. The change of the solid-to-liquid ratio has the highest impact on the rate. The transformed kinetic curves of the SKN carbon experiments at 50 °C and 3 mol/l HNO_3 presented in the coordinates of the second order are displayed in Fig. 2.

Figure 2. 1 - S/L=1/10, 2 - S/L=1/20, 3 - S/L=1/30, 4 - S/L=1/40
Kinetic curves of DFH decomposition using SKN carbon

All the curves are adequately defined with second order reaction equations. Reducing the solid-to-liquid ratio increases the oxidation rate. All oxidation rate constants, calculated by means of a graphical approach are shown in Table 1.

Table 1. Summarized table of kinetic data

Nº	Type	T (°C)	S/L	HNO_3 , mol/l	$K, \text{l}^* \text{mol}^{-1} \text{sec}^{-1}$
1	SKN	40	1/10	3	12.872
2		40	1/20	3	6.148
3		40	1/30	3	3.787
4		40	1/40	3	1.972
5		20	1/20	3	0.628
6		35	1/20	3	1.713
7		50	1/20	3	3.209
8		50	1/20	2	2.838
9		50	1/20	3	2.111
10		50	1/20	4	1.762
11	SKNO	35	1/20	3	0.029
12		40	1/20	3	0.073
13		45	1/20	3	0.097
14		50	1/20	3	0.173
15		50	1/10	3	0.176
16		50	1/30	3	0.079
17	OS-3	50	1/40	3	0.014
18		50	1/20	3	0.019
19		50	1/15	3	0.022
20	VNIITU-1	50	1/10	3	0.047
21		50	1/20	3	0.840
22		50	1/20	4	0.861
23		50	1/20	5	0.502
24		30	1/20	3	0.460
25		40	1/20	3	0.565

Static experiments also showed differences in oxidation capabilities of different types of carbon catalysts. Results of the experiments with different types of coal at 50 °C, 3 mol/l HNO_3 , S/L = 1/20 and a starting concentration of DFH ~0.2 mol/l are depicted in Fig.3.

1 - SKN, 2 - SKNO, 3 - OS-3, 4 - VNIITU-3
Figure 3. Kinetic curves of DFH oxidation with different types of carbon

The calculated second order of reaction constants for all the experiments are displayed in Table 1. The oxidation process of DFH with all types of carbons may be described using a second order equation; therefore, the reaction mechanism does not depend on the

surface shape. The oxidation rate of the types of carbon is displayed as follows: SKN > VNIITU-1 > SKNO > OS-3.

SKN carbon (which exhibited the highest rate of DFH decomposition) was chosen for conducting dynamic experiments. These experiments were conducted in a temperature-controlled glass column of 10 ml. Because of the active gas evolution, the solution was delivered via the peristaltic pump from the bottom to the top. Nitric acid solution (3 mol/l) containing DFH (0.2 mol/l) and Pu (III) (10 g/l) was supplied at 0.1 l per hour. After passing through the column, the solution changed from light blue to brown, proving the oxidation of Pu (III) to Pu (IV). This hypothesis is also proved by the spectral analysis. The specters of the solutions before and after passing through the catalytic oxidation column are shown in Fig. 4. The spectrophotometer used was a Lambda 55 by Perkin Elmer.

Figure 4. Specters of the plutonium solutions before and after treatment in the catalytic column

Distinctive peaks of the solution after the catalytic column at 538, 657, 700, 790, 852, 1065 nm signify the presence of Pu (IV). The slight peak at a wavelength of 830 nm, characteristic of Pu (VI) should also be noted.

250 ml of solution passed through the column in this experiment, which corresponds to 30 column volumes. Increasing the rate of passing from 0.1 l/h to 0.19 l/h did not increase the plutonium oxidation rate.

CARBOHYDRAZIDE DECOMPOSITION USING AG-3 CARBON

The Pu (III) oxidation method consisted of pouring the nitric acid solution (until its concentration reached 1 mol/l in the final solution), carbohydrazide aliquot (2 mol/l), reserve plutonium solution aliquot (37.5 g/l), neptunium (21.8 g/l), technetium (13.7 g/l) and quadrivalent uranium (480 g/l) into a 20ml vessel. The plutonium concentration in the working solution was chosen taking into account the ease of observing the absorption spectrum, that is, without any extra mixing. After that, the solution was sustained in 40 °C for half an hour. According to the observations, the plutonium reduction occurs fast, in the span of one minute. The reduction completeness was monitored via absorption spectrum recordings using a Shimadzu 1201UV spectrophotometer.

After sustaining the solution, a concentrated nitric acid aliquot was added for increasing the overall acidity up to the required concentration (2.8-4 mol/l) and the resulting solution was poured into a different temperature-controlled AG-3 carbon-containing vessel. This event was recorded as the beginning of the

oxidation reaction. During the experiment 3ml- portions of the solution were drawn into a sample cell with a 10mm optical path length. The sample cell was inserted into the spectrophotometer and an absorption specter between 1100 and 400 nm was registered. After registering the specter, the solution in the sample cell was poured back into the main vessel. The concentration of the trivalent plutonium was determined by the characteristic peak at the 601 nm wavelength, considering the specter base change due to gas emission. The conducted experiments' specifications are shown in Table 2 and the kinetic curves of the Pu (III) concentration changes are depicted in figs. 5-7.

The oxidation rate of Pu (III) was assessed via the half-oxidation reaction time ($t_{1/2}$). All the changeable parameters affect the Pu (III) oxidation rate (Table 2).

Table 2. Pu (III) oxidation in carbohydrazide experiment conditions in 1/20 solid-to-liquid ratio

No	[HNO ₃], mol/l	T, °C	[CH], mol/l	[Pu(III)], g/l	$t_{1/2}$, min
1	2.86	50	0.1	3.15	2
2	4	50	0.1	4.0	3
3	4	50	0.5	3.8	~70
4	4	40	0.25	3.7	4
5	4	50	0.25	3.63	2.5
6	3	50	0.5	3.94	~125
7	4	50	0.5	12.8	9

Figure 5. Dependency of Pu (III) content in the solution on AG-3 carbon contact time at [CH] = 0.5 mol/l; 50 °C and differing concentrations of nitric acid

Figure 6. Dependency of Pu (III) content in the solution on AG-3 carbon contact time at [HNO₃] = 4 mol/l; 50 °C and [CH] 0 mol/l: 1 - 0.1; 2 - 0.25; 3 - 0.5

Figure 7. Dependency of Pu (III) content in the solution on AG-3 carbon contact time at $[CH]_0 = 0.5$ mol/l; $[HNO_3] = 4$ mol/l; $50^\circ C$ and differing starting plutonium concentrations $[Pu]$, g/l: 1 – 3.8; 2 – 12.8

Intense gas evolution and froth buildup are observed at the start of the reaction. During this moment, a rapid decrease in plutonium concentration by 10–20% occurs, depending on the initial concentration of carbohydrazide. Afterwards, the rate of oxidation decreases and the concentration of Pu (III) changes fractionally. The kinetic curves display this as a plateau. After a certain amount of time (depending on the initial amount of carbohydrazide – $[CH]_0$), a rapid decrease in trivalent plutonium occurs (up to its complete disappearance), which signifies complete oxidation. Visually, this may be noted as an ending to any gas evolution and a transfer of solution color from light blue to brown. This Pu (III) oxidation process is explained by the presence of a stabilizer in the solution (carbohydrazide). Pu (III) begins the oxidation only after carbohydrazide has been oxidized.

The Pu (III) half-oxidation time decreases when the acidity of the solution, temperature or plutonium concentration are increased (see Table 2).

In this study [5], the IR-specters of activated carbon, treated with varying concentrations of nitric acid, were researched in detail. The spectrum absorption lines, characteristic of -C-H, -C-O and -C=C- groups were identified. An increase in $-NO_3$ group absorption lines may be observed in the 0.1–2.0 mol/l nitric acid concentration interval, but, with any further increase in nitric acid concentration, the $-NO_3$ absorption line intensity decreases and at a 4 mol/l nitric acid concentration these lines are almost completely displaced by the $-NO_2$ group absorption lines.

The data obtained from our research allow the assumption of the reducing agent decomposition and oxidation of Pu (III) as a series of consecutive reactions:

Reaction №2 passes rapidly because hydrazine derivatives prevent nitric acid decomposition. After that, the following reactions ensue:

after which reaction №1 repeats itself.

CONCLUSION

The possibility of using carbon catalysts for oxidating organic reductants and Pu (III) was proved experimentally. Optimal conditions for conducting the process in enlarged setups were selected. Other experiments using different hydrazine substituting solutions (carbohydrazine, hydrazine nitrate) yielded similar decomposition rate dependencies from core parameters.

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² Red-reducing agent