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# Chemical Analyses of Uranium Impurities in NaF

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## 1. Introduction

We studied the characteristics of uranium impurities in NaF powder prepared with reaction of NaOH and $NH_4F$ in waste which was generated from nuclear fuel production process [1]. NaF is generated from the reconversion process and contains a small quantity of uranium impurities. The uranium impurities are important, since the uranium content in the NaF waste should be less than the approval limit for self disposal of NaF wastes. The approval standard of its own disposal is known to be less than 7.4 Bq/g.

Besides the self disposal of NaF, The characteristics of uranium impurities are also interesting from the viewpoint of uranium stability in NaF powders. There is a possibility for uranium impurities to form either precipitates or a solid solution with NaF. So our goal is to perform chemical analyses of uranium impurities in NaF and find the chemical/physical states of uranium impurities for the application to reducing uranium impurities in NaF.

## 2. Experiment and Results

### *2.1 The experimental method*

NaF waste, which was supplied from KNFC, contains about 20~30% of water. To analyze uranium quantity using ICP, a uranium separation experiment was performed using $H_2O$ and $HNO_3$, respectively. A uranium separation experiments were carried out successively to reduce activity in NaF waste. NaF is dissolved in a solvent of $H_2O$ or $HNO_3$. Small amount of sample was extracted continuously, while 10g of NaF was dissolved continuously, to water(or $HNO_3$). Solution samples were drawn out at the solution volume of 75, 150, 200, 300 and 500ml respectively. The amounts of uranium dissolved in the solution sample were compared to that of Na dissolved.

### *2.2 Dissolution of Uranium into NaF*

Ten grams of NaF are dissolved in 500ml of $H_2O$ and $HNO_3$, respectively. NaF is dissolved in $HNO_3$ better than in $H_2O$. No remnant could be found in either of them.

In the case of the $H_2O$ solution, the total amounts of dissolved U were increased proportionally as increasing $H_2O$ amount. However, in the case of 1M $HNO_3$ solution, uranium was almost dissolved in just 75 mL of $HNO_3$.

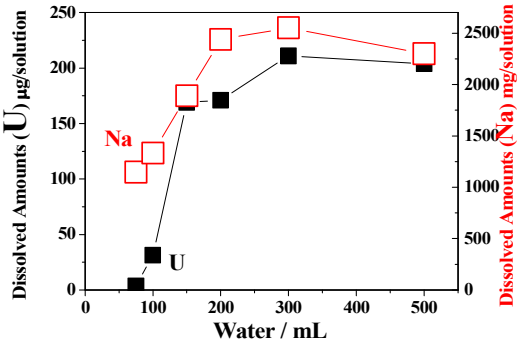


Fig 1. Dissolved amounts of U & Na in water

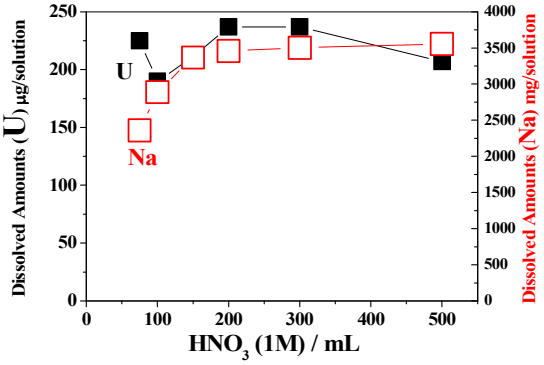


Fig 2. Dissolved amounts of U & Na in $HNO_3$

Based on this difference, it can be seen that uranium impurities have a good possibility of existing as precipitates. If the uranium impurities exist in NaF lattice, dissolution behaviors in the continuous-dissolving method are the same in both $H_2O$ and $HNO_3$ solution. This experiment demonstrated that the NaF and uranium compounds ware isolated from each other.

And when uranium compounds were extracted from a liquid state to a solid state, it can't exist in a state of solid solution in NaF crystallization because uranium's ion size and oxidation state are different from those of NaF [2].

### *2.3 Analysis by SEM*

To analyze the type of uranium compounds, SEM which uses primary electron and backscattered electron is used. Using primary electrons couldn't find uranium compound. Using backscattered electron, however, did find uranium compounds. To confirm the uranium compound's presence, EDX is used. Because the range

of electron is several ㎛ [3].it is certain that sure the brilliant part is the uranium compound [4].

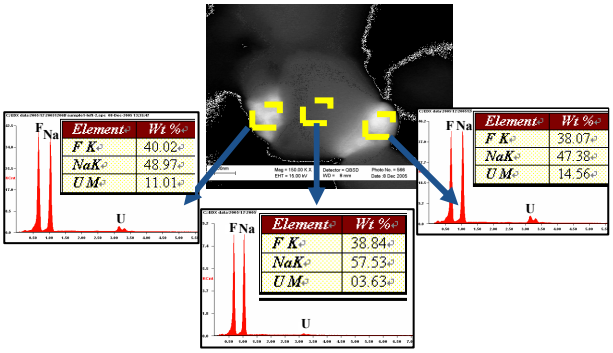


Fig 3. The result of EDX

In order to analyze the NaF compound, X-ray diffraction is carried out after drying for 8 hours. From the result, however, uranium's peak couldn't be found because the amount of uranium compounds is very small. The interesting things are existence of $NH_4NO_3$ whose amount couldn't be estimated. Before 1992, actually, the facility used as the $CaF_2$ production plant. So there is good possibility that $NH_4NO_3$ exists in NaF wastes..

*2.4 Analysis by HSC*

HSC is used to analyze the possible chemical form of uranium impurities. HSC is a common thermodynamics program made in Outokumpu Research Corp. It solves chemical equilibrium by minimizing of the free energy of the system.[5]

Uranium ion was assumed to exist in the reaction. And the form of the uranium compound was investigated by the HSC program. It shows that $NH_3$, Na and F ions is existed. The uranium ion is the reduced form of the $UO_2$. The $UO_2$ form is shown in Fig 4. If the amount of NaOH is more than that of $NH_4F$, uranium exists in the form of $Na_2U_2O_7$.

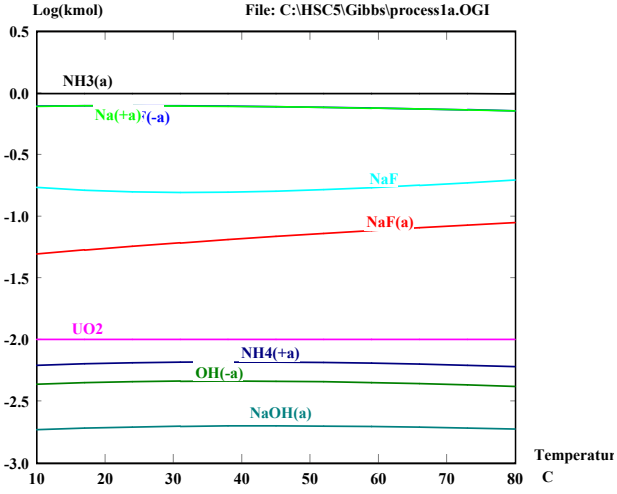


Fig 4. A product in the reaction

$Na_2U_2O_7$, $UO_2(OH)_2$ and $UO_2F_2$ are considered of the possible uranium compounds. If Yellow cake exists instead of $UO_2$, it shows low solubility. 0.1% of it dissolves and the remains exist in the solid form. About 50% of the $UO_2(OH)_2$ dissolved, And all of the $UO_2F_2$ dissolved.

*2.5 Thermodynamic analysis of solving successively in using $H_2O$ – effect of $NH_4HO_3$*

By the XRD analysis, the NaF compound contains $NH_4HO_3$ in a very small amount. As $NO_3$- ion dissolve the uranium compound, its solubility of uranium compound can be interpreted.

*2.6 The solving experiment and thermodynamic analysis of using 0.1M and 1M $HNO_3$*

0.1M $HNO_3$ dissolved the uranium compound less than 1M $HNO_3$, however, more than $H_2O$. This is difficult to interpret thermodynamically. So it is estimated that uranium impurities exist on the NaF crystallization face or its gap.

## 3. Conclusion

Chemical form of uranium impurities in NaF was studied by a continuous-dissolving method. uranium impurities were found to exist as precipitates on the NaF crystal face or gaps between NaF grains. HSC calculation indicates U impurities are $UO_2$, $Na_2U_2O_7$, $UO_2(OH)_2$, $UO_2F_2$ depending on the condition of NaF production.

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