

## A new carbonate process for recovery of uranium alone from spent nuclear fuel

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### 1. Introduction

A recovery of uranium from the spent nuclear fuel will become more important in the near future because of rapidly growing demand for uranium for the many nuclear power plants being built all over the world to cope with energy and environmental problems, and because of the volume reduction of the high level waste for a geological disposal.

A great deal of interest has been recently attracted on using alkaline carbonate media for the treatment of spent nuclear fuel instead of using acid media, because a process using carbonate media has several advantages such as enhanced safety, economic competitiveness, and minimal generation of waste as well as more proliferation-resistance. We have suggested a conceptual process called COL (Carbonate-based Oxidative Leaching) for a recovery of uranium alone from the spent nuclear fuel by using a high alkaline carbonate solution with H<sub>2</sub>O<sub>2</sub>, where the TRU elements are undissolved and precipitated together with most of other fission products and all the inorganic chemical salts including carbonate salt used in the system are recycled [1,2], as shown in Fig.1. Such a process is considered to have a high proliferation resistance and environmental friendliness.

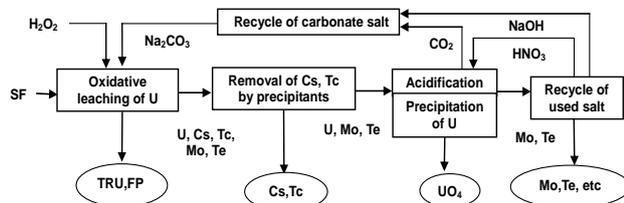
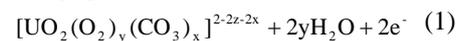
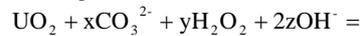


Fig.1 COL process diagram using a carbonate media to recover U from spent nuclear fuel.

### 2. Methods and Results

In the dissolution stage of Fig.1, U was evaluated to be dissolved with a sufficiently fast dissolution rate and a high solubility in a sodium carbonate solution of 0.5 ~ 1 M solution at pH of 11~12 containing hydrogen peroxide together with dissolution of a few impurity elements of only Cs, Tc, Mo, Te from spent nuclear fuel (See Fig.2 and Fig.3). At this time, because of the differences in the solubilities and redox potentials of the radio-nuclides, most of rare earth, TRU, and transient elements were evaluated or confirmed to be precipitated as insoluble residue or hydrolysates. The U leaching was very fast and increased with the H<sub>2</sub>O<sub>2</sub> concentration, and the dissolved uranium ions exist in the form of uranyl peroxy-carbonato complex, as

expressed in equation 1. To understand whether H<sub>2</sub>O<sub>2</sub> acts as a reductant or an oxidant in a solution, it is necessary to understand its redox chemistry. Figure 4 showing the redox potential-pH diagrams of H<sub>2</sub>O<sub>2</sub>, water, uranium oxide, and TRU (Pu, Np, Am) oxides means that only UO<sub>2</sub> among actinide element oxides can be oxidatively dissolved from spent fuel in the solution, the TRU oxides being undissolved. From the results of actual solubility of NpO<sub>2</sub> and simulated solubilities of actinide oxides in the carbonate solution (See Fig.5 and Fig.6), the leaching ratio of U and TRU from spent nuclear fuel in the carbonate solution was estimated to be able to be about 10<sup>9</sup> (See Fig.2, Fig.4, and Fig.5).



The Cs and Tc could be selectively removed from the solution by precipitants of such as sodium tetraphenyl borate and tetraphenyl phosphonium chloride, of which results are not present in this paper. After removal of Cs and Tc in the carbonate solutions, the uranyl peroxy-carbonato ions could be recovered as a precipitate of UO<sub>4</sub> with a high precipitation yield of more than 99% by acidification of the solution to pH of 3 to 5 with adding acid in the carbonate solution (See Fig.7). During the acidification of the uranyl carbonate solution, the de-carbonation and liberation of oxygen in uranyl peroxy-carbonato complex occurred. The CO<sub>2</sub> released during the acidification of the uranyl carbonate solution could be completely recovered as a sodium carbonate solution by using a gas absorption column into which a NaOH solution was fed [3]. After the recovery step of uranium, all the chemical salts used in the process such as the carbonate salt, NaOH, and acid could be almost completely recovered and recycled without any generation of secondary waste by using an electro dialysis reactor where the Mo and Te were finally separated from the solution.

Because of minimal generation of waste and the mixed precipitation of TRU elements together with other fission products without their dissolutions during recovery of U alone from the spent fuel, the COL process suggested in this work can said to be very helpful for the spent fuel management in view of a volume reduction of the high level active waste generated from the spent fuel with enhancing greatly the proliferation-resistance, environmental friendliness, and operational safety.

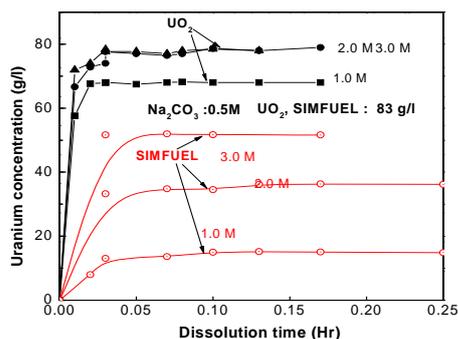


Fig.2 Dissolved U concentration from  $UO_2$  and SIMFUEL in carbonate solutions of 0.5 M  $Na_2CO_3$  with several  $H_2O_2$  concentrations.

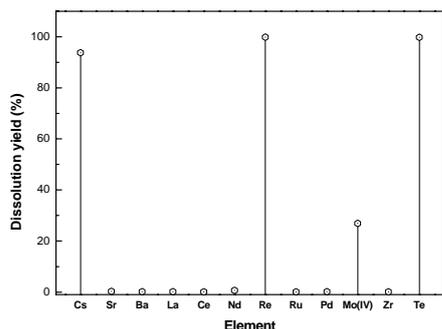


Fig.3 Dissolution yields of the major metal oxides in spent fuel in a carbonate solution of 0.5 M  $Na_2CO_3$  and 1.0 M  $H_2O_2$ .

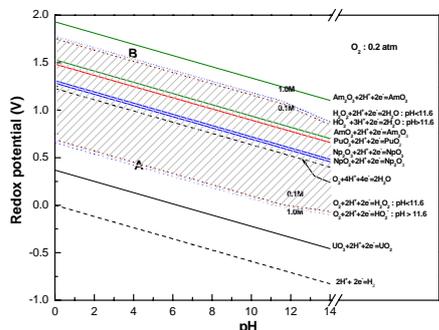


Fig.4 Redox potential-pH diagrams of U, Pu, Np, Am dioxides and  $H_2O_2$ .

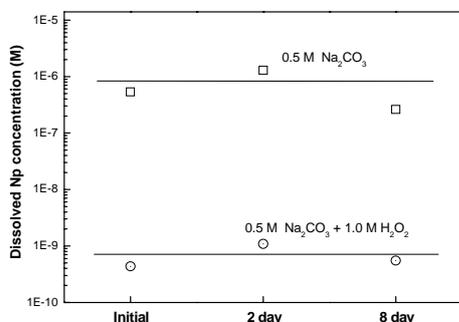


Fig.5 Concentration change of the Np ions dissolved from  $NpO_2$  in carbonate solution with time.

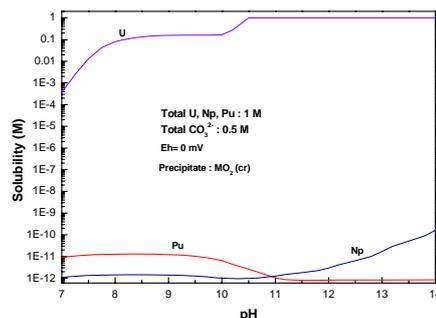


Fig.6 Simulated solubilities of TRU in a carbonate solution.

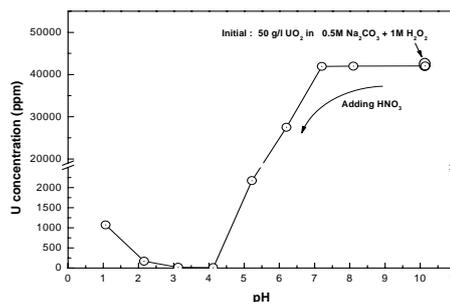


Fig.7 Change of the uranium concentration in the solution according to pH-adjustment a uranyl peroxy-carbonato complex ion solution.

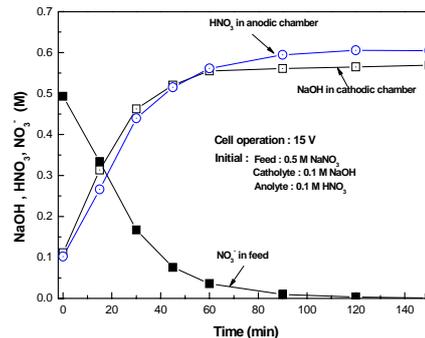


Fig.8 Concentration changes of the  $NaNO_3$ ,  $HNO_3$ , and  $NaOH$  in feed, anodic, and cathodic solutions in an electro dialysis cell with time (feeding 0.5 M  $NaNO_3$  in the cell).

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