



Oxidative dissolution of triuranium octaoxide in hydroxide-peroxide media

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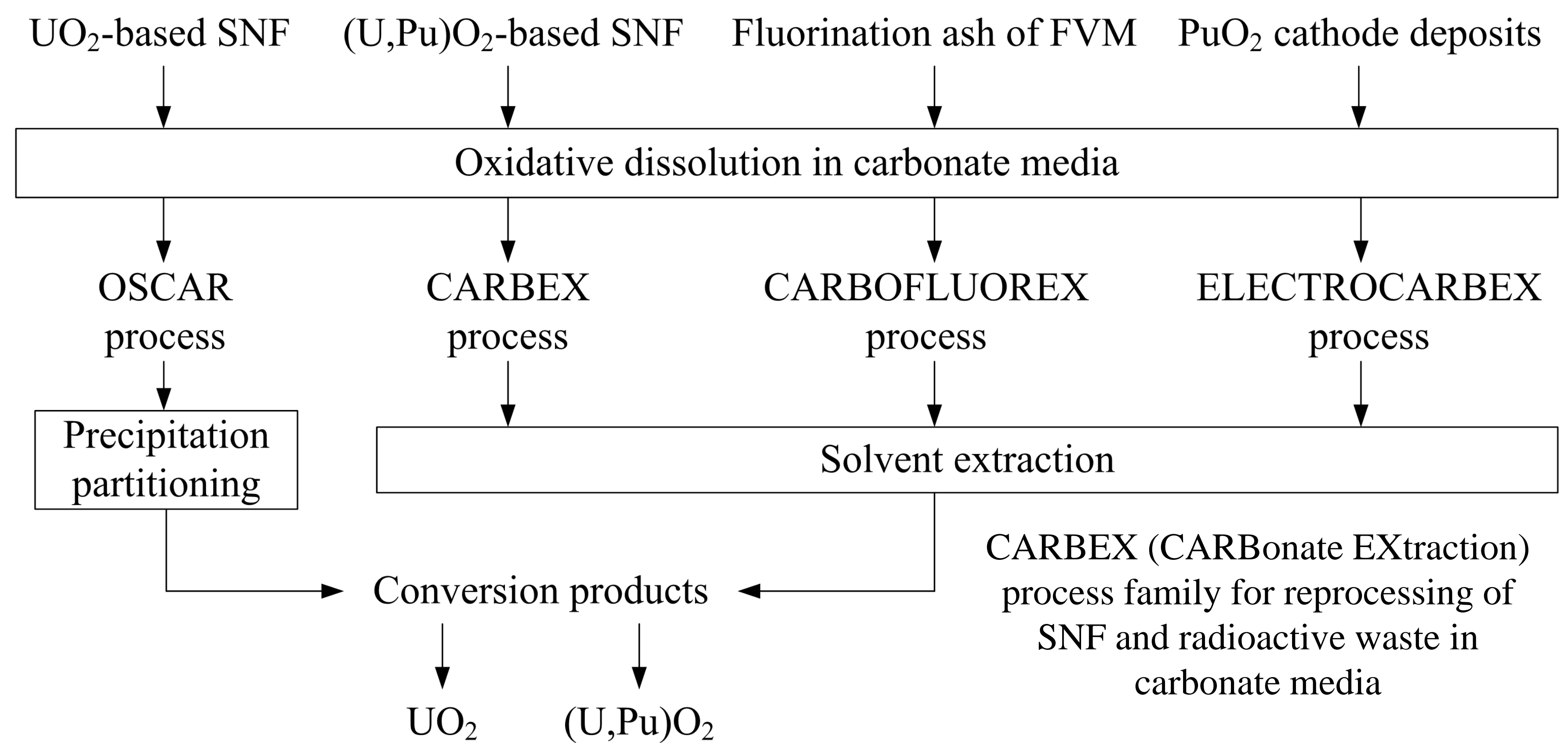
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Background

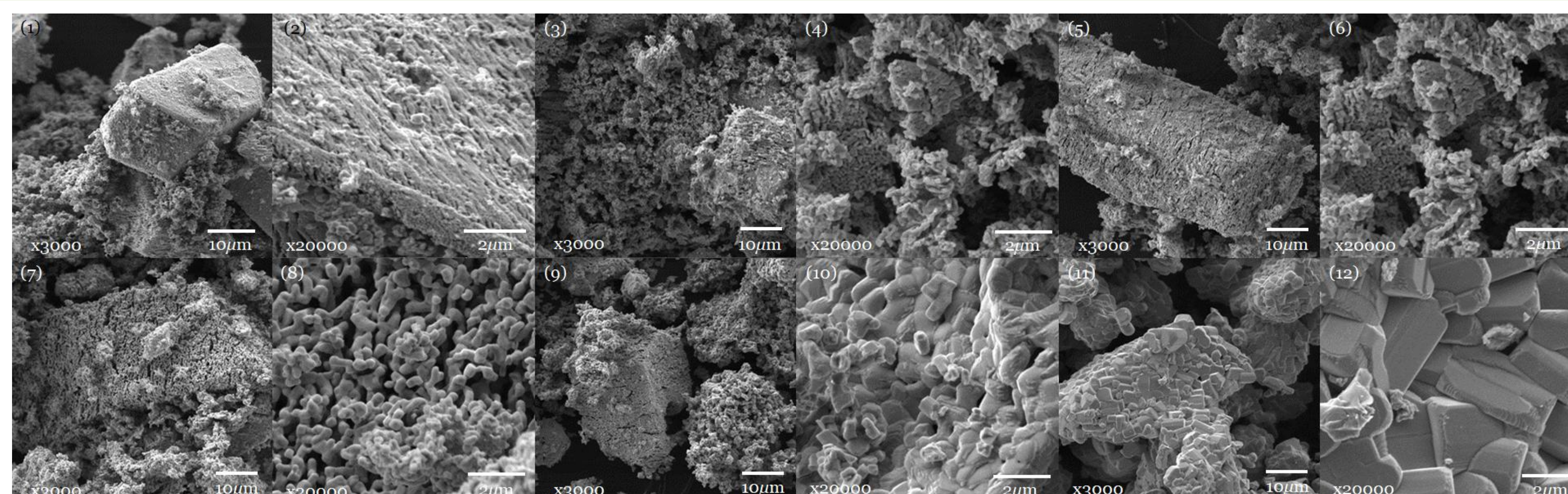
The main direction of spent nuclear fuel (SNF) reprocessing in carbonate media (including CARBEX process) is related to its dissolution in carbonate or carbonate-alkaline solutions and is considered as an alternative to hydro-chemical reprocessing in various options of the PUREX process.

An oxidizing agent is required to dissolution UO_2 and U_3O_8 in carbonate and carbonate-alkaline media. The applying of H_2O_2 in dissolution process allows the rapidly and quantitatively dissolution of UO_2 and U_3O_8 in aqueous solutions of alkali metal or ammonium carbonates. Addition of the peroxide ion to the U(VI)-containing carbonate solution results in highly soluble mixed peroxo-carbonate complexes. Soluble mixed peroxo-hydroxide complexes are formed in aqueous alkaline solutions.

Aim: Study of the kinetic of U_3O_8 powder oxidative dissolution in NaOH solutions and determine the conditions for complete dissolution of U_3O_8 in alkaline media containing hydrogen peroxide.



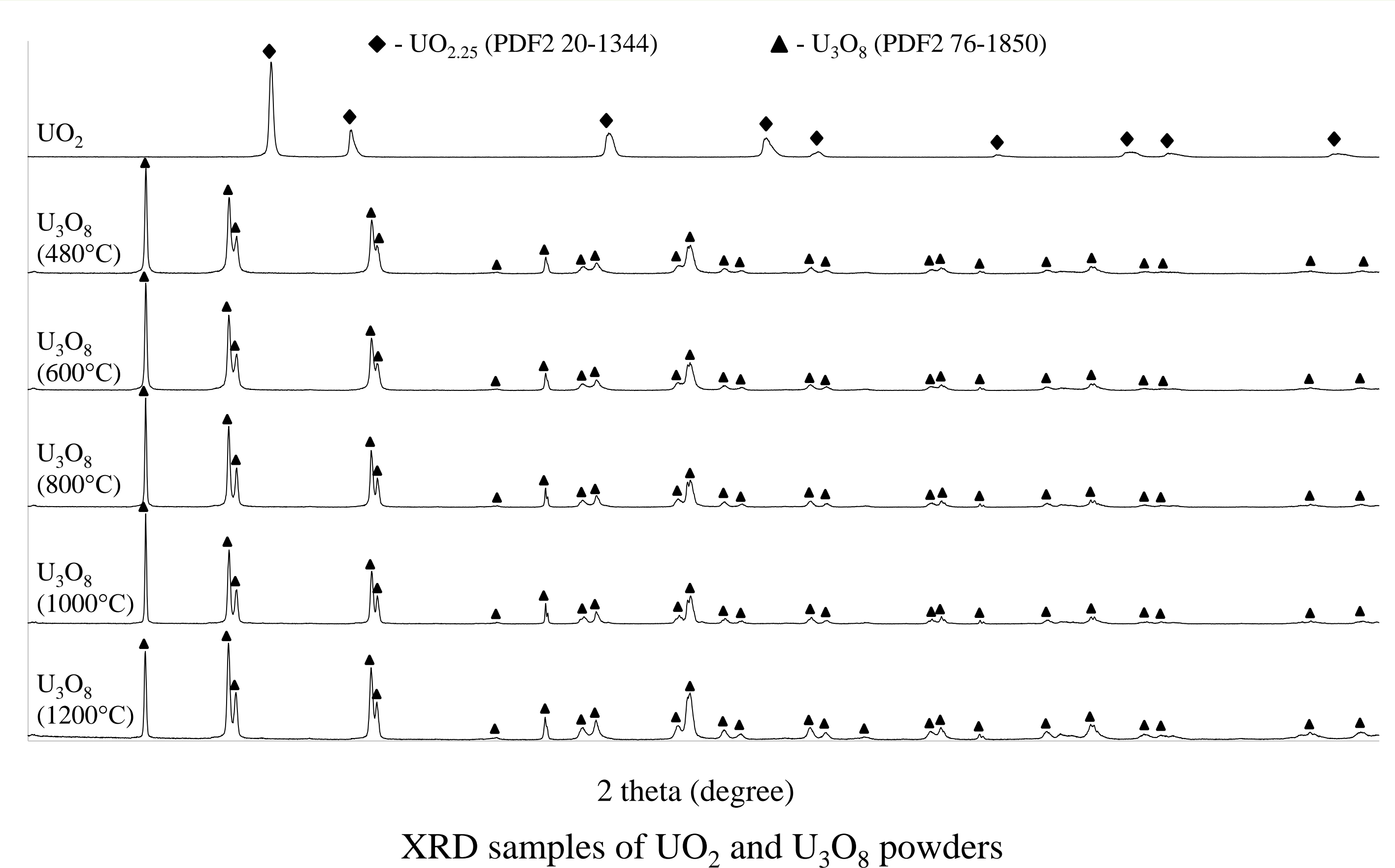
Materials and Methods



SEM micrographs of initial UO_2 powder sample (1,2) and U_3O_8 powders samples obtained at 450°C (3,4), 600°C (5,6), 800°C (7,8), 1000°C (9,10), and 1200°C (11,12)

Specific surface area (SSA) of U_3O_8 samples obtained at different temperature treatment of $\text{UO}_{2.25}$ initial powder in air atmosphere for 240 min

$t, ^\circ\text{C}$	480	600	800	1000	1200
$SSA_{BET}, \text{m}^2/\text{g}$	3.8	3.7	1.8	0.8	0.1



XRD samples of UO_2 and U_3O_8 powders

Results and discussion

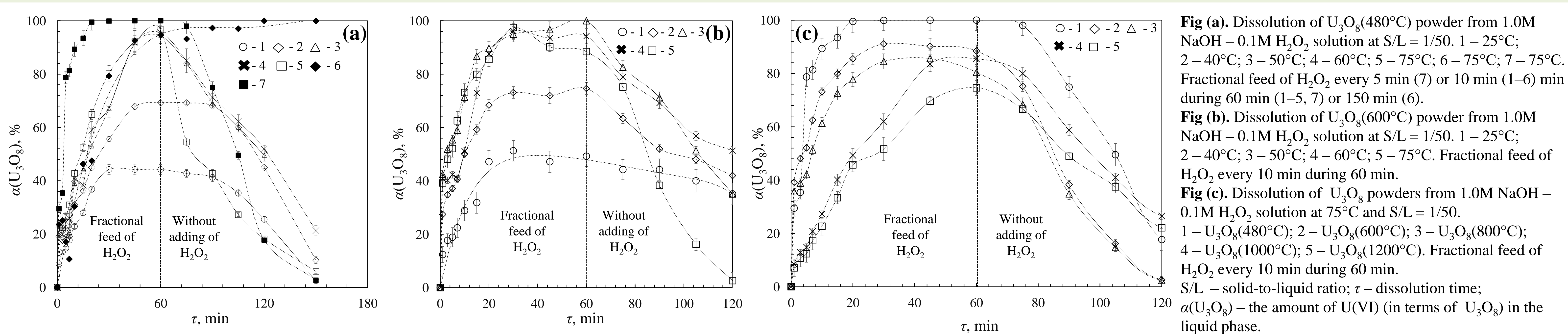


Fig (a). Dissolution of $\text{U}_3\text{O}_8(480^\circ\text{C})$ powder from 1.0M NaOH – 0.1M H_2O_2 solution at S/L = 1/50. 1 – 25°C; 2 – 40°C; 3 – 50°C; 4 – 60°C; 5 – 75°C; 6 – 75°C; 7 – 75°C. Fractional feed of H_2O_2 every 5 min (7) or 10 min (1–6) min during 60 min (1–5, 7) or 150 min (6).
Fig (b). Dissolution of $\text{U}_3\text{O}_8(600^\circ\text{C})$ powder from 1.0M NaOH – 0.1M H_2O_2 solution at S/L = 1/50. 1 – 25°C; 2 – 40°C; 3 – 50°C; 4 – 60°C; 5 – 75°C. Fractional feed of H_2O_2 every 10 min during 60 min.
Fig (c). Dissolution of U_3O_8 powders from 1.0M NaOH – 0.1M H_2O_2 solution at 75°C and S/L = 1/50. 1 – $\text{U}_3\text{O}_8(480^\circ\text{C})$; 2 – $\text{U}_3\text{O}_8(600^\circ\text{C})$; 3 – $\text{U}_3\text{O}_8(800^\circ\text{C})$; 4 – $\text{U}_3\text{O}_8(1000^\circ\text{C})$; 5 – $\text{U}_3\text{O}_8(1200^\circ\text{C})$. Fractional feed of H_2O_2 every 10 min during 60 min.
S/L – solid-to-liquid ratio; τ – dissolution time; $\alpha(\text{U}_3\text{O}_8)$ – the amount of U(VI) (in terms of U_3O_8) in the liquid phase.

The oxidative dissolution of U_3O_8 powders (obtained at 480°C, 600°C, 800°C, 1000 °C, and 1200°C) in aqueous NaOH solutions in the presence of H_2O_2 in the temperature range of 25-75°C. An increase in the temperature and the specific surface area of the U_3O_8 powder leads to an increase in the dissolution rate. Fractional feed of H_2O_2 is necessary for complete oxidation of U(IV) and dissolution of U_3O_8 in NaOH solutions. This is due to rapid decomposition (increased alkalinity and temperature) and a decrease in the concentration of oxidizer and complexing reagent (H_2O_2) in an alkaline solution. Maintaining the required concentration of H_2O_2 in an alkaline solution during oxidative dissolution of U_3O_8 powder is a key condition for achieving high process rate, completeness of dissolution of the oxide and stabilization of uranium(VI) in an alkaline solution.

Conclusion

The possibility of complete dissolution of U_3O_8 (480°C) and U_3O_8 (600°C) powder samples in 1.0M NaOH – 0.1M H_2O_2 solutions at 75°C and H_2O_2 fractional feeding due to the formation of soluble mixed peroxo-hydroxide complexes of uranium(VI) is shown. It has been found that stopping the H_2O_2 feed leads to the decomposition of soluble peroxo-hydroxide complexes of uranium(VI) and the quantitative distribution of uranium(VI) from the alkaline solution to the precipitate.

Obtained data makes it possible to develop approaches to the processes of selective leaching of uranium from voloxidized spent nuclear fuel and its hydrolytic reagent-free precipitation from alkaline solutions in the form of a preliminary concentrate purified from the bulk of highly radioactive fission products. Such an approach may be one alternative to replacing the first solvent extraction cycle of uranium(VI) from carbonate and alkaline solutions after oxidative dissolution of spent nuclear fuel in the CARBEX process.

References

- [1] G.S. Goff et al., First identification and thermodynamic characterization of the ternary U(VI) species, $\text{UO}_2(\text{O}_2)(\text{CO}_3)_2^{4-}$, in $\text{UO}_2\text{--H}_2\text{O}_2\text{--K}_2\text{CO}_3$ solutions, *Inorg. Chem.* vol. 47, no. 6, pp. 1984–1990, 2008.
- [2] T. Watanabe, Y. Ikeda, A study on identification of uranyl complexes in aqueous solutions containing carbonate ion and hydrogen peroxide, *Energy Proc.* vol. 39, pp. 81–95, 2013.
- [3] P.L. Zanonato et al., Chemical equilibria in the uranyl(VI)-peroxide-carbonate system; identification of precursors for the formation of poly-peroxometallates, *Dalton Trans.* vol. 41, pp. 11635–11641, 2012.
- [4] P.L. Zanonato, et al., Chemical equilibria in the binary and ternary uranyl(vi)-hydroxide-peroxide systems, *Dalton Trans.* vol. 41, pp. 3380–3386, 2012.
- [5] S.I. Stepanov, A.V. Boyarintsev, “Reprocessing of spent nuclear fuel in carbonate media: Problems, achievements, and prospects”, *Nucl. Eng. Technol.*, vol. 54, no. 7, pp. 2339-2358, 2022.

Acknowledgments

The work was carried out with the financial support of the Russian Science Foundation. Grant number 20-63-46006.