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New applications of the hot compressed water method for the chemistry of the nuclear fuel cycle

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The hot compressed water (HCW) is a remarkable reaction medium. In the nuclear field, the HCW method has been successfully applied in chemical synthesis and separations, nuclear waste treatment, studies of accelerated corrosion of cladding materials, etc. Moreover, the supercritical water (SCW) reactor is a concept of GenIV reactors under consideration.
We have employed the HCW (here pressured water above 120 oC) method in chemical reactions relevant to the nuclear fuels production. Thus, we have proved for the first time that the hydrothermal attack of the An(IV)-oxalates take place under HCW, with formation of AnO2 (An= Th, U, Np, Pu) nanocrystals (NC's). This new synthetic method is uncomplicated, fast, versatile, close to quantitative, and reproducible. With respect of other hydrothermally methods employing organic solvents, this one presents the advantage that the decomposition path does not lead to residual carbon impurities which can be absorbed to the NC's surface. But the main achievement consists in the destructuring of the plates-like agglomerates specific to the oxalate-to-oxide thermal conversion, with direct effect on the sintering behavior of the NC's. Even extremely effective in the case of the actinides, the hydrothermal decomposition of cerium oxalate does not lead to the desired reaction product.
It was shown that HCW supports water elimination from molecules such us carbohydrates and alcohols. Very intriguing, on have found that also Ce(IV), Th(IV) and U(IV) hydroxides dehydrates under HCW, forming even smaller correspondent NC's than compared with the hydrothermal decomposition of the oxalates. Thus, we have proposed the hydrothermal decomposition of Ce(IV)-hydroxide at temperatures above 120 oC as an effective method to manufacture CeO2 NC's. Moreover, the method proved to be successful for the production of (U,Ce)O2 noncrystalline solid solution.
For the synthesis of the uranium and thorium carbides, we are currently developing a method of reacting U(VI), U(IV) and Th(IV) with different dicarboxylic acids, and subsequent decomposition of the formed complexes under inert/ reducing atmosphere.
Safety assessment for a lead-bismuth eutectic cooled reactor requires detailed knowledge of potential Pb,Bi/MOX interaction products that could form in the event of a pin breach. Investigations on the phase relation in the Bi-U-O ternary system have shown that the formation of Bi2UO6 is likely under mild thermal conditions. Beside the classical reaction in solid state, we have also synthesized this phase by reacting different components under HCW.
In the field of radioactive and nuclear wastes, remediation of uranium contaminated waters by using magnetite and zero-valent iron particles is a well-established treatment method. We have shown that magnetite NC's may form by the decomposition of a number of inorganic compounds under SCW conditions. Presently we are studying the reductive incorporation of uranium in the magnetite structure concurrently with the decomposition reaction under HCW.
Mineral-like hydrated phosphates (relevant for the dissolution of the phosphate based ceramic waste forms) could be also obtained by using this method.

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