



Management of zirconium rod claddings with process of electrochemical breakdown

Yury Pokhitonov (Khlopin Radium Institute, St. Petersburg, Russia)

Introduction

One of the waste types formed during reprocessing of irradiated nuclear power plant fuel is fuel element claddings, which in the conventional chop-leach process remain in the apparatus after dissolution of the fuel. The most commonly-used method of isolating spent fuel claddings is to encapsulate them in concrete and inter them in metal containers.

In view of the high cost of the cladding material (zirconium), there have been a number of proposals for this material to be recovered and re-used. However, the residual contamination of the claddings and the chemical stability of the zirconium militate against any proposal for a recycling process that might be economically justifiable. Use of reagents such as hydrofluoric acid is not really feasible on a commercial scale because of the problems in finding materials to build the dissolver unit and in dealing with the resulting wastes.

There is, however, information on the synthesis of mineral-like materials based on zirconium. The idea of using zirconium, which is contained in irradiated fuel, to synthesize compounds that would be suited to TPE long-term storage or underground disposal is conceptually attractive.

Objectives of research

The aim of this work was to investigate the process of electrochemical dissolution (breakdown) of fuel rod claddings in nitric acid solutions. A successful outcome to this task would enable zirconium separated from claddings to be utilized at the stage of encapsulation of high-level waste in a matrix based on zirconium dioxide, which features a high level of chemical stability.

Experimental results

Peak breakdown rates were achieved using 1M calcium nitrate in 1M nitric acid as the electrolyte. The reason for the increase in the zirconium breakdown rate should probably be seen as lying in the formation of calcium zirconate, the properties of which are different from those of zirconium oxide. The increase in dissolution rate is brought about by a fragmentation of the surface oxide layer, this increases the effective surface and reduces the insulation due to the oxide film.



The rate of dissolution rises with temperature, reaching ~40-70 mg/cm²·h at 90°C. The current yield under these conditions is 0.6-0.7 g/A·h.

X-ray phase analysis was used to determine the composition of the oxide film formed on the surface of the specimens, following electrochemical dissolution at different acidities

Conclusion

The mechanism of the electrochemical breakdown process is fairly complex and the results obtained do no more than provide us with an idea of some of the features of the physical/chemical process under consideration.

The process of electrochemical dissolution (destruction) of zirconium claddings may nevertheless be carried out in nitric acid, preferably in dilute solutions and with calcium nitrates present.

At the same time these experimental results allow conclusion that the use of zirconium (cladding material) at the stage of encapsulation of high-level waste seems to be quite justified.