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Head-End Scheme for Reprocessing of Advanced Nuclear Fuels by Direct Dissolution in Nitric Acid

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Advanced nuclear fuels—mixed carbides MC, mixed carbonitrides M(C, N), mixed nitrides MN ($M = U_{0.8}Pu_{0.2}$)—show promise for use in future fast breeder reactors (FBR). One precondition for their acceptability as fuels is the mastering of the complete fuel cycle, especially the reprocessing step. In principle, the Purex solvent extraction process, developed for LWR fuel, is also applicable to the recovery of uranium and plutonium from mixed oxide FBR fuel. Additional preparative steps in the head-end of the process are needed for advanced fuels, if the reprocessing is based on the controlled oxidation of the fuel to MO_2 with O_2 or CO_2. Another way of preparing the feed to meet the requirements of the Purex process is the direct dissolution of the carbides or nitrides in nitric acid, as described in this paper.

Specimens of 5–10 g of MC, M(C, N) or MN with burn-ups between 0 and 6.7 at % were dissolved under reflux in 2–12 *M* HNO_3 kept at constant temperatures between 30 and 85 °C for up to 24 hours. The evolved gases were continuously measured by infrared absorption (Miran-80) or samples were taken during and after the dissolution and analysed by mass spectrometry. In the case of MC- and M(C, N)-dissolutions, the CO_2 formed was trapped in NaOH and the carbonate/bicarbonate titrated with HCl under computer control [1].

The resulting solutions were analysed for uranium and plutonium by titration (unirradiated MC), according to the methods of Eberle *et al.* [2] and Davies and Townsend [3], respectively. Additionally, spectrophotometric measurements in the range 400–850 nm were made.

The remotely controlled spectrometer (Cary 17D and HP 9835A) was used to determine the oxidation states of U and Pu along with the total concentrations of these elements by multicomponent analysis, taking the carbon containing compounds in the solution into account [1]. The organic species, mainly mellitic acid and oxalic acid [4], were also identified by ion chromatography (Dionex D 10) [5].

The solutions were filtered through 1.6 μm fritted glass filters, the residues determined by weighing and characterized by x-ray diffraction analyses. After dissolution of the residue in H_2SO_4 and $(NH_4)_2SO_4$ the radioactive fission products were determined by γ-spectrometry, the uranium concentration was measured by isotope dilution mass spectrometry and the plutonium concentration by α-spectrometry.

Gaseous Phase

The off-gas from MC dissolution contains the gases N_2O, NO, NO_2 and CO_2; no hydrocarbons are formed when the nitric acid molarity is above 2 *M*. About 50% of the carbide carbon is released as CO_2, the remainder forms soluble organic compounds. The evolution of the predominant gas, NO, ceases at the end of the carbide dissolution, whereas the formation of NO_2 and CO_2 continues for many hours, indicating an oxidation of the carbonaceous by-products in the solution. Only small amounts of N_2O are found in the off-gas.

Liquid Phase

The MC-fuel dissolves in nitric acid producing a solution containing U(VI), Pu(IV) and carbon containing species [1]. Unirradiated or low burn-up fuels dissolve completely (>99.9%), whereas high burn-up fuels (>4 at%) give rise to minor amounts of residues, which can be removed by filtration. The oxalic acid complexes the plutonium and decreases its extractability with tributylphosphate (TBP) [6]. The carbon containing species can, however, be destroyed by oxidizing chemicals, such as MnO_2 or BiO_3^- [7], or by photochemical treatment [8]. The nuclear radiation absorbed by the sample solution also affects the organic compounds, so that their deleterious influence on the Pu-extraction disappears after storage. MN-fuels dissolve faster than MC under violent NO_x evolution. The solution obtained contains U(VI) and Pu(IV). During M(C, N)-dissolution large amounts (20%) of Pu(VI) were occasionally observed; however Pu(VI) is unstable and transforms to Pu(IV) upon standing.

Solid Phase

The amounts of residues found by dissolution of high burn-up MC and MN are minimized in 8 *M* HNO_3 at 80 °C (*e.g.* 0.5% and 0.3%, respectively). The MC residues contain only very small amounts of uranium and plutonium (*e.g.* 0.04% and 0.3% of the initial fuel amounts, respectively), with a U/Pu ratio in the residue of 0.6, strongly deviating from the U/Pu ratio in the solution (about 3.9). Small amounts of PuO_2 were also found in the residue.

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The Use of RE-O-S Phase Stability Diagrams in Gaseous Desulfurisation and Iron and Steel Production

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The thermodynamic properties of rare earth (RE) compounds containing oxygen and/or sulfur are of industrial significance in the high temperature desulfurisation of gaseous fuels by rare earth oxides [1], the control of graphite morphology in cast irons [2] and sulfide inclusion control in steels [1]. The initial form of the phase stability diagrams was based on the thermochemical data of Gschneidner *et al.* [3] using cerium as a 'representative' rare earth [4]. More recently [5], the high temperature standard free energies of formation of some RE–O–S compounds have been determined using oxygen concentration cells with calcia stabilised zirconia (CSZ) as the solid electrolyte, and the phase stability diagrams extended to higher oxygen potentials.

The La–O–S and Ce–O–S Diagrams. Updated versions of the La–O–S and Ce–O–S phase stability diagrams at 1100 K [5] are given in Fig. 1 and 2, respectively.

For the La–O–S diagram, oxygen concentration cells of the type:

$Pt/La_2O_3(s), La_2O_2S(s), La_2O_2SO_4(s)/CSZ/Air/Pt$ and $Pt/La_2O_2S(s), La_2O_2SO_4(s), Ag(s), Ag_2S(s)/CSZ/Air/Pt$ were used [5] to generate thermodynamic data on the equilibrium:

$$La_2O_2S(s) + 2O_2(g) = La_2O_2SO_4(s) \qquad (1)$$

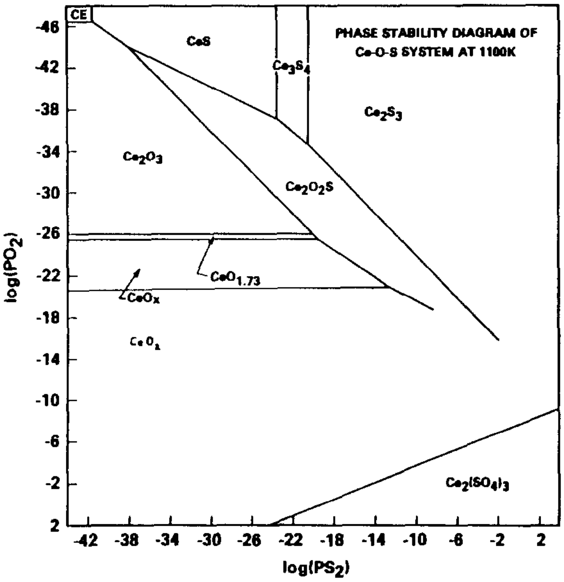

Fig. 2. The Ce–O–S phase stability diagram at 1100 K [5].

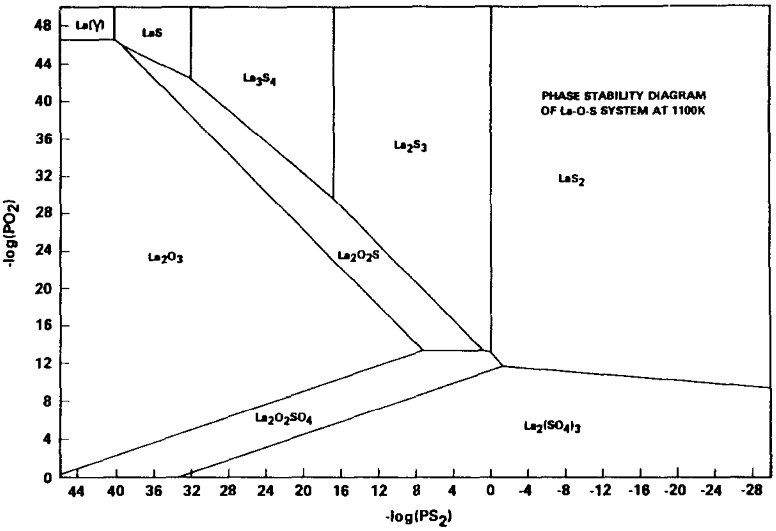

Fig. 1. The La–O–S phase stability diagram at 1100 K [5].