In India, Department of Atomic Energy is establishing Fast Breeder Reactor (FBR) technology with an objective to meet the increasing requirement of nuclear power. As a first step in this development, an experimental Fast Breeder Test Reactor (FBTR) was built up at Kalpakkam and it reached criticality in October 1985. In Breeder Reactors, more fissile material is produced than what is burnt out, by neutron capture reactions taking place in the fertile material as the power generation is in progress. The success of the FBR technology lies in the efficient and economic recovery of the fissile material from the spent fuel of the Breeder Reactor, in reprocessing plant. This plant employs the following steps, namely dissolution (Head-end) solvent extraction-separation of U and Pu from fission products, partitioning (separation of U and Pu streams), precipitation and calcination into oxides.

The FBTR employs a full core of mixed-carbide fuels (that too of unique composition namely 30% UC-70% PuC) for the first time in the world. Once the spent fuel is brought into nitric acid solution and is free from interfering organics, then rest of the steps which follow are similar to those employed at present for mixed oxide fuels. Thus, it is obvious that the challenge in the reprocessing of the mixed-carbide fuels rests mainly on the head-end step. Dissolution of mixed-oxide fuels in the traditional
dissolvent namely HNO₃-HF, is severely limited by fluoride complexing with Pu, U and some fission products like Zr, in addition to the problems of corrosion. Ruthenium, a fission-product has been reported to interfere in the oxidative dissolution of mixed oxide fuels in HNO₃-Ce(IV) solution by the catalytic reduction of Ce(IV). Despite this limitation, lack of other desirable alternatives has warranted further work on oxidative dissolution. The R&D efforts in our laboratory resulted in the development of the present Electro-Oxidative Dissolution Technique (EODT).

The Head-end processes so far investigated for the carbide fuels, namely, pyrohydrolysis, pyrolytic oxidation, low temperature hydrolysis, direct dissolution in nitric acid and photochemical process have been reviewed bringing out the merits and demerits of the processes. Pyrolytic oxidation and pyrohydrolysis are high temperature operations to be carried out on the pyrophoric mixed-carbide pellets. In addition, during the pyrohydrolysis process, hydrogen is evolved which is likely to pose problems related to safety. However, the advantage of this method is that the product is a free flowing powder of mixed-oxide which readily dissolves in nitric acid. Low-temperature hydrolysis is another desirable method. But, irradiated uranium monocarbide becomes passive to hydrolysis with water at 80 to 90°C. When carbide is dissolved in nitric acid, it dissolves completely, but about 44 to 68% of carbide-carbon is converted
into the soluble organic acids such as oxalic acid, mellitic acid and other unidentified products. Only oxalic acid has been reported to interfere in the solvent extraction of Pu, owing to complexation of Pu(IV) by oxalic acid. Nevertheless, one of the main limitations of this method lies in the incomplete destruction of the organics, even on refluxing the nitric acid solution along with KMnO₄. Further the precipitate of MnO₂ formed during refluxing may adsorb Pu. The photochemical destruction of these organic acids is a rather time-consuming process (34 to 45 h) thus making this approach unsuitable for plant application. Incorporation of the fragile glass or quartz window in the dissolver equipment in order to irradiate the solution with light, is also hazardous.

The EODT has been compared with the other Head-end processes highlighting the advantage and problems of the present method. The EODT is found to destroy the oxalic acid completely in about 2h and destroy the soluble organics from an initial level of 44 to 60%, to a level which is less than 0.2%. The conventional thermosyphon dissolver with modifications for electrolytic processes is found to be adequate for this method. In the present EODT, it has been demonstrated that the PuO₂ solid dissolves completely in 15 minutes in 4M HNO₃ under suitable conditions. The dissolution of other nuclear materials such as UC pellets, fresh FBTR mixed-carbide fuel pellets and an unirradiated FBTR fuel pin chopped into 1/2" pieces have been carried
out employing the EODT and the results of these experiments are reported in this thesis. A comparison of the time required for complete dissolution of all the above mentioned fuel materials is furnished. The extent of destruction of soluble organics with respect to time of electro-oxidation, in experiments with UC pellets, are included. The experimental conditions and the effect of different parameters such as temperature, concentration of the redox intermediate and of the nitric acid and the nature of the anode materials are also presented.

The dissolvent HNO₃-Ce(IV) investigated by the American Workers, as an alternate to the traditional HNO₃-HF, has dissolved completely the unirradiated mixed-oxide fuels whereas it has failed for the irradiated ones. This failure has been reported to be due to the presence of Ru which is a fission-product. Ruthenium catalytically reduces Ce(IV) to Ce(III) and makes the dissolvent ineffective for the irradiated fuel. Since irradiated fuel at present is not available with us, interference of Ru in the present EODT is investigated by simulation studies. In presence of Ru, Ce as well as Cr in nitric acid medium can be oxidised to their higher oxidation states. Under simulated conditions Ru in metallic as well as in oxide form is observed not to interfere either in the electro-oxidative destruction of organics from UC dissolution or in the electro-oxidative dissolution of PuO₂. It is attempted to probe into the
possible reactions and mechanism of the dissolution of the pluonium dioxide and destruction of the soluble organics.

The advantages of the EODT over other techniques are highlighted. The present technique eliminates the use of corrosive HF in case of mixed-oxide fuels. In case of mixed-carbide fuels, high temperature operation as in pyrohydrolysis or pyrolytic oxidation is avoided. Use of sodium nitrite or NO₂ gas for adjusting the Pu valency, in a separate step is also eliminated in the EODT. The present technique seems to overcome the interference by Ru unlike the HNO₃-Ce(IV) dissolvent. Like any other electrochemical process, the EODT is also easily amenable for remote operation and control. The electrochemical dissolution techniques so far developed/employed by others and the operations of the equipment namely Electrolytic Dissolver-cum-Conditioner employed in the scaled-up version of the present EODT are described.

The problems faced in the EODT and how they are solved are described. The insoluble residue obtained in the dissolution studies with UC pellets are characterised by X-ray diffraction and thermogravimetric analyses. The above studies indicated the residue to be uranyl oxalate monohydrate. These residues are also dissolved on further electro-oxidation under suitable conditions.

Noble metal fission products such as Ru, Rh, and Pd are
known to form insoluble intermetallic alloys with U and Pu, of the general formula M₃(U, Pu) in spent fuels. It is necessary to study the dissolution behaviour of these compounds in the EODT. From Eₒ values it is expected that the high solution potential in the anode compartment may facilitate leaching of the baser U and Pu from the insoluble alloys. In order to confirm this, the compound U₃Pd₃ has been prepared and its dissolution in nitric acid has been studied. Contrary to the expectation, the U₃Pd₃ alloy is found to readily dissolve in pure nitric acid itself, at 65°C. Probably, the intermetallic alloys with other noble metals (Ru & Rh) may be insoluble. Since no H₂ or hydrocarbon has been reported to be evolved, when carbides are dissolved in nitric acid, it is suggested that the EODT is suitable for adoption in the head-end step of reprocessing even from the safety considerations. Since the condition of anodic oxidation prevails in the electrolytic dissolver, the conventional construction material namely AISI 304L stainless steel is found to be unsuitable. This is revealed by the excessive corrosion rate (1705 micrometre per year) which has been observed for this material. The corrosion data for the titanium-5% tantalum alloy and zircaloy-2 have been generated which show them to be equally suitable as construction material. Development of anode material has been taken up under the collaborative work with Materials Development Laboratory at Kalpakkam. In the initial studies of the present technique Pt anode has
been used. Later studies with Titanium Substrate Insoluble Anode (TSIA) have shown that the costly Pt anode can be substituted with TSIA. Recent experiments on electrolysis, reveal that TSIA is not suitable anode, in nitric acid medium above 65°C. By applying a corrosion-resistant oxide mixture of suitable composition, designated as the Mixed Oxide Coated Titanium Anode (MOCTA) the maximum temperature of use has been successfully enhanced to 100°C.