SUMMARY

The thesis entitled: "Production of Some Long-Lived Fission-Product Radionuclides" comprises three chapters; introduction, experimental, and results and discussion.

Chapter 1, introduction, includes brief accounts on nuclear fission, chemistry, radiochemistry and nuclear chemistry of uranium, Periodic Table and ^{235}U-fission products, chemical processing for separation of some ^{235}U-fission products (including radioiodine, radioruthenium, radiocesium, radiomolybdenum, and radio-zirconium and –niobium), some beneficial applications of ^{235}U-fission products (including $^{137}Cs/^{137m}Ba$ and $^{99}Mo/^{99m}Tc$ radioisotope generators, sealed sources, nuclear batteries, and miscellaneous applications).

Chapter 2, experimental, includes description of the chemicals and solutions as well as specifications of the equipments used. It includes also description of processes related to the target preparation, irradiation, and dissolution, preparation of 6-tungstocerate(IV), 6-WCe, gel matrix, separation methods of radioiodine, radioruthenium, radiocesium, radiomolybdenum, and radio-zirconium and –niobium from the aged and/or hot irradiated natural-abundance UO_3 targets, some beneficial applications of ^{235}U-fission products (including $^{137}Cs/^{137m}Ba$ and $^{99}Mo/^{99m}Tc$ radioisotope generators as well as $^{99}Mo/^{99m}Tc$-$^{137}Cs/^{137m}Ba$ dual radioisotope generator) and quality control investigations of the product radionuclides (including elution profiles of generator-produced radionuclides, separation and elution yields, recovery yield, radionuclidic purity, radiochemical purity, chemical purity, and pH-value).

Chapter 3, results and discussion. The uranium targets, consisted of 4×0.025 g of natural-abundance UO_3, were irradiated in ETRR-2 Research Reactor-Egypt for 4 h at a thermal neutron flux of 1×10^{14}

$n.cm^{-2}.s^{-1}$. Thereafter, they were cooled for 10 d (hot sample) or for ~ 2.5 y (aged sample) before alkali/acid dissolution process to obtain hot and aged fission-product (FP) feeding solutions, respectively. These solutions were submitted to gamma-ray spectrometric analysis. The obtained spectra were identified and quantified according to the characteristic gamma-ray photopeaks of the corresponding radionuclides. The feeding FP solutions were radiochemically processed by sequential distillation from nitric acid media of controlled chemical composition for separation of volatile species (radioiodine and radioruthenium) and in-situ precipitation reactions of e.g., $Al(OH)_3$ for separation of radiomolybdenum and/or radiocesium. Redissolution of the formed matrix precipitated from the hot FP solution followed by suitable chemical processing reactions led to separation of the $^{95}Zr/^{95}Nb$ couple. All the processing steps were followed and assessed by radiometric methods. The validity of the corresponding separation procedure was controlled by carrying out the respective quality control investigations for the product radionuclide. The obtained data were discussed and interpreted. Peaceful uses of the separated FP radionuclides were illustrated in preparation of $^{137}Cs/^{137m}Ba$ and $^{99}Mo/^{99m}Tc$ radioisotope generators as well as $^{99}Mo/^{99m}Tc$-$^{137}Cs/^{137m}Ba$ dual radioisotope generator.

Iodine-131 ($T_{1/2}$ = 8.04 d, Y_f =2.89 %) was separated from the hot FP solution by distillation form 20 % HNO_3 containing 0.5 ml 30 % H_2O_2, as an oxidant, via boiling for 4 h. The distilled off radioiodine was recovered in ice-cooled 15 ml 0.1 M NaOH-0.01 M $Na_2S_2O_3$ solution after passing through an acid trap containing 15 ml 3 M H_2SO_4. The separation yield of ^{131}I was ≥ 99.99 % with a recovery yield of 82.7 %. The corresponding radionuclidic purity was found to be 65.60 % ^{131}I (determined immediately after recovery) with the presence of 34.40 %

^{132}I, as an isotopic radiocontaminant, and ≥ 99.99 % ^{131}I (determined after ~ 40-h decay time) due to decay of ^{132}I with $T_{1/2}$ = 2.28 h. Radiochemical purity of the ^{131}I product solution was found to be 99.4 % (onto Whatman No. 1 paper chromatogram) and 99.2 % (onto thin layer chromatogram) as I^-. pH-value of the product solution was 12.8 containing radioactivity and radioactive concentration of 11.7 MBq ^{131}I and 0.8 MBq ^{131}I /ml, respectively. However the same procedure was followed for the separation of ^{129}I ($T_{1/2}$ = 1.57 ×10^7 y, Y_f = 0.511 %) from the aged FP solution, it was not detected in the product solution.

Ruthenium-106 ($T_{1/2}$ = 1.02 y, Y_f = 0.402 %) was separated from the aged FP solution, after separation of ^{129}I, by distillation from 40 % HNO_3 containing 0.01 g $KMnO_4$, as an oxidant, via boiling for 2.5 h. The distilled off radioruthenium was recovered in ice-cooled 15 ml 0.1 M NaOH solution with a separation yield of 91.8 % ^{106}Ru (no more ^{106}Ru was distilled off after boiling for further 0.5 h), and a recovery yield of 74.3 %. The product solution had a radionuclidic purity of ≥ 99.99 % ^{106}Ru, pH-value of 12.3, radioactivity and radioactive concentration of ~ 13.9 kBq ^{106}Ru and ~ 0.9 kBq ^{106}Ru/ml, respectively. On the other hand, ^{103}Ru ($T_{1/2}$ = 39.27 d, Y_f = 3.03 %) was separated from the hot FP solution, after separation of ^{131}I, by distillation from 40 % HNO_3-10 % H_2SO_4 containing 0.01 g $KMnO_4$, as an oxidant, via boiling for 1 h. The distilled off radioruthenium was recovered in ice-cooled 15 ml 0.1 M NaOH solution with a separation yield of ≥ 99.99 % ^{103}Ru and a recovery yield of 77.5 %. The product solution had a radionuclidic purity of 98.49 % ^{103}Ru (with the presence of 1.51 % of $^{106}Ru/^{106}Rh$ radioactive couple as an isotopic radiocontaminant), pH-value of 12.5, radioactivity and radioactivity concentration of 5.1 MBq ^{103}Ru and 0.3 MBq ^{103}Ru /ml, respectively.

Cesium-137 ($T_{1/2}$ = 30.07 y, Y_f = 6.19 %) was separated from the aged FP solution, after separation of ^{106}Ru, by addition of NaOH solution to pH-value of 9.5 to precipitate the $Al(OH)_3$-MnO_2-$Na_2U_2O_7$ matrix which selectively retained the remaining FP radionuclides leaving, mainly, ^{137}Cs in the supernatant solution with a seaparation yield (or a recovery yield) of 97.3 %. Radionuclidic purity of the product solution was found to be ~ 99.75 % ^{137}Cs with the presence of ~ 0.25 % ^{134}Cs as an isotopic radiocontaminant and ~1.4 × 10^{-3} % ^{152,155}Eu as non-isotopic radiocontaminants separated and identified by 6-WCe chromatographic column operations. Radioactivity and specific activity of the final ^{137}Cs product loaded onto 1.5 g of 6-WCe matrix were found to be ~ 54.4 kBq ^{137}Cs and ~ 36.3 kBq ^{137}Cs /g, respectively. Cesium-137 was also separated from the hot FP solution, after separation of ^{103}Ru, by raising pH-value of the solution to 9.5 to precipitate the $Al(OH)_3$-MnO_2-$Na_2U_2O_7$ matrix as mentioned above. Thereafter, HNO_3 was added to the supernatant solution (to obtain a FP solution in 1 M HNO_3) followed by addition of Ba carrier to precipitate $BaSO_4$ from the solution. Finally, scavenging of radiocesium as a ferrocyanide complex was carried out by addition of $Na_4[Fe(CN)_6]$ and $NiCl_2$ solutions and raising the solution pH-value to 10 with NaOH solution to precipitate $Ni_2[Fe(CN)_6]$. The separation yield of ^{137}Cs was ≥ 99.99 % with a recovery yield of 87.7 %. Radionuclidic purity of ^{137}Cs in the ferrocyanide complex was found to be 43.25 % with the presence of 0.26 % ^{134}Cs and 50.77 % ^{136}Cs as isotopic radiocontaminants, and 5.72 % ^{132}I as non-isotopic radiocontaminant. The radioactivity and specific activity of the ^{137}Cs product in the obtained ferrocyanide complex was found to be 51.9 kBq and 129.8 kBq/g, respectively.

All the aforementioned dissolution and chemical processing steps of the hot UO_3 targets were basic steps for establishing a procedure for separation of ^{99}Mo ($T_{1/2}$ = 2.75 d, Y_f = 6.11 %) from the hot FP solution. The final supernatant solution (66.8 ml of 1.7 M Na_2SO_4-2.3 M $NaNO_3$), obtained after precipitation of nickel ferrocyanide, was found to contain the radioactivity of ^{99}Mo. The separation yield of ^{99}Mo was found to be 97.5 % with a recovery yield of 66.1 %. The corresponding radionuclidic purity was found to be 99.05 % ^{99}Mo with the presence of 0.91 % ^{132}I and 0.04 % $^{95}Zr/^{95}Nb$ as radiocontaminants. The ^{99}Mo product solution had pH-value of 10, radioactivity and radioactive concentration of 12 MBq ^{99}Mo and 0.2 MBq ^{99}Mo /ml, respectively.

Zirconium-95 ($T_{1/2}$ = 64.02 d, Y_f = 6.5 %) and niobium-95 ($T_{1/2}$ = 34.97 d, Y_f =6.5 %) were separated from the $Al(OH)_3$-MnO_2-$Na_2U_2O_7$ matrix precipitated from the hot FP solution at pH9.5 (after a cooling time of 70 d). The matrix was dissolved in 30 ml 1 M H_2SO_4. Then, $BaCl_2$ was added to precipitate $BaSO_4$ from the solution. Purification of the separated $^{95}Zr/^{95}Nb$ couple (which remained in the supernatant solution) from traces of ^{137}Cs radiocontaminat was carried out by raising the solution pH-value to 9.5, to precipitate $Al(OH)_3$, which retained the $^{95}Zr/^{95}Nb$ couple leaving ^{137}Cs in the supernatant. Finally, $Al(OH)_3$ precipitate containing pure $^{95}Zr/^{95}Nb$ copule was dissolved in 30 ml 1 M HNO_3 solution. The separation yield of the $^{95}Zr/^{95}Nb$ couple was ≥ 99.99 % with a recovery yield of 95.3 %. Radionuclidic purity of the $^{95}Zr/^{95}Nb$ couple was found to be 99.96 % with the presence of 0.02 % ^{60}Co, 0.005 % ^{65}Zn, 0.005 % ^{125}Sb, and 0.01 % ^{144}Ce as radiocontaminants. Radioactivity and radioactive concentration were found to be 4.6 MBq and 0.15 MBq/ml for ^{95}Zr and 10.1 MBq and 0.34 MBq/ml for ^{95}Nb, respectively.

^{137}Cs recovered from the aged FP solution and ^{99}Mo recovered from the hot FP solution were loaded onto 6-WCe and chromatographic alumina columns for preparation of radioisotope generator systems from

which the generated ^{137m}Ba ($T_{1/2}$ = 2.55 min) and ^{99m}Tc ($T_{1/2}$ =6.01 h) daughter radionuclides were eluted, respectively. On the other hand, the mixture of ^{99}Mo and ^{137}Cs radionuclides recovered from the hot FP solution was loaded onto 6-WCe chromatographic column for preparation of a dual radioisotope generator from which ^{99m}Tc and ^{137m}Ba were sequentially eluted. The elution performance of the generated daughter radionuclides from the radioisotope generator systems was controlled as a function of some preparational and operational parameters such as column matrix, chemical composition of the eluent, flow rate, elution frequency, generator age, etc.

For $^{137}Cs/^{137m}Ba$ radioisotope generator based on 6-WCe column, the ^{137m}Ba eluates with 0.9 % NaCl-0.1 M HCl eluent had higher elution yields and radionuclidic purity than with 0.1 M NH_4Cl-0.1 M HCl eluent. The elution profiles of ^{137m}Ba had two components; maximum elution peak and continuous elution plateau. The generator has been repeatedly eluted for 311 days by passing 4810 ml of the saline eluent (10 ml × 481 elution operations) at a flow rate of 3.0 ml/min and 25°C. ^{137m}Ba eluates of reproducible elution yields (from 63.9±1.0 to 68.9±0.2 % at the maximum elution peaks, obtained in the second ml of the eluate, and from 41.2±0.5 to 44.8±1.0 % for 1 ml eluate of the continuous elution regions) and a high radionuclidic purity of ≥ 99.99 % were obtained. The eluates had pH-value of 1 with undetected W and Ce as chemical contaminants from the column matrix.

For $^{99}Mo/^{99m}Tc$ radioisotope generator based on alumina column, 20 elution operations were carried out, over a period of 26 days. In each elution operation, 10 ml 0.9 % NaCl solution, as eluent, was passed through the column bed at a flow rate of 0.5 ml/min (except for the 2nd, 3rd, and 4th elutions which were conducted at flow rates 1.0, 2.0, and 3.0 ml/min, respectively) and 25 °C. ^{99m}Tc eluates with high elution yield

(88.4 ± 0.4 %), radionuclidic purity (≥ 99.99 %), radiochemical purity (98.6-99.0 % as $^{99m}TcO_4^-$), and low Al contamination level (1-3 μg/ml) where obtained at flow rate 0.5 ml /min. pH-value of the ^{99m}Tc eluates ranged from 6.2-6.5.

For the ^{99}Mo/^{99m}Tc-^{137}Cs/^{137m}Ba dual generator based on 6-WCe column, ^{99m}Tc was firstly eluted for 14 times over a period of 18 days with passing 10 ml 0.9 % NaCl solution, in each elution operation, at a flow rate of 0.5 ml/min (except for the 2nd, 3rd, and 4th elutions which were conducted at flow rates 1.0, 2.0, and 3.0 ml/min, respectively) and 25°C. ^{99m}Tc eluates with elution yield of 76.9 ±0.3 %, radionuclidic purity of ≥ 99.99 %, radiochemical purity of 97.3-98.1 %, and low W and Ce contamination levels (1.5-2.7 and 0 μg/ml, respectively) were obtained at flow rate 0.5 ml/min. pH-value of the ^{99m}Tc eluates ranged from 3.2-4.5. After complete decay of ^{99}Mo (~ 90 d from loading the column with the mixture of ^{99}Mo and ^{137}Cs radionuclides), ^{137m}Ba was eluted for 250 days by passing 3300 ml of 0.9 % NaCl-0.1 M HCl eluent (10 ml × 330 elution operations) at a flow rate of 3.0 ml/min and 25°C. ^{137m}Ba eluates of reproducible elution yields (from 62.4±2.1 to 68.2±2.3 % at the maximum elution peaks, obtained in the second ml of the eluate, and from 41.4±1.1 to 44.3±1.1 % for 1 ml eluate of the continuous elution regions) with radionuclidic purity of ≥ 99.99 %, undetected W and Ce contamination levels, and pH-value of 1 were obtained.