CHAPTER V

SUMMARY AND CONCLUSION

The present work is concerned with the chemical processing of Egyptian monazite sand concentrate (~96% purity) produced from Rosetta beach black sand. The concentrate is prepared by NMA pilot plant using different physical dressing techniques as based upon the specific gravity, the magnetic and the electrostatic characteristics of the beach mineral constituents. The purpose of the chemical processing is to separate U, Th and REE in their maximum possible purity to ensure successfully marketable concentrates of adequate purity suitable for various applications. For U and Th concentrates, their preparation in nuclear pure forms suitable for nuclear fuel would represent the final target.

Two main chemical methods for monazite processing are competitive and have actually been commercially applied. These include the alkali process using caustic soda and the acid processing using sulfuric acid. The former has been applied on a pilot scale at Inchass Facility of NMA since the sixties. In this process, the phosphate component of the mineral is converted to trisodium phosphate while the metal values remain insoluble in the form of what is called the hydrous oxide cake. The latter is then dissolved in HCl and subjected to gradual neutralization fist at pH 5.8 to obtain the U/Th cake and then at a pH of about 8 to precipitate the REE cake. In the sulfuric acid process, the whole mineral is dissolved resulting in U, Th and REE sulfates and phosphates. Various recovery techniques have been studied for the separation of these metal values. However, in the eighties of the last century, it was proven that the primary amines are capable of selectively extracting U and Th values from sulfate liquors and it was therefore found necessary to carry out the present work. In the latter, it was also required to develop a rapid, sensitive and reliable method for U, Th and total REE analysis of the working mineral concentrate as well as during its breakdown and recovery of its metal values.

This thesis is therefore divided into three main topics, the first is the development of an IC method for U, Th and total REE analysis while the second topic involves the acid breakdown of the monazite concentrate by sulfuric acid and investigating the relevant parameters. The recovery of the metal values from the obtained sulfuric liquor represents the third topic.

The developed IC method for U, Th and ΣREE was studied using a Dionex 200 system fitted with an Ion Pac CS5A analytical column and an Ion Pac CG5A guard column. A gradient elution protocol was applied and the eluent used was composed of HCl and $(NH_4)_2SO_4$. The concentration of both eluent composition was studied as well as the effect of the flow rate to determine the optimum retention time and efficient resolution of the three analytes. The obtained results revealed that the optimum flow rate is 0.7 mL/min. Separation of U from Th and ΣREE was obtained by solution assaying of 0.1 M HCl and 0.1 M $(NH_4)_2SO_4$ while separation of Th from ΣREE was achieved using a solution assaying of 0.1 M HCL and 0.2 M $(NH_4)_2SO_4$. Using these optimum conditions, the necessary standard curves obeying Beer's law have been plotted in the range of 5.79 to 174.5 mg/L for U and in the range of 5 to 150 mg/L for Th and ΣREE. The analyzed monazite sand concentrate used in this work assayed 61.12% RE_2O_3, 4.70% ThO_2 and 0.42% U_3O_8.

For the breakdown of the study monazite by the sulfuric acid process, several conditions have been studied including the effects of the acid input, the sand grain size, the solid/liquid ratio as well as the effects of time and temperature. From the obtained results, it has been concluded that about 96% monazite dissolution would be obtained by applying the following optimum conditions upon the Egyptian monazite sand concentrate (as received); viz,

- Sulfuric acid concentration (v/v): 80%
- Solid/liquid ratio : 1/3
- Reaction time : 2.5 hr
- Reaction temperature : 180 °C

For studying the recovery of U, Th and ΣREE from monazite sulfate liquor, various techniques have actually been applied. The selective precipitation of Th and REE was first tried using a sulfate liquor assaying (in g/L) 32.20 REE, 2.47 Th, 0.2 U while SO_4^{2-} and PO_4^{3-} assayed 200.12 and 8.94 respectively. Using 10% NH_4OH solution, several sulfate solution samples have been neutralized to varying pH values. At pH 2, it was found that all Th and about 90% REE have been precipitated together with about 10% U. After filtering and proper washing of the latter, the pH of he obtained filtrate (120 mg/L U)was re-adjusted to 1.8 and was then passed through an anion exchange column (Amberlite IRA400) for U adsorption. However due to the high sulfate content (about 200 g/L) beside phosphate (about 9 g/L) the resin capacity for U did not exceed 5g/L i.e. less than 5% of its theoretical capacity. Uranium was almost readily eluted by 1 M NaCl acidified with H_2SO_4 to 0.1M. A contact time of 2 min which corresponded to 7.5 mL/min was used for U elution.

Failure to achieve economic results for U recovery by the ion exchange resin and due to the fact that primary amines (> 10 carbon atoms) are capable of extracting both U and Th from sulfate liquors it was decided to investigate the potentiality of applying this technique to working monazite sulfate leach liquor. For this purpose dodecylamine was used and the relevant extraction and stripping conditions were studied. The former included the amine concentration, the pH of the sulfate liquor, the extraction temperature as well as the nature of the diluent. For studying the effect of the amine concentration, various solutions assaying between 0.1 up to 5.4% amine in benzene were prepared and allowed to contact the aqueous phase (room temperature ≈25 °C, 1/1 for the O/A ratio and using a contact time of 5 min). The obtained results revealed the improvement of the extraction coefficient with increasing the amine concentration. The effect of the pH of the working sulfate liquor was also investigated between pH values ranging from -0.5 to 1.0 and indicated that the distribution coefficient is greatly improved by increasing the pH. Regarding the diluent, toluene, kerosene and methanol were used beside benzene. Benzene has indeed resulted in the best coefficients for both U and Th. On other hand, the equilibrium data of U and Th obtained by applying different O/A ratios during extraction were used to construct the corresponding McCabe_Thiele extraction diagrams. An operating line of slope 0.575 (equivalent to organic/aqueous flow rate)was found suitable for both curves. From the two diagrams, it would be clearly evident that 2 to 3 theoretical stages would be sufficient. Finally, nitric acid with different concentration was applied as a possible selective stripping agent. A suitable loaded organic phase sample assaying 0.79 g U/L and 11.314 g Th/L was prepared for this purpose. However, it was recommended to apply NaCl or NH_4NO_3 in presence of a low concentration of the corresponding acid.