



دراسات فيزيائية و كيميائية على التمعينات اليورانيومية  
بمنطقة السيلا بغرض عمليات الإذابة و الاستخلاص  
رسالة مقدمة من

احمد سعيد بيومى الشيخ

إلى

كلية العلوم – جامعة عين شمس  
ضمن متطلبات الحصول على درجة الدكتوراه الفلسفية فى الكيمياء

تحت إشراف

أ.د. محمد محمود ابو على  
أستاذ الكيمياء غير عضوية- كلية العلوم  
جامعة عين شمس

أ.د. احمد محمود السيد ضاهر  
أستاذ الكيمياء غير العضوية  
هيئة المواد النووية

2015



**PHYSICAL AND CHEMICAL STUDIES ON THE URANIFEROUS  
MINERALIZATION OF EL- SELLA AREA FOR ITS LEACHING  
AND RECOVERY PROCESSES**

A Thesis Presented  
To Chemistry Dept., Faculty of science  
Ain Shams University

*By*

**Ahmed Said Bayoumi El-Sheikh**

M. Sc. Chemistry 2006  
For the Degree of Doctor of Philosophy (Ph. D.) in Chemistry

**Supervised by**

*Prof Dr. Ahmed Mahmoud El-Sayed Daher*

*Professor of inorganic Chemistry  
Nuclear Materials Authority*

*Prof Dr. Mohamed Mahmoud Abo-Aly*

*Professor of inorganic Chemistry  
Faculty of Science- Ain shams University*

**2015**



كلية العلوم

قسم الكيمياء  
جامعة عين شمس

اسم الطالب: احمد سعيد بيومى الشيخ

الدرجة العلمية: دكتوراه الفلسفة فى العلوم

القسم التابع له: الكيمياء

اسم الكلية: كلية العلوم

اسم الجامعة: جامعة عين شمس

سنة الحصول على الماجستير: ٢٠٠٦



كلية العلوم  
قسم الدراسات العليا والبحوث

رسالة دكتوراه فى الكيمياء غير العضوية

اسم الطالب/ احمد سعيد بيومى الشيخ

عنوان الرسالة  
دراسات فيزيائية و كيميائية على التمعينات اليورانيومية بمنطقة السيلا بغرض  
عمليات الإذابة و الاستخلاص

اسم الدرجة/ الدكتوراه فى الكيمياء غير العضوية

لجنة الاشراف

ا.د. / محمد محمود محمد ابو على استاذ الكيمياء غير العضوية-كلية العلوم-جامعة عين شمس

ا.د./ احمد محمود السيد ضاهر استاذ الكيمياء غير العضوية -هيئة المواد النووية

لجنة الحكم

اجيزت الرسالة بتاريخ / / ٢٠١٥

الدراسات العليا

ختم الاجازة

موافقة مجلس الجامعة

موافقة مجلس الكلية



**PHYSICAL AND CHEMICAL STUDIES ON THE URANIFEROUS  
MINERALIZATION OF EL- SELLA AREA FOR ITS LEACHING  
AND RECOVERY PROCESSES**

Thesis advisors

***SIGNATURE***

***Prof Dr. Mohamed Mahmoud Abo-Aly***

***Prof Dr. Ahmed Mahmoud El-Sayed  
Daher***

**Head of chemistry department**

**Prof Dr/ Hamed Ahmed Derbala**



# Contents

<b>Abstract</b>	<b>v</b>
<b>Abbreviations</b>	<b>vi</b>
<b>Acknowledgment</b>	<b>vii</b>
<b>LIST OF FIGURES</b>	<b>viii</b>
<b>LIST OF TABLES</b>	<b>xii</b>
<b>CHAPTER I INTRODUCTION AND LITERATURE REVIEW</b>	<b>1</b>
<b>Part I Introduction</b>	<b>1</b>
<b>I.1.General Statement</b>	<b>1</b>
<b>I.2. Mode of Occurrence OF EL-Sella Mineralization</b>	<b>2</b>
<b>I.3. Aim and Scope of the Work</b>	<b>4</b>
<b>PART II The Hydrometallurgical Characteristics of Uranium and Rare Earth Elements –Theoretical Aspects and Literature Review</b>	<b>5</b>
<b>I.4. Extractive metallurgy of uranium ores</b>	<b>5</b>
<b>I. 4.1. Uranium leaching</b>	<b>5</b>
<b>I.4.1.1. Leaching reagents</b>	<b>6</b>
<b>I.4.1.2. Leaching techniques</b>	<b>9</b>
<b>I.4.1.2.1.Atmospheric agitation leaching</b>	<b>12</b>
<b>I.4.1.2.2. Pressure leaching</b>	<b>13</b>
<b>I.4.1.2.3. Strong acid pugging and curing</b>	<b>15</b>
<b>I.4.1.2.4. Percolation leaching</b>	<b>16</b>
<b>I.4.1.2.5. In-situ mining</b>	<b>17</b>
<b>I.4.1.2.6. In-situ underground leaching</b>	<b>18</b>
<b>I.4.1.2.7. Bacterial leaching</b>	<b>18</b>
<b>I.4.1.2.8. Heap leaching</b>	<b>18</b>
<b>I.4.1.2.9. Solvent leaching</b>	<b>19</b>
<b>I.4.2. Recovery of uranium from its leach liquors</b>	<b>21</b>
<b>I.4.2.1. Ion exchange technique:</b>	<b>21</b>
<b>I.4.2.1.1. Chemistry of ion exchange:</b>	<b>21</b>
<b>I.4.2.1.1.1. Adsorption reactions</b>	<b>22</b>
<b>I.4.2.1.1.2. Elution reaction</b>	<b>22</b>
<b>I.4.2.2. Ion exchange systems</b>	<b>23</b>
<b>I.4.2.2.1. Fixed bed system</b>	<b>23</b>

<b>I.4.2.2.2. moving bed system</b>	<b>23</b>
<b>I.4.2.2.3. Resin in pulp system (RIP)</b>	<b>24</b>
<b>I.4.2.2.4. Continuous ion exchange (CIX)</b>	<b>25</b>
<b>I.4.2.2. Uranium recovery by solvent extraction</b>	<b>26</b>
<b>I.4.2.2.1 Chemistry of uranium extraction by organic solvents</b>	<b>28</b>
<b>I.4.2.2.3. Diluents</b>	<b>32</b>
<b>I.4.2.2.3 Chemistry of uranium re-extraction (stripping) from loaded solvents</b>	<b>32</b>
<b>I.4.2.2.4. Multistage operation</b>	<b>34</b>
<b>I.4.2.3. Uranium precipitation</b>	<b>35</b>
<b>I.5. Extractive metallurgy of rare earth elements</b>	<b>38</b>
<b>I.5.1. Rare earths ores</b>	<b>39</b>
<b>I.5.1.1. Bastnasite</b>	<b>39</b>
<b>I.5.1.2. Monazite</b>	<b>40</b>
<b>I.5.1.2 Xenotime</b>	<b>43</b>
<b>I.5.2. Separation and recovery procedures of REEs</b>	<b>45</b>
<b>I.5.2.1. Separation of rare earths by ion exchange technique</b>	<b>46</b>
<b>I.5.2.2. Solvent extraction separation of rare earths</b>	<b>48</b>
<b>I.5.2.2.1. Cation exchangers</b>	<b>51</b>
<b>I.5.2.2.2. -Carboxylic acids</b>	<b>52</b>
<b>I.5.2.2.3. Organophosphorous acids</b>	<b>53</b>
<b>I.5.2.2.4. Chelating extractant</b>	<b>56</b>
<b>I.5.2.2.5. Solvation extractant</b>	<b>56</b>
<b>I.5.2.2.6. Anion exchangers</b>	<b>57</b>
<b>I.5.2.2.6. Synergistic solvent extraction</b>	<b>58</b>
<b>CHAPTER II EXPEREMENTAL</b>	<b>59</b>
<b>II.1. Chemicals and reagents</b>	<b>59</b>
<b>II.2. Materials</b>	<b>60</b>
<b>II.3. Experimental procedure</b>	<b>60</b>
<b>II.3.1. Acid leaching procedures</b>	<b>60</b>
<b>II.3.1.1. Acid agitation leaching procedures</b>	<b>60</b>
<b>II.3.1.1. Acid pug leaching procedures</b>	<b>62</b>
<b>II.3.2. Solvent extraction of uranium and REEs</b>	<b>62</b>
<b>II.3.2.1. A/O Solvent extraction of uranium and REEs</b>	<b>63</b>
<b>II.3.2.2. Solvent extraction leaching of uranium</b>	<b>63</b>
<b>II.4. Analytical procedure</b>	<b>63</b>
<b>II.4.1. Analysis of the working ore material</b>	<b>63</b>
<b>II.4.2. Control analysis</b>	<b>64</b>



<b>II.4.2.1. Uranium analysis</b>	<b>64</b>
<b>II.4.2.2. REEs analysis</b>	<b>64</b>
<b>II.4.3. Instrumentation</b>	<b>65</b>
<b>CHAPTER III RESULTS AND DISCUSSION</b>	<b>66</b>
<b>III.1.Characteristics of the working El-Sella ore material</b>	<b>66</b>
<b>III.1.1. Mineralogical characteristics</b>	<b>66</b>
<b>III.1.2. Chemical composition</b>	<b>67</b>
<b>III.2. Results of acid leaching relevant factors</b>	<b>72</b>
<b>III.2.1. Effect of sulfuric acid concentration</b>	<b>72</b>
<b>III.2.2. Effect of solid/ liquid ratio</b>	<b>74</b>
<b>III.2.3. Effect of the leaching time</b>	<b>75</b>
<b>III.2.4. Effect of the leaching temperature</b>	<b>77</b>
<b>III.3. Uranium extraction by Trioctyl Amine</b>	<b>79</b>
<b>III.3.1 Optimization of the uranium extraction parameters by TOA</b>	<b>79</b>
<b>III.3.1.1 Effect of pH value</b>	<b>79</b>
<b>III.3.1.2 Effect of shaking time</b>	<b>81</b>
<b>III.3.1.3 Effect of TOA concentration upon uranium extraction</b>	<b>83</b>
<b>III.3.1.4 Effect of O/A phase ratio -construction of McCabe Thiele extraction diagram</b>	<b>84</b>
<b>III.3.2. Optimization of the uranium stripping parameters from loaded TOA</b>	<b>88</b>
<b>III.3.2.1. Uranium stripping using sulfuric acid</b>	<b>88</b>
<b>III.3.2.1.1. Effect of sulfuric acid concentration</b>	<b>88</b>
<b>III.3.2.1.2. Effect of shaking Time</b>	<b>90</b>
<b>III.3.2.1.3. Effect of A/O phase ratio upon uranium stripping construction of McCabe-Thiele stripping diagram</b>	<b>91</b>
<b>III.3.2.2. Uranium stripping using sodium carbonate</b>	<b>93</b>
<b>III.3.2.2.1. Effect of sodium carbonate concentration</b>	<b>93</b>
<b>III.3.2.2.2. Effect of shaking time</b>	<b>95</b>
<b>III.3.2.2.3. Effect of A/O phase ratio - construction of McCabe-Thiele stripping diagram</b>	<b>96</b>
<b>III.4. REEs extraction by DEHPA</b>	<b>98</b>
<b>III.4.1. Optimization of the REEs extraction parameters by DEHPA</b>	<b>99</b>
<b>III.4.1.1. Effect of DEHPA concentration upon REEs extraction</b>	<b>99</b>
<b>III.4.1.2. Effect of the shaking time</b>	<b>101</b>
<b>III.4.1.3. Effect of O/A phase ratio-construction of McCabe-Thiele extraction diagram</b>	<b>102</b>

<b>III.4.2. Optimization of the REEs stripping parameters from loaded DEHPA</b>	<b>104</b>
<b>III.4.2.1. Effect of the stripping agent</b>	<b>105</b>
<b>III.4.2.2. Effect of the shaking time</b>	<b>106</b>
<b>III.4.2.3. Effect of O/A Phase ratio -construction of McCabe Thiele stripping diagram</b>	<b>108</b>
<b>III.5. Solvent leaching results of uranium from El-Sella mineralization</b>	<b>110</b>
<b>III.5.1 Results of relevant pug leaching parameters</b>	<b>110</b>
<b>III.5.2. Solvent leaching of uranium</b>	<b>110</b>
<b>III.5.2.1. Effect of curing time</b>	<b>111</b>
<b>III.5.2.2. Effect of curing temperature</b>	<b>114</b>
<b>III.5.2.3. Effect of input acid amount</b>	<b>117</b>
<b>III.5.2.4. Effect of solvent flow rate</b>	<b>119</b>
<b>III.5.2.5. Effect of solvent concentration</b>	<b>122</b>
<b>III.5.3. Results of uranium stripping</b>	<b>125</b>
<b>III.5.3.1. Effect of sodium carbonate concentration</b>	<b>126</b>
<b>III.5.3.2. Effect of shaking time</b>	<b>127</b>
<b>III.5.3.3. Effect of A/O phase ratio and construction of McCabe-Thiele stripping diagram</b>	<b>129</b>
<b>III.6. Kinetic Studies</b>	<b>132</b>
<b>CHAPTER IV SUMMARY AND CONCLUSION</b>	<b>139</b>
<b>REFERENCES</b>	<b>146</b>
<b>ARABIC SUMMARY</b>	

## *Abstract*

**Key words:**, uranium, rare Earths, solvent extraction, solvent leaching,

trioctyl amine, DEHPA

The present work is concerned with the chemical processing of El-Sella mineralization in order to recover its two metal values; namely uranium and REEs. For this purpose acid leaching using sulfuric acid has been studied to determine the optimum conditions to obtain their maximum possible leaching efficiencies. The obtained leach liquor was then subjected to two solvent extraction circuits; viz a Trioctyl amine circuit for selective anionic uranium extraction whereas in the second circuit, REEs have been extracted using the cationic extractant (di-2-ethyl hexyl phosphoric acid, DEHPA).

Due to the specific nature of El-Sella ore material, which is highly argillic in a manner to require a low solid/liquid ratio in the leaching circuit with consequent expensive solid/liquid separation and filtration, it was found necessary to directly apply the solvent leaching procedure. The latter was applied herein for uranium after proper acid pug leaching of the working ore material using TOA.

## **ACKNOWLEDGEMENT**

Praise to Allah, Al-Rahman Al-Rahem, by whose grace this work has been completed.

I am indeed very grateful to Prof. Dr. Mohammed Mahmoud Abo-Aly, Chemistry Dept., Faculty of Science, Ain Shams University for his excellent interest and supervision. In the mean time, I wish to express my gratitude to my supervisor Prof. Dr. Ahmed Daher, Head of Materials of Reactor Treatment Section, (Nuclear Materials Authority) for suggesting the subject, supervision, the help and advice he gave to me during the progress of the work. I also thank him for his continuous support and valuable ideas.

Great thanks for Prof. Dr. Nabil El-Hazek, Ex-Present of Nuclear Materials Authority for his excellent help and efforts in revising the manuscript and finishing this work. Finally, my deepest gratitude is offered to my family.

# Abbreviations

<b>Suffexx</b>	<b>Abbreviation</b>
<b>B</b>	<b>Benzene</b>
<b>DEHPA</b>	<b>Di Ehtyl Hexyl Phosphoric acid</b>
<b>DCHPA</b>	<b>Dicyclohexylphosphinic acid</b>
<b>HDP A</b>	<b>Mono heptadecyl phosphoric acid</b>
<b>K</b>	<b>Kerosene</b>
<b>REEs</b>	<b>Rare earth elements</b>
<b>S/L</b>	<b>Solid/liquid</b>
<b>TBP</b>	<b>Tri butyl phosphate</b>
<b>TOA</b>	<b>Trioctyl amine</b>
<b>U</b>	<b>Uranium</b>
<b>v/v</b>	<b>Volume/volume</b>
<b>XRF</b>	<b>X ray fluorescence</b>

## *LIST OF Figures*

<b>Fig. (1)</b>	<b>The location map of El-Sella area.</b>	<b>3</b>
<b>Fig. (2)</b>	<b>Selection of leaching processes.</b>	<b>11</b>
<b>Fig. (3)</b>	<b>Distribution isotherms for extraction of uranium from a Plateau leach liquor with alkyl phosphate .</b>	<b>28</b>
<b>Fig. (4)</b>	<b>Typical McCabe-Thiele diagram for three-stage countercurrent extraction.</b>	<b>35</b>
<b>Fig. (5)</b>	<b>Chemical processing of Bastnasite.</b>	<b>40</b>
<b>Fig. (6)</b>	<b>Monazite processing by acid treatment.</b>	<b>43</b>
<b>Fig. (7)</b>	<b>Monazite processing by alkali treatment.</b>	<b>43</b>
<b>Fig. (8)</b>	<b>Chemical processing of Xenotime.</b>	<b>44</b>
<b>Fig. (9)</b>	<b>XRF of El-Sella sample.</b>	<b>69</b>
<b>Fig. (10)</b>	<b>Scanning Electron microscope of El-Sella sample (1).</b>	<b>70</b>
<b>Fig. (11)</b>	<b>Scanning Electron microscope of El-Sella sample (2).</b>	<b>71</b>
<b>Fig. (12)</b>	<b>Effect of sulfuric concentration upon uranium. and rare earth leaching efficiency From El-Sela composite sample.</b>	<b>73</b>
<b>Fig. (13)</b>	<b>Effect of solid/liquid upon uranium and rare earth leaching efficiency from El-Sela composite sample.</b>	<b>75</b>
<b>Fig. (14)</b>	<b>Effect of leaching time upon uranium and rare earth leaching efficiency from El-Sela composite.</b>	<b>77</b>
<b>Fig. (15)</b>	<b>Effect of temperature upon uranium and rare earth leaching efficiency from El-Sela composite sample.</b>	<b>78</b>
<b>Fig. (16)</b>	<b>Effect of pH on uranium extraction efficiency from the leach liquor of El-Sella composite sample.</b>	<b>81</b>
<b>Fig. (17)</b>	<b>Effect of shaking time upon uranium extraction efficiency from the leach liquor of El-Sella composite sample.</b>	<b>82</b>
<b>Fig (18)</b>	<b>Effect of TOA concentration (M) upon uranium extraction from the Leach liquor of El Sella mineralization composite sample.</b>	<b>84</b>

<b>Fig. (19)</b>	<b>Effect of O/A phase ratio upon uranium extraction efficiency of uranium by TOA in benzene from the loaded liquor of El Sella mineralization composite sample.</b>	<b>87</b>
<b>Fig. (20)</b>	<b>McCabe-Thiele diagram for uranium extraction from the acid leach liquor of El Sella composite sample.</b>	<b>88</b>
<b>Fig. (21)</b>	<b>Effect of sulfuric acid concentration upon uranium stripping efficiency for the loaded 1.2 g U/l by 0.088 M TOA/B solvent sample.</b>	<b>89</b>
<b>Fig. (22)</b>	<b>Effect of shaking time upon uranium stripping efficiency by 15% H<sub>2</sub>SO<sub>4</sub> from the loaded (1.2 g U/l) 0.088M TOA/K solvent sample.</b>	<b>91</b>
<b>Fig. (23)</b>	<b>Effect of A/O phase ratio upon uranium stripping efficiency by 15% H<sub>2</sub>SO<sub>4</sub> from the loaded 1.2 g U/l 0.088M TOA/K solvent sample.</b>	<b>92</b>
<b>Fig. (24)</b>	<b>McCabe-Thiele diagram for uranium stripping by 15% H<sub>2</sub>SO<sub>4</sub> v/v from the loaded 1.2g/l 0.088M TOA/K solvent sample.</b>	<b>93</b>
<b>Fig. (25)</b>	<b>Effect of sod. Carbonate conc. upon uranium stripping efficiency for the loaded 1.2 g/l 0.088 M TOA/benzene solvent sample.</b>	<b>95</b>
<b>Fig. (26)</b>	<b>Effect of shaking time upon uranium stripping efficiency for the loaded 1.2 g/l 0.088 M TOA/benzene solvent sample.</b>	<b>96</b>
<b>Fig. (27)</b>	<b>Effect of phase ratio upon uranium stripping efficiency for the loaded 1.2 g/l 0.088 M TOA/benzene solvent sample.</b>	<b>97</b>
<b>Fig. (28)</b>	<b>McCabe-Thiele diagram for uranium stripping by sod. Carbonate v/v from the loaded 1.2g/l 0.088M TOA/K solvent sample.</b>	<b>98</b>
<b>Fig. (29)</b>	<b>Effect of DEHPA/K concentration upon REEs extraction efficiency from the uranium-free El Sella leach liquor.</b>	<b>101</b>
<b>Fig. (30)</b>	<b>Effect of shaking time in upon REEs extraction efficiency from the uranium-free El Sella leach liquor.</b>	<b>102</b>
<b>Fig. (31)</b>	<b>Effect of A/O ratio upon REEs extraction efficiency by DEHPA/K from the uranium-free El Sella leach liquor.</b>	<b>103</b>