

Recovery of Rare Earths from Uranium Ion Exchange Effluent Solutions

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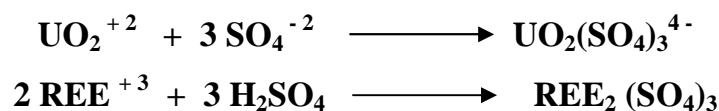
Summary. Sulphate effluent solutions from anion exchange resin after uranium extraction were containing about 115 ppm of rare earth elements (REE), so a trial to recover these amounts was studied. Precipitation of rare earths from these solutions using sodium hydroxide was firstly studied to prepare hydrous cake concentrate followed by studying upgrading for this concentrate by selective precipitation from different acidic media using hydrofluoric or oxalic acids. More than 99% of the REE were precipitated from the effluent solutions using sodium hydroxide at pH 8.5 while the same precipitation efficiency was achieved at lower pH value (6.5) in presence of 2.5% hydrogen peroxide. However, it is benefit to firstly precipitate most of the iron cations at pH 3.0 also washing the produced REE hydroxide cake by water of pH 9.5 to decrease the co-precipitated aluminum as well as upgrading the constituents of REE in the cake from 16% to more than 27%. Rare earths selective precipitation using hydrofluoric acid from nitrate medium was the most effective while the precipitation using oxalic acid from hydrochloric acid medium was effective where about 98% precipitation efficiency were achieved in the two cases. On the other hand, the rare earths fluoride precipitate was high grade and containing minimum co-precipitated of the other constituents than that of rare earths oxalate.

Introduction

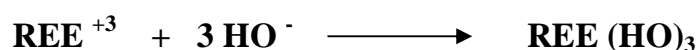
Rare earth elements comprise fifteen elements of lanthanides on the periodic table with atomic numbers from 57 to 71 in addition to scandium of atomic number 21 and yttrium of atomic number 39 because of their similar properties.^(1, 2) The chemistry of rare earths is generally discussed not as individual element but as a group where they are classified mainly into two groups as enriched in their minerals and namely light rare earths (or cerium group) and heavy rare earths (or yttrium group).^(3, 4)

Igneous rocks and the deposits derived from weathering of pegmatite represent the main sources of rare earths.⁽²⁾ However, about 95% of the rare earths occur in three minerals namely; monazite, bastnasite (cerium group source) and xenotime (yttrium group source). The other rare earth mineral resources involved are euxenite, gadolinite, pyrochlore and the non rare earth mineral especially that of igneous rocks containing uranium and thorium as well as that associated with iron ores.^(1,2) The markets account for 59% of the total worldwide consumption of rare earths for catalysts, glassmaking, lighting, and metallurgy.^(1,5) On the other hand, high-growth markets of battery alloys, ceramics and permanent magnets as well as application in the nuclear reactors account for the other 41%.^(6, 7,8)

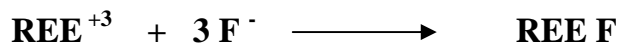
Extractive hydrometallurgy of ores, especially uranium which also associated with yttrium group rare earths, is a hydro-chemical process including leaching followed by recovery processes for the required element. Sulphuric acid is widely used all over the world for leaching uranium ores without prior separation by physical upgrading techniques.⁽⁹⁾ The reactions of uranium and rare earths with sulphuric acid can be represented as follow:⁽¹⁰⁾



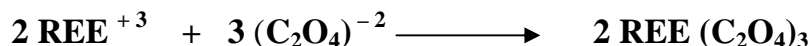
The commonly methods used for separating the rare earths from their pregnant solutions involve selective and fractional precipitation and extraction using either ion exchange resins or organic solvents.⁽¹¹⁾ However, the extraction techniques may require preparation of high grade concentrates of rare earths through the precipitation methods.⁽¹⁾ Rare earths can be separated through precipitation by different precipitating agents namely; hydroxide, fluoride and oxalate.⁽²⁾ By a suitable combination of these precipitation methods, separation of rare earths is accomplished. Ammonium, sodium or potassium hydroxides and calcium or magnesia milk can be used for precipitation of rare earths as hydroxide, but these precipitation methods are the least selective.⁽¹²⁾ Hydroxide precipitation proceeds according to the following equation:



Precipitation of the rare earths as fluoride is particularly useful for the collection of trace amounts due to their low solubility particularly for the heavier rare earths.⁽²⁾ Fluoride precipitation proceeds according to the following equation:



Precipitation of the rare earths as oxalate is most useful for separating from the majority of accompanying elements.^(2,13) Large amounts of ferric iron tend to inhibit precipitation of the rare earths because oxalic acid was consumed in reduction of the ferric iron. Oxalate precipitation proceeds according to the following equation:



In precipitation using fluoride or oxalate, as the precipitating agent concentration increases the rare earth solubility decreases considerably.

Experimental

Materials, chemicals and reagents used

All chemicals and reagents were analytical grade and double distilled water was used except that used in the pilot unit.

Instrumentation and analytical

Hot plate magnetic stirrer model Fisher Scientific was used for samples agitation. pH–mV–temp. meter, HAANA instruments provided with H1 1270 combination electrode and temperature sensor was used for pH adjustment. Determination of total rare earths using Arsenazo III method⁽¹⁴⁾ was accomplished using UV-spectrophotometer single, model SP-8001, Metretech Inc. Scanning Electron Microscope (SEM), model Philips XL 30 was used for identification of the prepared rare earth concentrates.

Raw materials preparation

Technological sample weighing 6 tons of an uraniferous mineralization, assay mean value of 1300 ppm U and 500 ppm REE, from Gattar (V) area, located at 35 km west of Hurghada City, Egypt, was batch treated on pilot unit. The solid material was firstly exposed to crushing and grinding to grain size of – 60 mesh "0.25 mm" then leaching by 100 g/l sulphuric acid without oxidant addition where the slurry of 50% solids was agitated for 6 h at about 50°C. At these conditions more than 96.0% of uranium and 59.0% of rare earths constituents were leached.⁽¹⁵⁾

After filtration and solids washing, the pH of the solutions was adjusted to 1.75 using 10% sodium hydroxide. These solutions were then passed through set of two columns packed with Amberlite IRA 400 anion exchange resin where the uranium content was completely extracted. The effluent solutions from the ion exchange columns were collected which containing about 115 ppm of REE.

Rare earths precipitation from the effluent solutions

Five liters of effluent solutions were subjected to hydroxide precipitation experiments at different pH values from 3.5 to 9.5 using 10% sodium hydroxide and also in presence of 2.5% hydrogen peroxide. After each precipitation experiment, the slurry was filtered out using filter paper (Whatman 41). The filtrate from each experiment was analyzed against the un-precipitated rare earths then precipitation efficiency was calculated according to the following equation:

$$\text{Precipitation efficiency, \%} = \frac{(\text{Original Conc. of REE} - \text{un-precipitated})}{\text{Original Conc. of REE}} \times 100$$

Samples from the hydroxide precipitation were then prepared for qualitative analysis against the major and rare earth elements using the SEM. These samples were prepared as follows:

Ten liters from the effluent solutions were subjected firstly for precipitation of its iron constituent at pH 3.0 then samples from the resultant clear solution each of one liter were then precipitated at different pHs of 7.5, 8.5 with NaOH and at pH 6.5 with NaOH in presence of H₂O₂. The produced precipitates filtered out and washed as summarized in table (1) then dried.

Table (1): conditions of precipitation and washing of the hydroxide cake

| Sample Number | | | | | | |
|---------------|--|--------|---|--|--------|---|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| Condition | pH 7.5 | pH 8.5 | pH 6.5 in presence of H ₂ O ₂ | pH 7.5 | pH 8.5 | pH 6.5 in presence of H ₂ O ₂ |
| | The precipitate was washed by normal water | | | The precipitate was washed by water adjusted to pH 9.5 with NaOH | | |

The suitable conditions of hydroxide precipitation were then applied upon the effluent solutions, to prepare hydroxide cake concentrate which was the raw material for the further selective precipitation experiments from different acids media. In this

regard, the pH was adjusted firstly to 3.0 using sodium hydroxide for iron removal, the resultant clear solutions was further adjusted to pH 8.5 for rare earths precipitation. The thickened slurry was filtered out and washed with water of pH 9.5 to minimize the aluminum content. Sample from the dry cake was qualitatively analyzed using the SEM.

Rare earths selective precipitation

Rare earths selective precipitation via hydrofluoric and oxalic acids were studied, after dissolution the dry hydroxide cake in the required acidic medium (chloride, nitrate or sulphate), where 100 ml from the prepared solution was used for each experiment.

Fluoride precipitation

Experiments of rare earths fluoride precipitation from the three acidic media were conducted using hydrofluoric acid (70% concentration) by adding 0.5, 1.0, 1.5, 2.0 and 3.0 ml and then filtered in polypropylene funnel using filter paper (Whatman 41). The filtrate from each experiment was analyzed against the remained un-precipitated rare earths. The precipitation efficiency was calculated for each experiment according to the previously mentioned equation. Rare earth dry precipitate samples were prepared then qualitatively analyzed by the SEM.

Oxalate precipitation

Experiments of rare earths oxalate precipitation from the three acidic media were also studied. Oxalic acid equivalent to 12% was gradually added as crystals to the sample with continuous stirring.⁽²⁾ The samples solution were firstly adjusted to pH 1.0 and 5.0 using 10% sodium hydroxide where the pH was re-adjusted to pH 1.0 by ammonium hydroxide after the addition of oxalic acid. Each sample was allowed to stand over night then the precipitate was filtered. The filtrate was analyzed against the remained un-precipitated rare earths. The precipitation efficiency was calculated according to the previously mentioned equation.

Rare earth oxalate precipitate samples prepared from chloride and nitrate acidic media were ignited at 650°C then qualitatively analyzed using the SEM.

Results and Discussion

The analysis of Gattar "V" host rock is shown in table (2). The data indicates that the rare earths present are mainly yttrium group (about 55% yttrium) and the total of rare earths represent about 85% of the present uranium.⁽²⁾

Table (2): Major oxides, trace elements and rare earths in Gattar "V" host rock

| M.E.* | % | T.E.* | ppm | T. E.* | ppm | REE* | ppm | % of Total | REE* | ppm | % of Total |
|--------------------------------|-------|-------|-----|--------|-------|------|------|------------|-------|-------|------------|
| SiO ₂ | 64.22 | As | 111 | Rb | 220.7 | Y | 518 | 54.82 | La | 42.7 | 4.52 |
| Al ₂ O ₃ | 14.71 | Ba | 174 | Sr | 140.6 | Sc | 16.0 | 0.11 | Ce | 87.2 | 9.28 |
| Fe ₂ O ₃ | 7.18 | Cr | 147 | Th | 22.54 | Gd | 30.1 | 3.18 | Pr | 10.5 | 1.11 |
| MnO | 0.07 | Cu | 65 | U | 1120 | Tb | 8.6 | 0.91 | Nd | 56.3 | 5.96 |
| MgO | 0.86 | Ga | 31 | V | 175 | Dy | 59.0 | 6.24 | Sm | 24.1 | 2.55 |
| CaO | 1.61 | Nb | 169 | Zn | 312 | Ho | 14.4 | 1.52 | Total | 959.7 | |
| Na ₂ O | 1.41 | Ni | 51 | Zr | 338.3 | Er | 44.4 | 4.70 | U | 1120 | |
| K ₂ O | 3.02 | Pb | 82 | | | Tm | 6.6 | 0.70 | | | |
| TiO ₂ | 0.81 | | | | | Yb | 37.3 | 3.95 | | | |
| P ₂ O ₅ | 0.18 | | | | | Lu | 4.7 | 0.50 | | | |
| LOI | 4.54 | | | | | | | | | | |
| Total | 98.59 | | | | | | | | | | |

earth element

*M. E. = Major Element

T. E. = Trace Element and

REE = Rare

Precipitation of rare earths from sulphate effluent solutions

Results of rare earths precipitation from effluent sulphate solutions (after uranium extraction) using sodium hydroxide and its qualitative analysis using SEM will be herein discussed.

Precipitation using sodium hydroxide

Results of rare earths precipitation efficiency from sulphate effluent solutions at different pH were indicated in figure (1).

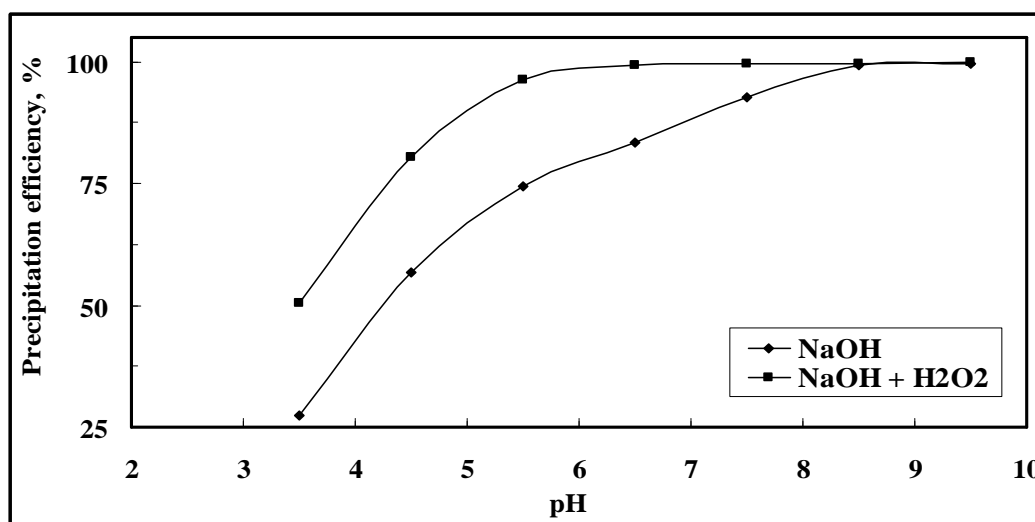


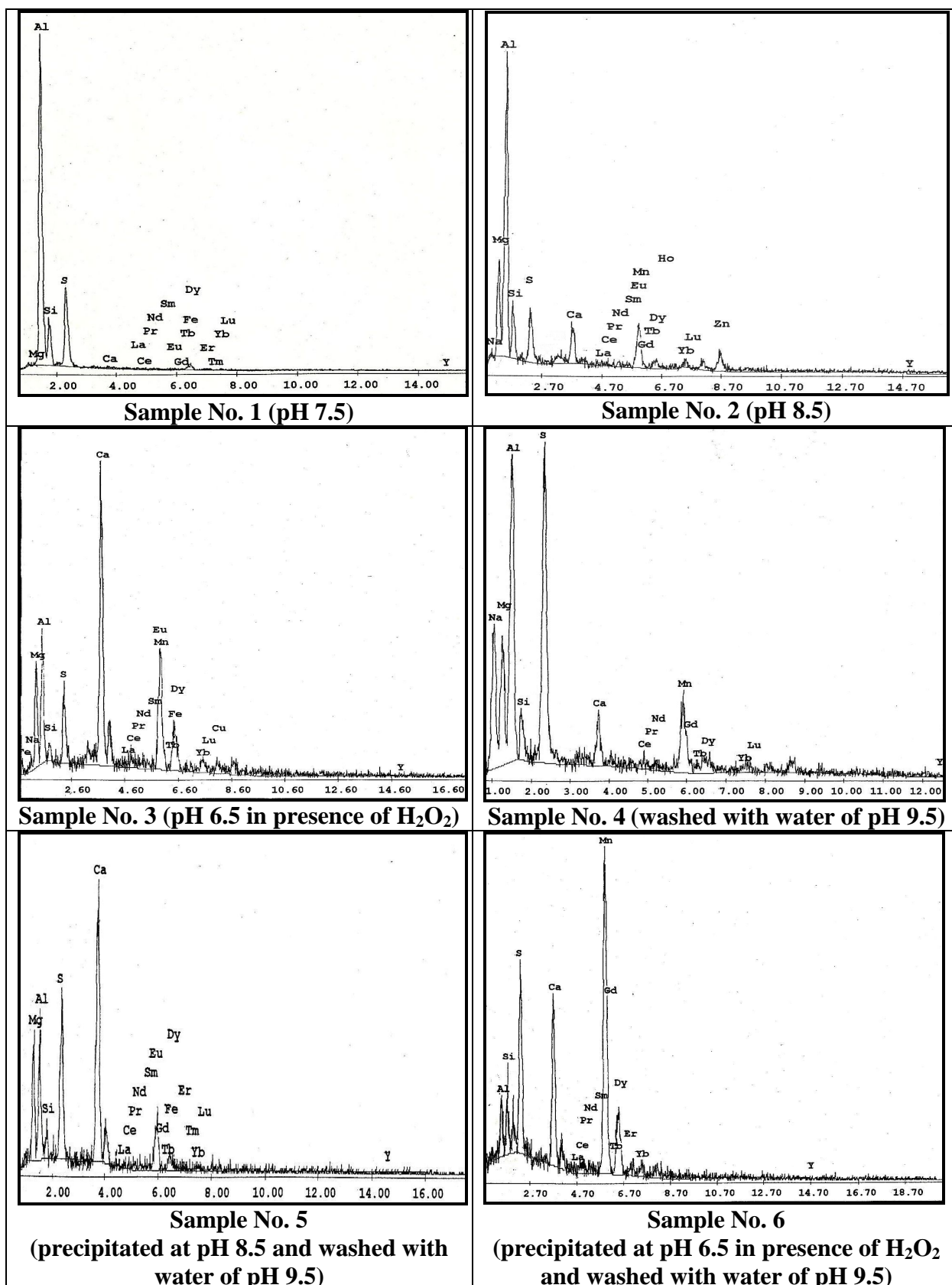
Figure (1): Rare earths precipitation from the sulphate effluent solutions

From these results it is obvious that at pH 3.5 more than 27% of the rare earths were precipitated by NaOH while in case of hydrogen peroxide addition was reached to more than 50%. Almost complete precipitation of the rare earths was achieved at pH of 8.5, but in presence of hydrogen peroxide this was achieved at lower pH of 6.5.

Specification of hydroxide precipitates at different pH

Results of the Scanning Electron Microscope qualitative analysis (after iron precipitation at pH 3.0) at different pH values of 7.5, 8.5 with NaOH and at pH 6.5 with NaOH in presence of H₂O₂ were discussed in figure (2) and table (3).

From these results it is obvious that the cake precipitated at pH 7.5 (sample No. 1) containing more than 55% "Al" and about 8.27% total rare earths. After washing with water of pH 9.5 (sample No. 4), aluminum was decreased to about 25 and the total rare earths were upgraded to 13.7%. The precipitated cake at pH 8.5 (sample No. 2) containing about 38% "Al", 12% "Mg" and 6% "Mn" and the total rare earths was about 16%, while the washed cake with water of pH 9.5 (sample No. 5), aluminum was decreased to about 13% and the total rare earths was upgraded to more than 27%. The latter cake sample precipitated at pH 6.5 in presence of H₂O₂ (sample No. 3), aluminum was decreased to about 19% while "Mn" increased to more than 12% and "Mg" was about 12% (as sample No. 2) and its total rare earths content was reached to about 19%. After washing with water of pH 9.5 (sample No. 6), aluminum was decreased to about 6% and the total rare earths were upgraded to more than 24%.



Samples No. 1, 2 and 3: water washed precipitates at pH 7.5, 8.5 and 6.5 in presence of H₂O₂ respectively
 Samples No. 4, 5 and 6: washed precipitates with water of pH 9.5

Fig. (2): Scanning electron microscope charts for water washed hydroxide cake precipitated at different conditions

Table (3): Results of the qualitative analysis of scanning electron microscope for major elements and rare earth elements in the prepared hydroxide cakes

| Element, % | Sample Number | | | | | |
|------------------|---------------|--------------|--------------|--------------|--------------|--------------|
| | 1 | 2 | 3 | 4 | 5 | 6 |
| Mg | 0.55 | 12.36 | 12.03 | 3.81 | 14.97 | 7.11 |
| Al | 55.33 | 37.98 | 18.89 | 24.92 | 12.69 | 5.94 |
| Si | 12.90 | 10.17 | 6.25 | 10.05 | 4.17 | 6.03 |
| S | 11.30 | 7.53 | 11.40 | 16.88 | 12.12 | 10.76 |
| Ca | 7.27 | 3.76 | 14.01 | 8.20 | 8.51 | 16.46 |
| Mn | 3.30 | 5.98 | 12.51 | 5.66 | 9.84 | 20.63 |
| Na | ---- | 6.40 | 1.44 | 11.99 | 9.17 | 2.17 |
| Fe | 1.08 | ---- | 5.05 | 4.82 | 0.90 | 4.79 |
| La | 0.58 | 0.54 | 1.26 | 0.80 | 1.26 | 1.43 |
| Ce | 0.66 | 0.79 | 2.06 | 1.38 | 1.06 | 2.11 |
| Pr | 0.27 | 0.30 | 0.80 | 0.86 | 1.18 | 0.87 |
| Nd | 0.37 | 1.26 | 1.05 | 0.84 | 1.58 | 1.18 |
| Sm | 0.22 | 0.21 | 0.68 | ---- | 1.12 | 0.59 |
| Gd | 0.36 | 1.85 | ---- | 0.88 | 3.08 | 0.69 |
| Tb | ---- | 1.01 | ---- | 0.19 | 2.39 | 0.88 |
| Dy | 0.92 | 1.61 | 1.24 | 1.54 | 2.61 | 3.01 |
| Tm | 0.36 | ---- | ---- | 0.95 | 0.45 | ---- |
| Yb | 1.14 | 2.84 | 2.23 | 1.88 | 4.23 | 5.10 |
| Lu | 0.90 | ---- | 2.73 | 1.30 | 0.92 | 2.20 |
| Y | 2.49 | 5.41 | 6.70 | 3.05 | 7.75 | 8.05 |
| Total REE | 8.27 | 15.82 | 18.75 | 13.67 | 27.63 | 26.11 |

Result of SEM qualification for the hydroxide cake prepared from the whole effluent solutions, which represent the raw material for the further studies study, was shown in figure (3) and the corresponding table.

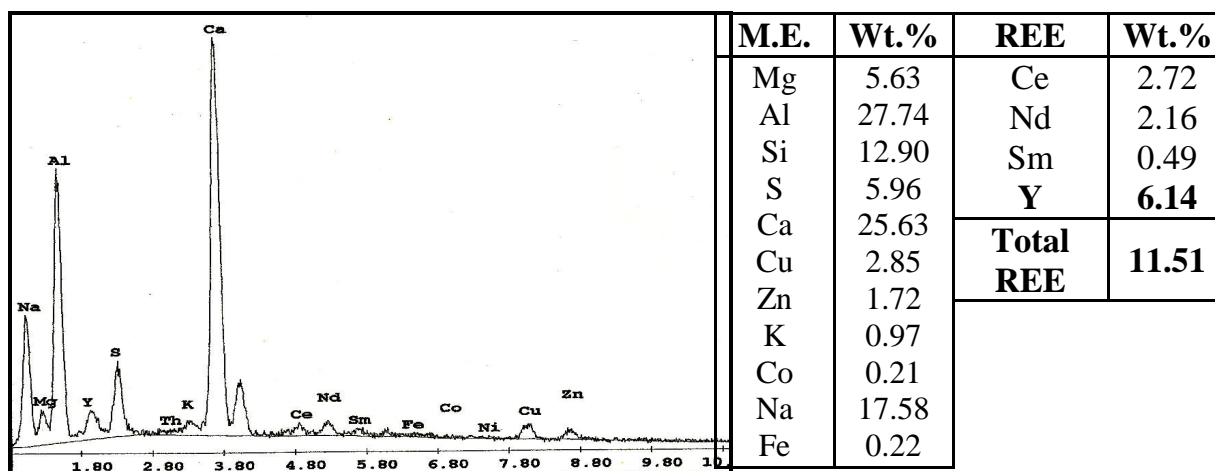


Fig. (3): Scanning Electron Microscope qualification for the prepared dry hydroxide cake containing major of the rare earths

Selective precipitation of rare earths using hydrofluoric acid

Results of rare earths selective precipitation from the three acid media (HCl, HNO₃ and H₂SO₄) were represented in Fig. (4) and the corresponding table.

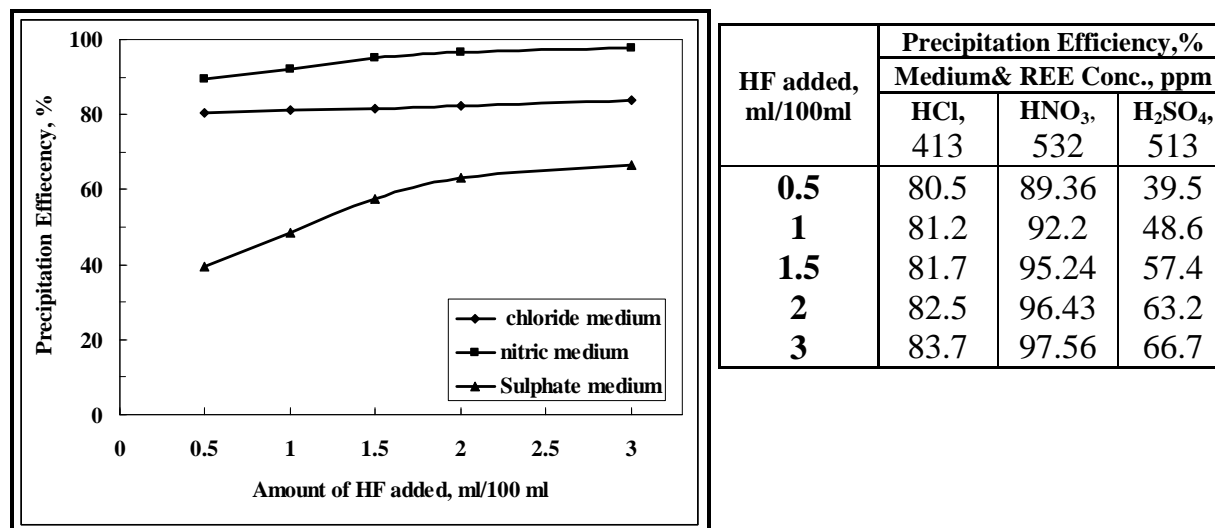


Fig. (4): Results of precipitation of rare earths using hydrofluoric acid from HCl, HNO₃ and H₂SO₄ media

The results reveal that more than 80% of rare earths were precipitated from hydrochloric acid medium when 0.5 ml of 70% HF is added per 100 ml solution and the precipitation efficiency not increase than about 84% with increasing the added amount of HF to 3.0 ml. From nitric acid medium, about 89% of rare earths were precipitated by adding 0.5 ml HF and the precipitation efficiency was increased to about 98% at 3.0 ml HF. From sulphuric acid medium only 40% of rare earths were precipitated by adding 0.5 ml HF and the precipitation efficiency didn't increase than 67% at 3.0 ml HF.

Samples precipitated using 3.0 ml HF from hydrochloric and nitric acid media were subjected to qualitative analysis by the SEM. The result illustrated in the figures (5, 6) and the corresponding tables. From these results, it is clear that the major co-precipitated elements in hydrochloric acid medium were Al, Mg and Ca. Yttrium which represents the heavy REE of the studied ore material was reached to 8.7% while the total rare earths about 15%. In case of nitric acid medium the major co-precipitated elements were Ca and Si, however, yttrium was more than 16.0% and the total REE more than 28.0%. It is worthy to mention that calcium was considered as carrier during precipitation of rare earths using the hydrofluoric acid [2]. Accordingly,

rare earths selective precipitation using hydrofluoric acid from nitrate medium was the most effective.

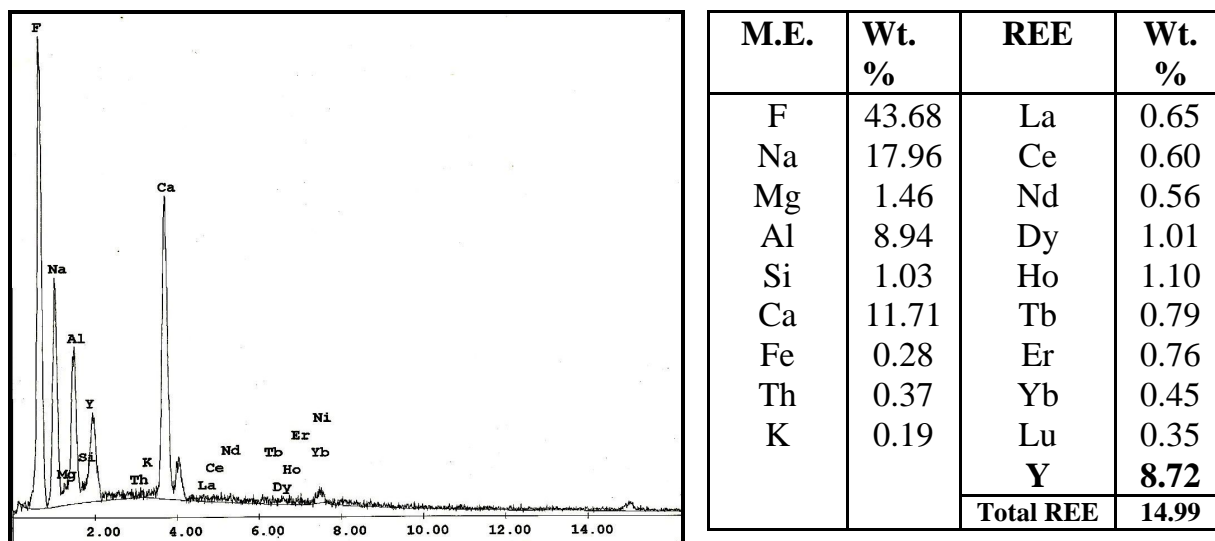


Fig. (5): Scanning electron microscope qualitative analysis for REE-fluoride precipitated from HCl medium

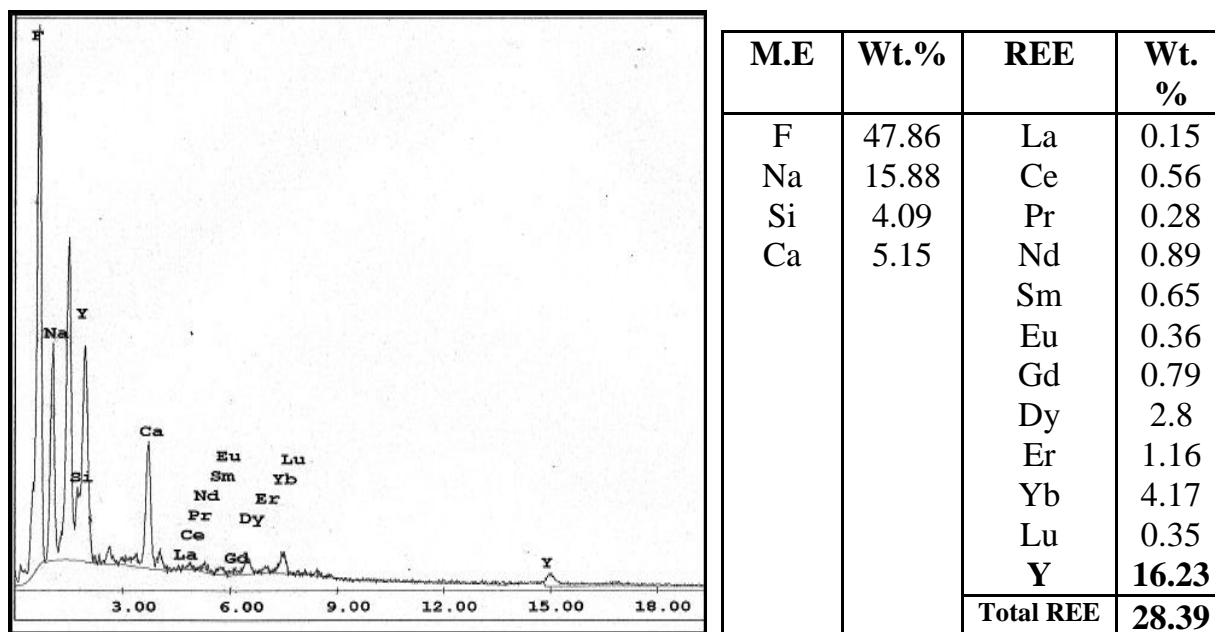


Fig. (6): Scanning electron microscope qualitative analysis for REE-fluoride precipitated from HNO₃ medium

Selective precipitation of rare earths using oxalic acid

Results of selective precipitation of REE using oxalic acid was indicated in table (4) which reveal that rare earths precipitation efficiency from hydrochloric medium, in case of initial pH of 5.0 was the most efficient (about 99%).

Table (4): Results of precipitation efficiency of rare earths using oxalic acid from different acidic media

| Acidic medium | REE Conc., ppm | Precipitation Efficiency, % | |
|---------------|----------------|-----------------------------|----------------|
| | | Initial pH 1.0 | Initial pH 5.0 |
| Hydrochloric | 413 | 91.8 | 98.86 |
| Nitric | 532 | 83.76 | 96.85 |
| Sulphuric | 513 | 61.6 | 82.73 |

Rare earth oxalate precipitates from hydrochloric and nitric acid media were ignited to remove oxalate at 650°C. Results of the qualitative analysis for samples using the SEM were shown in figures (7, 8) and the corresponding tables. From these results it is clear that the precipitate prepared from hydrochloric acid containing high percent of the total rare earths than that prepared from nitric acid medium. However, oxalate precipitation does not achieve the required selectivity where the precipitate containing high percent of aluminum (more than 30%) and other impurities.

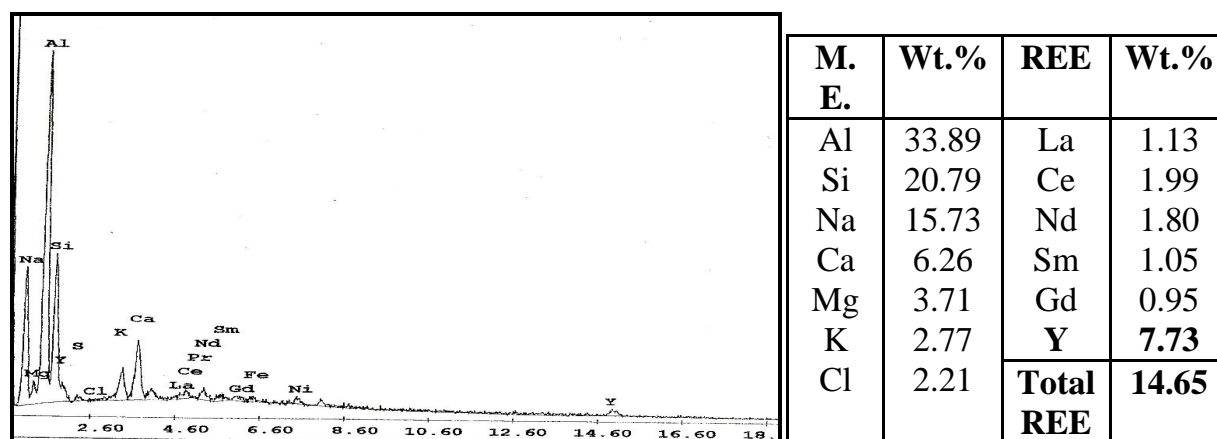


Fig. (7): Scanning electron microscope qualitative analysis for REE-oxalate precipitated from chloride acid medium

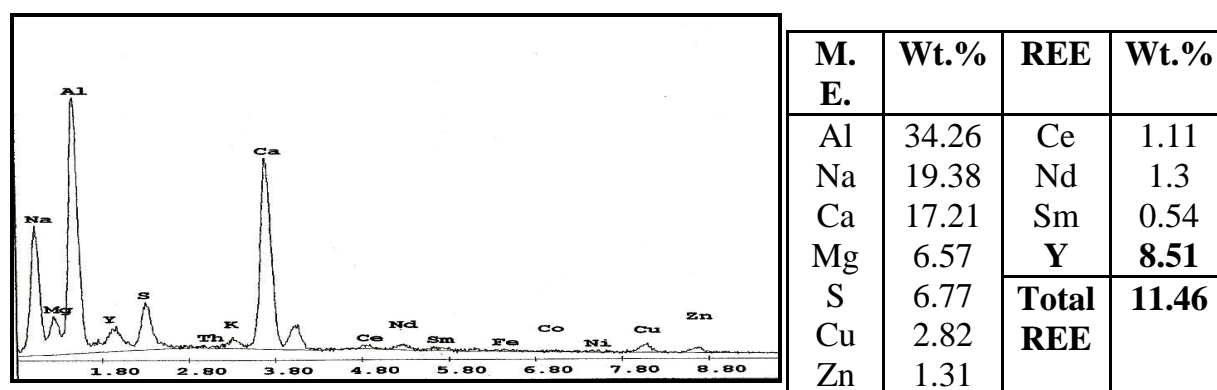


Fig. (8): Scanning electron microscope qualitative analysis for REE-oxalate precipitated from nitric acid

Conclusion

Technological sample from Gattar (V) uraniferous material, assayed 1300 ppm of uranium and 500 ppm of rare earths was treated on pilot unit. Sulphate effluent solutions, from the anion exchange resin Amberlite IRA 400 after uranium extraction, which containing about 115 ppm rare earths were subjected to study recover of these values. Precipitation using sodium hydroxide achieve more than 99% precipitation efficiency at pH 8.5 and in case of presence 2.5% hydrogen peroxide the same efficiency achieved at lower pH value (6.5). However, it is benefit to firstly precipitate major of the iron at pH 3.0 then the pH of the resultant solution increased to 8.5. On the other hand, the produced hydroxide cake containing REE washed by water of pH 9.5 to decrease the co-precipitated aluminum. In this regard, aluminum decreased from 38% to 13% and the total REE were upgraded from 16% to more than 27%.

Rare earths selective precipitation using hydrofluoric acid from nitrate medium was the most effective while the precipitation using oxalic acid from hydrochloric was the effective where about 98% precipitation efficiency were achieved in the two cases. However, the rare earths fluoride precipitate contained minimum co-precipitated of the other constituents than that of RE-oxalate.

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