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Subject: Chemistry

Topic – Occurrence and Extraction of Lanthanides from Monazite Sands

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Ans. Major Minerals containing lanthanides are (i) Monazite (ii) Bastnaesite (iii) Cerite
Lanthanides are best extracted from monazite.

Monazite sand consists of mixture of Th, Ce, Nd, Pr and La – phosphate along with impurities. The mineral is powdered and digested with conc. H_2SO_4 until a paste of sulphates containing phosphoric acid and an excess of (H_2SO_4) sulphuric acid is formed. The paste is centrifused and then treated with cold water when silica being insoluble precipitated out. The solution is neutralised with a previously prepared mixture of Lanthanide Oxides when Thorium, Zirconium and Titanium precipitated out as pyrophosphates. Sodium sulphate is added to the clear mother liquor so that the light lanthanides (Ln to Sm) may be precipitate out as double salts while the heavy lanthanides (Gd to Lu) still remain in solution.

Hot solution of sodium hydroxide is added to the precipitated double sulphates of light lanthanides to form a mixture of hydrated oxides.

This is washed till free from Na_2SO_4 and dried in air at 373 K where by cerium is completely oxidized to CeO_2 while other lanthanides change into their oxides. At these stage the approximate composition of residual solids is CeO_2 (50%) Nd_2O_3 (20%) La_2O_3 (17%) Pr_2O_3 (8%) Sm_2O_3 (5%). This mixture is reacted with dilute nitric acid when all the lanthanide oxides (except CeO_2) get dissolved and filtered out. The crude CeO_2 is dissolved in 85% HNO_3 and cerium is precipitated from it as the red basic nitrate, $\text{Ce}(\text{OH})_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ by the addition of excess of dilute H_2SO_4 . After the removal of cerium, the filtrate containing lanthanides are separated into individual components.

Separation of Lanthanides by ion exchange method:

This is the most rapid and effective method for the separation and purification of the lanthanides.

This method is based on the following principles.

- (i) Lanthanide ions on contact with synthetic resins containing – COOH or SO₃H group undergo proton exchange.
- (ii) $\text{Ln}^{+3} + 3\text{H} - \text{Resin} \longrightarrow \text{Ln} (\text{Resin})_3 + 3\text{H}^+$. The bonding of the lanthanide ion to the resin depends on its size i.e. Smaller the size of lanthanides firmly it is bound to the resin and vice – versa. Since lanthanide ions are hydrated. Therefore size of the hydrated ions are considered. Smaller is the size of ions, more is the hydration. Hence La⁺³ is least hydrated and Lu⁺³ is most hydrated. Hence La⁺³ is strongly bounded with resin and Lu⁺³ weakly bounded.

A solution containing several lanthanide ions is dropped slowly down a column of synthetic ion exchange resin so that the lanthanide ions are bound less firmly to the resin in the order La⁺³ to Lu⁺³. They are then eluted from the column by using a solution containing citric acid and ammonium citrate. Firstly, the ammonium ions elute the metal ions from the resin as $3\text{NH}_4^+ + \text{Ln} (\text{Resin})_3 \longrightarrow 3\text{NH}_4 \text{ resin} + \text{Ln}^{+3}$. The metal ion then forms a complex with the citrate ions.

$\text{Ln}^{+3} + \text{Citrate ion} \longrightarrow \text{Ln} - \text{citrate complex}$ since Ln⁺³ is the least firmly bound to resin, therefore on elution, Lu – citrate complex is obtained first from the bottom of the column while La – citrate complex emerges last of all from the bottom of the column.

Complexing agents such as EDTA, amino – carboxylic acids and hydroxy carboxylic acids have also been found to be convenient elutants.

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Subject: Chemistry, Part – II B.Sc.

Topic – Comparison in Properties of Lanthanides and Actinides

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Ans.

Similarities:

- i. Oxidation state of +3 dominates in both the series.
- ii. In both the series f orbitals are being progressively filled.
- iii. Just like Lanthanide contraction, we have actinide contraction.
- iv. The nitrates, perchlorates and sulphates of trivalent actinides as well as Lanthanides are soluble while the hydroxides, fluorides and carbonates are insoluble.
- v. In the absorption spectra of the elements of both the series sharp line – like bands appear due to f-f transitions.

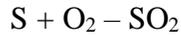
Differences:

Lanthanides	Actinides
1. Binding energy of 4f are higher.	1. Binding energy of 5f are lower.
2. 4 f electrons have comparatively greater shielding effect.	2. 5f – electrons have poor shielding effect.
3. Maximum oxidation state exhibited by Lanthanides is + 4 eg Ce^{+4}	3. Due to lower binding energies they show higher oxidation states such as +4, +5 & +6
4. They do not form Oxocations	4. They form oxocations such as UO_2^{2+} PuO_2^+
5. Except promethium they are non-radioactive	5. All are radioactive
6. They do not form complexes easily	6. They form stable complexes with π – bonding ligands.
7. They are paramagnetic but magnetic properties can be easily explained	7. They are also paramagnetic but it is difficult to explain magnetic properties.

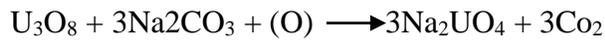
Extraction of Uranium from its ore Pitchblende (U_3O_8)

The various steps involved in the extraction of uranium are as under

- (a) Concentration : The ore is crushed to a fine powder and then concentrated by gravity separation in order to remove lighter impurities.
- (b) Roasting : the concentrated ore is then roasted in reverberatory furnace in excess of air to remove S, As etc as their oxides.



The roasted ore is then mixed with sodium carbonate and sodium nitrate. The whole mass is then fused on the hearth of a reverberatory furnace resulting in the formation of Na_2UO_4 .



- (c) Leaching with sulphuric acid: the fused mass is leached with dilute H_2SO_4 whereby sodium uranate changes into soluble uranyl sulphate while impurities $PbSO_4$ and $RaSO_4$ remain insoluble and $Na_2UO_4 + 2H_2SO_4 \rightarrow UO_2SO_4 + Na_2SO_4 + 2H_2O$

- (d) Treatment with sodium carbonate: the solution containing uranyl sulphate is treated with excess of Na_2CO_3 to precipitate iron, aluminium, nickel, cobalt and manganese as their insoluble carbonates while uranyl sulphate reacts with Na_2CO_3 to form $Na_4 [UO_2(CO_3)_3]$

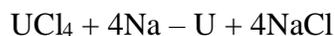
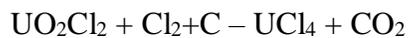
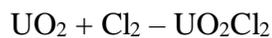
- (e) $Na_4 [UO_2(CO_3)_3]$ is bailed with dilute H_2SO_4 , $Na_2U_2O_7 \cdot 6H_2O$ yellow crystal is obtained.

- (f) Treatment with $(NH_4)_2CO_3$ with $(NH_4)_2CO_3$

yellow crystal above obtained gives double ammonium uranyl carbonate.

- (g) Conversion into U_3O_8 and then UO_2 on calcinations of above compound we get U_3O_8 and UO_2 .

Conversion of UO_2 into U



Thus uranium is obtained.