

The Amex Process

for Extracting Thorium Ores with Alkyl Amines

Solvent extraction processes offer

- ▶ better purity
- ▶ high recoveries
- ▶ good separation of by-product uranium and rare earths

THORIUM, which is a potentially useful fertile material for breeder reactors, has been obtained chiefly from monazite. A further major source was recently discovered in the uranium-thorium ores of the Canadian Blind River district. The amine extraction (Amex) processes developed at the Oak Ridge National Laboratory for uranium recovery (5, 6, 9-12) have been extended to achieve efficient low-cost recovery from both sources. Through choice of amine type and alkyl structure, these processes provide good control over extraction power and metal selectivity (Table I).

As with uranium, a number of reagents are effective for stripping the extracted thorium from amines (13-15). Thorium is present in the extract as a thorium-amine-sulfate complex, with excess amine sulfate and/or bisulfate. This complex contains three to four amine sulfates per thorium, depending on amine type (17). When the extract is treated with Cl or NO₃, thorium is displaced from the organic phase. When the extract is treated with neutral or acidic nitrate or chloride solutions, thorium is displaced with the nitrate or chloride anion.

Nitrate is the more effective stripping anion. Following nitrate stripping the amine is regenerated to the free amine form for recycle by contact with a base such as ammonium hydroxide. This recovers the relatively expensive nitrate for recycle and maintains extraction efficiency by preventing contamination with nitrate. Regeneration after chloride stripping is optional.

Hydroxide solutions precipitate thorium directly from the solvent. However, the slimy thorium precipitate is difficult to separate from the solvent.

Carbonate solutions strip thorium as a soluble carbonate complex, provided there is sufficient excess carbonate. With insufficient carbonate excess, part or essentially all of the stripped thorium precipitates, but if phase contact is

made with the organic as the continuous phase (water-in-oil dispersion), this precipitate separates readily. Extending the contact time from 2 to 10 minutes increases stripping and precipitation.

Recovery from Monazite

Battelle Memorial Institute and Ames Laboratory previously developed methods for recovering thorium, uranium, and rare earths from monazite sands. The Battelle process (4) uses caustic, and the Ames process (2, 3, 22, 24) uses sulfuric acid to open up the sands. The elements are partially separated by precipitation and the thorium-rich precipitate is redissolved and purified by tributylphosphate (TBP) extraction (16).

The Amex process (7, 13, 15) provides essentially complete recovery and separation of the elements, and the relatively pure thorium product is more amenable to TBP extraction. By adjustment of operational procedures, it may be possible to produce nuclear grade thorium oxide as a direct result of the amine extraction treatment, thus obviating need for TBP purification.

Digestion of Monazite Sand. The liquors used in these studies were prepared by digesting Indian monazite sand in 93% sulfuric acid, followed by water dilution to solubilize the metal

Alkyl amines are versatile extractants for economical recovery of relatively high grade thorium products from ore process sulfate liquors.

Relative extraction power for thorium and for other metal values is strongly dependent on the amine type and alkyl structure. Thus, appropriate choice of amine permits efficient recovery and separation in multi-cycle extraction operations.

sulfates (2). The digest slurries were filtered to provide clear liquors analyzing 5 to 7 grams of thorium, 0.2 gram of uranium, and 35 to 45 grams of rare earth oxides per liter (Table II).

Extraction of Thorium. Owing to the high acidity and relatively high concentrations of sulfate and phosphate, coefficients for extraction of thorium from monazite liquors are appreciably lower than those shown in Table I; the relative extraction power of amine classes is similar (Table III). The strong affinity ($E_s^0 > 500$) of the primary amines for thorium is again apparent. In comparison, the extraction coefficient for di-(tridecyl)amine is low (~ 5) although adequate for process use.

Table I. Degree of Extraction and Metal Selectivity Depends on Amine Type and Alkyl Structure

1M SO₄, pH 1, ~ 1 gram metal ion/liter; phase ratio 1/1, 0.1M amine in kerosine

Amine Type	Example Amines	Metal Ion Extr. Coefficient, $E_s^0(M) = \frac{[M]_{org}}{[M]_{aq}}$		
		U(VI)	Th	Ce(III)
Branched primary	Primene JM ^a and 1-(3-ethylpentyl)-4-ethyl-octylamine	5-30	>20,000	10-20
Secondary with alkyl branching distant from the nitrogen	Di(tridecyl)amine ^b	80	>500	<0.1
Secondary with alkyl branching on the first C	Amberlite LA-1 ^c and bis(1-isobutyl-3,5-dimethylhexyl)amine	80-120	5-15	<0.05
Tertiary with no branching or branching no closer than the third C	Alamine 336 ^{d,e} and triisooctylamine ^f	140	<0.03	<0.01

^a Trialkylmethylamine, homologous mixture, 18-24 carbons. ^b Mixed C₁₃ alkyls from tetra-propylene by oxo process. ^c Dodecyl-trialkylmethylamine, homologous mixture, 24-27 carbons. ^d Trialkylamine with mixed *n*-octyl and *n*-decyl radicals. ^e Kerosine diluent modified with 3 vol. % tridecanol. ^f Mixed C₈ alkyls from oxo process.