Uranium Ores Processing

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<table>
<thead>
<tr>
<th>Type</th>
<th>Name</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxides</td>
<td>Uraninite</td>
<td>$(U^{+4}_{1-x},U^{+5}_x)O_2+x$</td>
</tr>
<tr>
<td></td>
<td>Pitchblende</td>
<td>Variety ofuraninite</td>
</tr>
<tr>
<td>Hydrated oxides</td>
<td>Becquerelite</td>
<td>$7\text{ UO}_2\cdot11\text{ H}_2\text{O}$</td>
</tr>
<tr>
<td></td>
<td>Gummite</td>
<td>Alteration product of uraninite$^a$</td>
</tr>
<tr>
<td>Nb-Ta-Ti complex oxides</td>
<td>Brannerite</td>
<td>$(U, Ca, Fe, Th, Y)(Ti, Fe)_2O_6$</td>
</tr>
<tr>
<td></td>
<td>Davidite</td>
<td>Ideally $\text{FeTi}_5\text{O}_7$</td>
</tr>
<tr>
<td>Silicates</td>
<td>Coffinite</td>
<td>$U(\text{SiO}<em>4)</em>{1-x}(\text{OH})_{4x}$</td>
</tr>
<tr>
<td></td>
<td>Uranophane</td>
<td>$\text{Ca}(\text{UO}_2)_2(\text{SiO}_3)_2(\text{OH})_2\cdot5\text{ H}_2\text{O}$</td>
</tr>
<tr>
<td></td>
<td>Uranothorite</td>
<td>Uranoan variety of thorite, $\text{ThSiO}_4$</td>
</tr>
<tr>
<td>Phosphates</td>
<td>Autunite</td>
<td>$\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2\cdot10-12\text{ H}_2\text{O}$</td>
</tr>
<tr>
<td></td>
<td>Torbernite</td>
<td>$\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2\cdot12\text{ HO}_2\text{O}$</td>
</tr>
<tr>
<td>Vanadates</td>
<td>Carnotite</td>
<td>$\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2\cdot1-3\text{ H}_2\text{O}$</td>
</tr>
<tr>
<td></td>
<td>Tyuyamunite</td>
<td>$\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2\cdot5-8\text{ H}_2\text{O}$</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>Thucholite</td>
<td>Uraninite complex with hydrocarbons</td>
</tr>
<tr>
<td></td>
<td>Asphaltite$^b$</td>
<td>Many varieties containing U-organic complexes</td>
</tr>
</tbody>
</table>

$^a$Gummite is a generic name for uraninite alteration products and may include silicates, phosphates, and oxides.

$^b$Actually a variety of thucholite but term may be used in broad sense to describe a number of solid uraniferous bituminous hydrocarbons.
<table>
<thead>
<tr>
<th>Type of deposit</th>
<th>Principal uranium minerals</th>
<th>Typical U.S. occurrences</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vein deposits</td>
<td>Uraninite, torbernite, autunite, and uranophane</td>
<td>Front Range, Colorado; Marysvale district, Utah; Spokane area, Washington.</td>
</tr>
<tr>
<td>Copper-bearing sandstones</td>
<td>Uraninite and uranium phosphates, vanadates, sulfates, carbonates, and silicates</td>
<td>San Rafael Swell area, Utah.</td>
</tr>
<tr>
<td>Other sandstones</td>
<td>Uraninite and coffinite; and uranium phosphates, silicates, arsenates, and carbonates</td>
<td>Grants-Laguna area, New Mexico.</td>
</tr>
<tr>
<td>Limestone</td>
<td>Uraninite, carnitide, tyuyamunite, and uranophane</td>
<td>Central Florida; Bear Lake area, Idaho; Utah; Wyoming; and western Montana.</td>
</tr>
<tr>
<td>Phosphate rock</td>
<td>Carbonate-fluorapatite</td>
<td>Western North and South Dakota; eastern Montana.</td>
</tr>
<tr>
<td>Lignite</td>
<td>Uranium hydrocarbons and minor secondary uranium minerals</td>
<td>Tennessee.</td>
</tr>
<tr>
<td>Bituminous shales</td>
<td>Uranium-hydrocarbon complex</td>
<td></td>
</tr>
</tbody>
</table>

*Early production from these areas was oxidized or "carnotite-type" ore, with the exception of the Big Indian area.
Figure 2-1.—Important uranium districts of the United States.
Source: R. L. Faulkner.17

Source: Evaluation, Interim Report (June 1979) Figure 3.2, and GJPO data files.
Mining Methods

https://geoinfo.nmt.edu/resources/uranium/mining.html

• Open Pit
• Underground
• In-Situ Recovery or In-Situ Leaching
Open Pit Uranium Mine
Reclaimed Tailings Piles
Uranium ore processing

• Drying
• Crushing
• Blending
• Fine Ore Storage
• Roasting
  to remove carbonaceous matter
  to convert vanadates to soluble form
  to alter clay minerals
Processing Methods

• Agitation Leaching (Selective Dissolution)
  – Acid leach
  – Basic Carbonate Leach
• Percolation Leach
• Pressure Leach
• Heap Leaching
• In-Situ Leach
Solubility of Uranium Minerals

- Hexavalent uranium oxides dissolve in acids
  \[ \text{UO}_3 + 2 \text{H}^+ = \text{UO}_2^{++} + \text{H}_2\text{O} \]

- Tetravalent Oxides require an oxidant
  \[ 2\text{Fe}^{3+} + 2\text{e} = 2\text{Fe}^{++} \]
  \[ \text{UO}_2 = \text{UO}_2^{++} + 2\text{e} \]

Overall reaction:

\[ \text{UO}_2 + 2\text{Fe}^{3+} = \text{UO}_2^{++} + 2\text{Fe}^{++} \]
FIG. 7.14. Diagram showing the relations among the metastable iron hydroxides and siderite at 25°C and 1 atmosphere total pressure. Boundary between solids and ions total activity of dissolved species = 10⁻⁶. Total dissolved carbonate species = 10⁻⁶. Dashed lines are boundaries between fields dominated by the labeled ion.
Stability domain of water

\[ 2\text{H}_2\text{O} = \text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e} \]

\[ E = E_0 + \frac{RT}{nF} \ln\left\{\frac{[\text{O}_2][\text{H}^+]^4}{[\text{H}_2\text{O}]^2}\right\} \]

\[ E = 1.23 - 0.059 \text{ pH} \quad \text{(b)} \]

\[ \text{H}_2(\text{g}) = 2\text{H}^+ + 2\text{e} \]

\[ E = 0.0 - 0.059 \text{ pH} \quad \text{(a)} \]

\[ \text{H}_2\text{O} = \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e} \]

\[ E = 1.77 - 0.059 \text{ pH} + 0.0295 \log(\text{H}_2\text{O}_2) \]
Fig. 1. Approximate positions of some natural environments as characterized by Eh and pH. (From R. M. Garrels, *Mineral Equilibria*, Harper, New York, 1960, p. 201.)
Oxidation of Ferrous Ions

- $6 \text{Fe}^{++} + \text{NaClO}_3 = \text{Fe}^{3+} + \text{NaCl} + 3\text{H}_2\text{O}$
- $2 \text{Fe}^{++} + \text{MnO}_2 + 4\text{H}^+ = 2 \text{Fe}^{3+} + \text{Mn}^{++} + 2\text{H}_2\text{O}$
Oxidizing Agents

- \( \text{H}_2\text{O}_2 + 2 \text{H}^+ + 2e = 2 \text{H}_2\text{O} \quad \text{E}^\circ = 1.77 \text{ V} \)
- \( \text{MnO}_4^- + 8 \text{H}^+ + 5e = \text{Mn}^{2+} + 4 \text{H}_2\text{O} \quad \text{E}^\circ = 1.52 \text{ V} \)
- \( \text{ClO}_3^- + 6 \text{H}^+ + 5e = \frac{1}{2} \text{Cl}_2 (g) + 3 \text{H}_2\text{O} \quad \text{E}^\circ = 1.47 \text{ V} \)
- \( \text{MnO}_2 (s) + 4 \text{H}^+ + 2e = \text{Mn}^{2+} + 2 \text{H}_2\text{O} \quad \text{E}^\circ = 1.23 \text{ V} \)
- \( \text{O}_2 (g) + 4 \text{H}^+ + 2e = 2 \text{H}_2\text{O} \quad \text{E}^\circ = 1.23 \text{ V} \)
- \( \text{NO}_3^- + 4 \text{H}^+ + 3e = \text{NO} (g) + 2 \text{H}_2\text{O} \quad \text{E}^\circ = 0.96 \text{ V} \)
- \( \text{ClO}^- + \text{H}_2\text{O} + 2e = \text{Cl}^- + 2 \text{OH}^- \quad \text{E}^\circ = 0.89 \text{ V} \)
- \( \text{Fe}^{3+} + e = \text{Fe}^{2+} \quad \text{E}^\circ = 0.77 \text{ V} \)
- \( \text{Cu}^{2+} + 2e = \text{Cu} (s) \quad \text{E}^\circ = 0.34 \text{ V} \)
- \( 2 \text{H}^+ + 2e = \text{H}_2 (g) \quad \text{E}^\circ = 0.0 \text{ V} \)
- \( \text{Fe}^{2+} + 2e = \text{Fe} \quad \text{E}^\circ = -0.44 \text{ V} \)
Fig. 7.27a. Stability relations among copper compounds in the system Cu-H₂O-O₂ at 25°C and 1 atmosphere total pressure. [Courtesy J. Anderson.]

Fig. 7.14. Diagram showing the relations among the metastable iron hydroxides siderite at 25°C and 1 atmosphere total pressure. Boundary between solids and ions total activity of dissolved species = 10⁻⁶. Total dissolved carbonate species = 10⁻⁷. Dashed lines are boundaries between fields dominated by the labeled ion.
Fig. 1. Potential-pH equilibrium diagram for the system zinc–water, at 25°C. [Established by considering Zn(OH)$_2$.]
Fig. 1. Potential–pH equilibrium diagram for the system manganese–water, at 25°C. [Considering β-MnO₂ (pyrolusite).]
A detailed study of uranium has been made previously [4] and Sillén [5] has published some redox diagrams for uranium, neptunium and plutonium.

Figures 1–5 are valid only in the absence of substances with which the metals of this group can form insoluble salts and soluble complexes.
Figs. 1–5. Potential–pH equilibrium diagrams for the systems actinides–water, at 25°C.
Fig. 1. Potential–pH equilibrium diagram for the system molybdenum–water, at 25°C.
FIG. 3b. Aqueous equilibrium diagram for vanadium minerals showing stability regions for various minerals, and the paths followed during weathering. (From H. T. Evans, Jr. and R. M. Garrels, loc. cit.)
FIG. 3a. Aqueous equilibria of vanadium, showing the major aspects of relations among solids and important dissolved species. (From H. T. EVANS, Jr. and R. M. GARRELS, Thermodynamic equilibria of vanadium in aqueous systems as applied to the interpretation of the Colorado Plateau ore deposits, *Geochim. and Cosmochim.* 15, 131–9 (1958).)
• Acid Leaching – Low carbonate ores

\[
\begin{align*}
\text{UO}_3 + 2\text{H}^+ &= \text{UO}_2^{++} + \text{H}_2\text{O} \\
\text{UO}_2 + 2\text{Fe}^{+++} &= \text{UO}_2^{++} + 2\text{Fe}^{++}
\end{align*}
\]

Uranyl ion forms complexes with sulfate ions

\[
\begin{align*}
\text{UO}_2^{++} + \text{SO}_4^{--} &= \text{UO}_2\text{SO}_4 \\
\text{UO}_2\text{SO}_4 + \text{SO}_4^{--} &= [\text{UO}_2(\text{SO}_4)_2]^{2--} \\
[\text{UO}_2(\text{SO}_4)_2]^{2--} + \text{SO}_4^{--} &= [\text{UO}_2(\text{SO}_4)_3]^{4--}
\end{align*}
\]
Acid Consuming Reactions

- Carbonates
- Sulfides
- Phosphates
- Vanadates
- Phosphates
- Some oxides
- Clays
Fig. 7-3. Diagram of Pachuca tank used in U.S. Atomic Energy Commission pilot-plant studies at Grand Junction, Colorado.
Fig. 7-4. Diagram of autoclave used in U. S. Atomic Energy Commission pilot-plant studies at Grand Junction, Colorado.
Pressure Oxidation of Pyritic Ores

- $2\text{FeS}_2 + 7.5\ \text{O}_2 + \text{H}_2\text{O} = \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4$

- $\text{UO}_2 + \text{Fe}_2(\text{SO}_4)_3 = \text{UO}_2\text{SO}_4 + 2\text{FeSO}_4$

- $4\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 + \text{O}_2 = 2\text{Fe}_2(\text{SO}_4)_3 + 2\text{H}_2\text{O}$

- $\text{CuFeS}_2 + 2\text{H}_2\text{SO}_4 + \text{O}_2 = \text{FeSO}_4 + \text{CuSO}_4 + 2\text{H}_2\text{O}$
Heap Leaching

- FeS₂ + H₂O + 3.5O₂ = FeSO₄ + H₂SO₄
- 2FeSO₄ + H₂SO₄ + ½ O₂ = Fe₂(SO₄)₃ + H₂O
  - Thiobacillus Ferrooxidants
  - Thiobacillus Thiooxidants
  - Ferrobascillus Ferrooxidants

Bacteria oxidize Ferrous ions to Ferric and help dissolve uraninite

UO²⁺ + 2Fe³⁺ = UO₂²⁺ + 2Fe²⁺
Figure 5-27.—Typical construction for heap leaching.
Injection wells (1) pump a chemical solution—typically groundwater mixed with sodium bicarbonate, hydrogen peroxide, and oxygen—into the layer of earth containing uranium ore. The solution dissolves the uranium from the deposit in the ground and is then pumped back to the surface through recovery wells (2) and sent to the processing plant to be processed into uranium yellowcake. Monitoring wells (3) are checked regularly to ensure that uranium and chemicals are not escaping from the drilling area.
Abandoned Injection Well
Recovery of Uranium from Acidic Solutions

- Solvent Extraction with both cationic (alkyl phosphoric acids) or anionic (tertiary amine) liquid ion exchangers:
  
  \[ \text{UO}_2^{++} + 2(R\text{H})_2(\text{org}) = \text{UO}_2R_4\text{H}_2(\text{org}) + 2\text{H}^+ \]

  \[ 4R_3\text{N}(\text{org}) + 2\text{H}_2\text{SO}_4 + \text{UO}_2(\text{SO}_4)_3^{4-} = (R_3\text{NH})_4\text{UO}_2(\text{SO}_4)_3(\text{org}) + 2\text{SO}_4^{2-} \]

- Uranium stripped with Na$_2$CO$_3$ solution and precipitated as Na$_2$U$_2$O$_7$
phoric acid (D2EHPA or usually just EHPA), heptadecyl phosphoric acid (HDPA), and dialkyl pyrophosphoric acid (OPPA). The latter reagent was used in the extraction of uranium from phosphoric acid liquors in Florida. The exchange reactions with the alkyl phosphoric reagents have been found to be not strictly analogous to cationic ion exchange. EHPA exists in the organic phase as a dimeric species $(\text{RH})_2^*$ and each extracted uranyl ion reacts with two dimers to form a complex containing the equivalent of two $(\text{RH})$ molecules in addition to two anions$^{55, 56}$ in accordance with the following reaction:

$$\text{UO}_2^{++} + 2(\text{RH})_2^{(\text{org})} = \text{UO}_2\text{R}_4\text{H}_2^{(\text{org})} + 2\text{H}^+$$

At higher uranium levels, increasingly long-chain polymers of the composition $(\text{UO}_2)_n\text{R}_{2n+2}\text{H}_2$ are evidently formed.$^{57}$ Monoalkyl phosphoric acids are believed to occur as larger polymers than EHPA.$^{58}$

Typical stripping reactions using sodium carbonate are:

$$\text{UO}_2\text{R}_4\text{H}_2^{(\text{org})} + 3\text{Na}_2\text{CO}_3 = 2\text{NaR}_2\text{H}^{(\text{org})} + \text{Na}_4\text{UO}_2(\text{CO}_3)_3,$$

and

$$2(\text{RH})_2^{(\text{org})} + \text{Na}_2\text{CO}_3 = 2\text{NaR}_2\text{H}^{(\text{org})} + \text{H}_2\text{O} + \text{CO}_2.$$ 

The alkali salts of the dialkyl phosphoric acids formed during stripping may either precipitate from the organic phase or, in the case of EHPA, tend to form a third liquid phase. To prevent this a modifying agent such as tributyl phosphate or a long-chain alcohol must be used with the active reagent. This is discussed in a subsequent section.

Anionic exchangers used industrially for uranium ore processing include either secondary amines with either normal or branched aliphatic chains or high-molecular weight tri-alkyl tertiary amines. Examples of some commercially available amines that have been used by the uranium industry are given in Table 6-14. These secondary and tertiary amines are similar in their exchange reactions to the weak basic resins. Formation of the amine sulfate and bisulfate salts and typical extraction and stripping reactions are shown following.

$$2\text{R}_3\text{N}^{(\text{org})} + \text{H}_2\text{SO}_4 = (\text{R}_3\text{NH})_2\text{SO}_4^{(\text{org})}$$

$$2(\text{R}_3\text{NH})\text{SO}_4^{(\text{org})} + \text{H}_2\text{SO}_4 = 2(\text{R}_3\text{NH})\text{HSO}_4^{(\text{org})}$$

\[\text{where } \text{R} = (2\text{-ethylhexyl-O})_2^\text{P-O}\]

$^*$
\[ 2(R_3NH)_2SO_4_{(org)} + UO_2(SO_4)_3^{4-} = (R_3NH)_4UO_2(SO_4)_3_{(org)} + 2SO_4^{2-} \]

\[ (R_3NH)_4UO_2(SO_4)_3_{(org)} + 5Na_2CO_3 = 4R_3N_{(org)} + Na_4UO_2(CO_3)_3 + 2H_2O + 2CO_2 + 3Na_2SO_4 \]

The quaternary amines have been found useful in the recovery of vanadium\(^{59}\) and in the scavenging of vanadium and molybdenum from basic liquors.\(^{60}\) Since the quaternary amines can act as strong bases they are capable of reactions in the high pH range and will extract uranium from carbonate solutions as shown on the following page.\(^{61}\)

**Table 6-14. Typical Reagents Used for Solvent Extraction of Uranium**

<table>
<thead>
<tr>
<th>Reagent name</th>
<th>Reagent type</th>
<th>Manufacturers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monododecyl phosphoric acid (DDPA)</td>
<td>Alkyl phosphoric acid</td>
<td>b</td>
</tr>
<tr>
<td>Di(2-ethylhexyl) phosphoric acid (EHPA)</td>
<td>Alkyl phosphoric acid</td>
<td>a b c</td>
</tr>
<tr>
<td>Heptadecyl phosphoric acid (HDPA)</td>
<td>Alkyl phosphoric acid</td>
<td>b</td>
</tr>
<tr>
<td>Diallyl pyrophosphoric acid (DPPA)</td>
<td>Alkyl phosphoric acid</td>
<td>b</td>
</tr>
<tr>
<td>Tributyl phosphate (TBP)</td>
<td>Alkyl phosphoric acid</td>
<td>b</td>
</tr>
<tr>
<td>Amine S-24, Amberlite LA-1, Amberlite LA-2</td>
<td>Secondary amines</td>
<td>b c d</td>
</tr>
<tr>
<td>Alamine 336 (Tricapryl)</td>
<td>Tertiary amines</td>
<td>c e f</td>
</tr>
<tr>
<td>Alamine 304 (Trilauryl)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adogen 364</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Triisoctylamine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aliquot 336</td>
<td>Quaternary amine</td>
<td>e f</td>
</tr>
<tr>
<td>Adogen 464</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\)Mobil Chemical Company.  
\(^{b}\)Stauffer Chemical Company.  
\(^{c}\)General Mills.  
\(^{d}\)Rohm and Haas Company.  
\(^{e}\)Union Carbide Corporation.  
\(^{f}\)Archer Daniels Midland Company.
Figure 6-23.—Generalized process flow diagram for the Amex process for uranium.
Source: K. B. Brown and others.⁹³
Carbonate Leaching

- $2\text{UO}_2 + \text{O}_2(\text{dissolved}) = 2\text{UO}_3$ (or $\text{H}_2\text{O}_2$)

- $\text{UO}_3 + \text{Na}_2\text{CO}_3 + 2\text{NaHCO}_3 = 4\text{Na}^+ + \text{UO}_2(\text{CO}_3)_3^{4-} + \text{H}_2\text{O}$

Sodium carbonate hydrolyzes in water to produce highly basic solutions. Bicarbonate added to neutralize excess $\text{OH}^-$ to prevent precipitation of sodium diuranate ($\text{Na}_2\text{U}_2\text{O}_7$ - yellowcake).
Ion Exchange Resins

- Both acidic or basic carbonate solutions

\[
4RX + [\text{UO}_2(\text{SO}_4)_3]^{4-} = R_4\text{UO}_2(\text{SO}_4)_3 + 4X^-
\]

\[
4RX + [\text{UO}_2(\text{CO}_3)_3]^{4-} = R_4\text{UO}_2(\text{CO}_3)_3 + 4X^-
\]

\[X : \text{NO}_3^- > \text{CN}^- > \text{HSO}_4^- > \text{Cl}^- > \text{HCO}_3^- > \text{OH}^-\]
In dilute sulfuric acid solution the uranyl cation, uranium sulfate, and both the divalent and tetravalent uranium sulfate complex anions will be present in accordance with the following equilibrium equations:

\[
\text{UO}_2^{++} + \text{SO}_4^{--} = \text{UO}_2\text{SO}_4 \\
\text{UO}_2\text{SO}_4 + \text{SO}_4^{--} = [\text{UO}_2(\text{SO}_4)_2]^{--} \\
[\text{UO}_2(\text{SO}_4)_2]^{--} + \text{SO}_4^{--} = [\text{UO}_2(\text{SO}_4)_3]^{-4}
\]

In carbonate solutions, the tetravalent uranyl tricarbonate complex anion, \([\text{UO}_2(\text{CO}_3)_3]^{-4}\) predominates, although a divalent ion, \([\text{UO}_2(\text{CO}_3)_2]^+\)
Ion Exchange Resin
Fig. 9-3. Typical ion-exchange column used in recovery of uranium [9].
Uranium Leaching, Counter Current Decantation, Solvent Extraction, Precipitation
Figure 15-20.—Map of Grants, New Mexico, area.
Figure 15-23.—Aerial view of Kerr-McGee Corporation Mill. Photo courtesy of Stearns-Roger Corporation, Denver, Colorado.
Uranium Precipitation and Purification

- Yellow cake (>70% U₃O₈) precipitated from carbonate solutions by MgO, NaOH or ammonia is dissolved.
- Phosphates, arsenates, molybdates, vanadates etc. removed by various methods.
- Uranium reprecipitated with ammonia.
- Ammonium diuranates decomposed.
- Oxides reduced by H₂(g) to UO₂.
- UO₂ converted to UF₄ then UF₆ (g).
- U²³⁵ enriched from U²³⁸ by gaseous diffusion or centrifuge.
Uranium Enrichment Centrifuges