URANIUM

A. Commodity Summary

Uranium is present in the earth's crust at approximately 2 ppm. Acidic rocks with a high silicate content, such as granite, have a uranium content that is above average, whereas the uranium contents of basic rocks such as basalts are lower than the average. However, 90 percent of the world's known uranium resources are contained in conglomerates and in sandstone.[1]

From 1980 to 1993, the domestic production of uranium declined from almost 44 million pounds U_3O_8 to about 3 million pounds (1,361 metric tons/yr).[2] A total of 17 uranium mines were operational in 1992; five conventional mines (both underground and open pit), four *in situ*, and eight reported as "other" (heap leach, mine water, mill tailings, or low-grade stock piles). Extraction/beneficiation operations produce yellowcake (precipitate containing uraniferous compounds), which is typically shipped to a Federal facility for processing. The number of mineral processing facilities is currently unknown. Uranium was also produced to a limited extent as a byproduct of phosphoric acid production at four sites. The primary demand for uranium is by commercial power generating facilities for use in fuel rods.[3]

B. Generalized Process Description

1. Discussion of Typical Production Processes

Uranium ore is recovered using either conventional milling or solution mining (*in situ leaching*). Beneficiation of conventionally mined ores involves crushing and grinding the extracted ores followed by placement in a leaching circuit. *In situ* operations use a leach solution to dissolve desirable uraniferous minerals from in-place deposits. Uranium in either case is removed from pregnant leach liquor and concentrated using solvent extraction or ion exchange and precipitated to form yellowcake. Yellowcake is then processed to produce uranium fluoride (UF_6), which is enriched and further refined to produce the fuel rods used in nuclear reactors.[4] Stockpiles of low grade ore removed from mines may be processed by heap leaching. It can also be economically feasible to separate the uranium as a by-product from the crude black acid (30% phosphoric acid) obtained from the leaching of phosphate for fertilizers.

2. Generalized Process Flow Diagram

Conventional Milling

Uranium ore is recovered by either open pit (for ore deposits close to the surface of the earth) or underground mining. The ore is blended, crushed, and ground. Ore high in vanadium is sometimes roasted with sodium chloride or soda ash prior to grinding in order to convert insoluble heavy metal vanadates (complex vanadium) into more soluble vanadate, which is then extracted with water. Two basic

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[1] "Uranium and Uranium Compounds," <u>Kirk-Othmer Encyclopedia of Chemical Technology,</u> 3rd ed., Vol. XXIII, 1983, p. 504.

[2] Department of Energy, <u>Decommissioning of U.S. Uranium Production Facilities</u>, February 1995, p. vii.

[3] U.S. Environmental Protection Agency, "Uranium," from <u>Technical Resource Document, Extraction and Beneficiation of Ores and Minerals,</u> Vol. 5, January 1995, pp. 3-5.

[4] U.S. Environmental Protection Agency, January 1995, <u>Op. Cit.,</u> pp. 13-16.

methods are employed to extract uranium from ore: acid leaching with sulfuric acid or alkaline leaching with a hot solution of sodium carbonate and sodium bicarbonate.[5] Exhibits 1 and 2 show process flow diagrams for open pit and underground acid-leach mills. A process flow diagram for an underground alkaline leach mill is shown in Exhibit 3. Most mills use acid leaching, which provides a higher uranium-removal efficiency. Alkaline leaching is used in the treatment of uranium ores when the lime content results in excessive acid consumption (alkaline leaching is preferred if acid consumption exceeds 68 kg/ton of ore treated).[6,7] Leaching involves bringing a solvent (lixiviant) in contact with the crushed ore slurry. Uranyl ions are then dissolved by the lixiviant. The pregnant lixiviant is separated from the residual solids (tails); typically the solids are washed with fresh lixiviant until the desired level of recovery is attained. The pregnant leach solution then enters a solvent extraction or ion exchange circuit.[8]

Solution Mining (*In Situ* Leaching)

In situ leaching, the most commonly employed solution mining technique, involves injecting a barren solution and lixiviant into the permeable ore zone. The solution penetrates the pores in the ore, leaching out the uranium and other metals.[9] The pregnant solution is then pumped up through production wells, passed through sand filters to remove any large particles, and transferred to ion exchange units. Ultimately, the uraniferous compounds are stripped from the ion exchange resins and precipitated to form yellowcake.[10] After the uranium is removed, the barren solutions are reconditioned and recycled. A typical *in situ* leach process is shown in Exhibit 4.

Solvent Extraction

Solvent extraction is typically employed by conventional milling operations since solvent extraction can be used in the presence of fine solids (slimes). The pregnant leach solution is mixed in tanks with the solvent. Normally, the solvents are organic compounds that can combine with either solute cations or solute anions. The uraniferous ions preferentially move from the aqueous pregnant leach solution into the organic solvent as the two are mixed and agitated. After the uraniferous compounds have been extracted, the barren lixiviant (raffinate) is typically recycled to the leaching circuit. After the solute exchange has taken place, the pregnant solvent extraction liquor is stripped using various agents such as nitrates, chlorides, sulfates, carbonates, and acids. The pregnant stripping liquor is then pumped to the precipitation step while the stripped organic solvent is recycled to the beginning of the solvent extraction circuit.

Ion Exchange

Ion exchange operations, used by most if not all *in situ* operations and some mills, make use of organic compounds to perform solute concentration. Generally, fixed organic resins contained within a column are used to remove uraniferous compounds from the leach solution by ion exchange. As the

[5] Werthman, P., and K. Bainbridge, "An Investigation of Uranium Mill Wastewater Treatability," Proceedings of the 35th Purdue Industrial Waste Conference, 1980, p. 248.

[6] "Uranium and Uranium Compounds," 1983, Op. Cit., pp. 516-517.

[7] "Uranium," in SME Mineral Processing Handbook, Vol. 2, 1985, p. 24-3.

[8] U.S. Environmental Protection Agency, January 1995, Op. Cit., pp. 18, 21.

[9] Department of Energy, February 1995, Op Cit., p. 30.

[10] U.S. Environmental Protection Agency, January 1995, Op. Cit., p. 27.

EXHIBIT 1

Process Flow Chart for an Open Pit Acid-Leach Mill

Graphic Not Available.

Source: U.S. Environmental Protection Agency, <u>Assessment of Environmental Aspects of Uranium Mining and Milling</u>, December 1976, p. 36.

EXHIBIT 2

Acid-Leach Process Flow Chart for an Underground Mine

Graphic Not Available.

Source: U.S. Environmental Protection Agency, <u>Assessment of Environmental Aspects of Uranium Mining and Milling</u>, December 1976, p. 38.

EXHIBIT 3

Alkaline-Leach Process Flow Chart for an Underground Mine

Graphic Not Available.

Source: U.S. Environmental Protection Agency, <u>Assessment of Environmental Aspects of Uranium Mining and Milling</u>, December 1976, p. 41.

EXHIBIT 4

Uranium *In Situ* Leach Process

Graphic Not Available.

Source: Department of Energy, <u>Decommissioning of U.S. Uranium Production Facilities</u>, February 1995, p. 31.

pregnant leach solution passes through the ion exchange resins, the uraniferous compounds bind to the resins. The barren leach solution is recycled back to the leaching circuit. After adsorption, the uraniferous compounds attached to the resins are released (eluted) by passing a concentrated chloride salt solution through the loaded resins. The pregnant elute liquor can then be directed to the precipitation circuit. The liquor may be acidified slightly to prevent the premature precipitation of uraniferous compounds.[11]

Yellowcake Production

Concentrated uraniferous ions from solvent extraction or ion exchange units are precipitated out of solution to produce yellowcake. Uranium is usually precipitated from acid solutions by neutralization with ammonia or magnesia.[12] Hydrogen peroxide may also be added to an acid pregnant stripping liquor or pregnant elution liquor to precipitate uranium peroxide. All forms of the uraniferous precipitate are known as yellowcake.

Alkaline pregnant stripping liquors or pregnant elution liquors typically contain uranyl carbonates. Prior to the precipitation of the uranyl ions, the carbonate ions are destroyed by adding hydrochloric acid. The carbonates are converted to carbon dioxide, which is vented off. The acidified solution is neutralized with an alkali or treated with hydrogen peroxide to precipitate the uraniferous compounds. The yellowcake is separated from the precipitation solution by filtration. Thickeners may be used in conjunction with filtration units. The filtered yellowcake is then dried and/or calcined and packaged for shipping. The supernatant generated from the precipitation and dewatering circuits can be recycled to the respective solvent extraction or ion exchange stripping solutions.[13]

Conversion and Purification Processes

Production of UF$_4$. The crude product from the refineries is purified to a degree that is usable in nuclear applications. The purified material is converted to uranium dioxide (UO$_2$) as shown in Exhibit 5. UO$_2$ is then converted to uranium tetrafluoride (UF$_4$) based on the following reaction:

$$UO_2(s) + 4HF(g) \ \text{-->} \ UF_4(s) + 2H_2O(g)$$
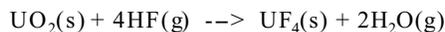
The process used to convert UO$_2$ to UF$_4$ is shown in Exhibit 6. Uranium tetrafluoride is then converted to either uranium metal or uranium hexafluoride (UF$_6$), the basic compound for isotope separation.

Production of UF$_6$. Uranium hexafluoride is prepared by direct fluorination of UF$_4$ with elemental fluorine in a fluorination tower based on the following reaction:

$$UF_4(s) + F_2(g) \ \text{--->} \ UF_6(g)$$
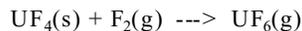
Solid UF$_4$ is fed through suitable locks into the top of the fluorination tower. Filtered and preheated fluorine is introduced into the side of the tower. Unreacted UF$_4$ is collected in a hopper at the bottom. This material is periodically removed and recycled.

Production of Uranium Metal. Uranium metal is produced by reduction of UF$_4$ by the Ames process as shown in Exhibit 7. The reduction process is carried out in a bomb. A charge consisting of anhydrous

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[11] U.S. Environmental Protection Agency, January 1995, Op. Cit., pp. 22-23.

[12] "Uranium and Uranium Compounds," 1983, Op. Cit., p. 522.

[13] U.S. Environmental Protection Agency, January 1995, Op. Cit., p. 23.

EXHIBIT 5

Production of Uranium Dioxide

Graphic Not Available.

Source: "Uranium and Uranium Compounds," <u>Kirk-Othmer Encyclopedia of Chemical Technology,</u> 3rd ed., Vol. XXIII, 1983, p. 523.

EXHIBIT 6

Flow Sheet for UF$_4$ Production

Graphic Not Available.

Source: "Uranium and Uranium Compounds," <u>Kirk-Othmer Encyclopedia of Chemical Technology,</u> 3rd ed., Vol. XXIII, 1983, p. 527.

EXHIBIT 7

The Ames Process

Graphic Not Available.

Source: "Uranium and Uranium Compounds," <u>Kirk-Othmer Encyclopedia of Chemical Technology,</u> 3rd ed., Vol. XXIII, 1983, p. 530.

UF_4 powder and magnesium chips is placed into the bomb. The charge is covered with MgF_2 powder, and the bomb is closed with a screwed-on flange cover. The charge is ignited spontaneously by heating, and the reduction of the UF_4 proceeds at a temperature of 700 °C.[14]

<u>Uranium-235 Enrichment</u>

Most nuclear reactors built for the generation of electric power are based on uranium fuel enriched in [235]U. Normally for such reactors, [235]U is enriched from a concentration of 0.7 percent to approximately 2-3 percent. The processes used to produce enriched uranium include the gaseous-diffusion process, centrifugal isotope separation, and electromagnetic separation.

3. Identification/Discussion of Novel (or otherwise distinct) Process(es)

An improved Eulex process for uranium extraction has been developed. In this process, a stage of uranium solvent extraction is coupled with each stage of resin elution rather than the elution and solvent extraction operations being conducted separately. The improved system reduces the number of stages, retention time, and resin inventory to about one-fourth or one-fifth that of other circuits.

A flotation technique also has been developed to extract uranium from seawater. Uranium is present in seawater in concentrations of 2.9 to 3.3 micrograms per liter. Sea water is the lowest grade but the most abundant source of uranium. However, it is unlikely that this source of uranium would be considered unless ore reserves become depleted.

Nuclear explosives have been used to increase the recovery of underground resources. The process may be useful in combination with solution mining of uranium ore bodies. However, the problem of radioactive contaminated waste would increase due to the production of artificial radionuclides.[15]

4. Beneficiation/Processing Boundary

EPA established the criteria for determining which wastes arising from the various mineral production sectors come from mineral processing operations and which are from beneficiation activities in the September 1989 final rule (see 54 Fed. Reg. 36592, 36616 codified at 261.4(b)(7)). In essence, beneficiation operations typically serve to separate and concentrate the mineral values from waste material, remove impurities, or prepare the ore for further refinement. Beneficiation activities generally do not change the mineral values themselves other than by reducing (e.g., crushing or grinding), or enlarging (e.g., pelletizing or briquetting) particle size to facilitate processing. A chemical change in the mineral value does not typically occur in beneficiation.

Mineral processing operations, in contrast, generally follow beneficiation and serve to change the concentrated mineral value into a more useful chemical form. This is often done by using heat (e.g., smelting) or chemical reactions (e.g., acid digestion, chlorination) to change the chemical composition of the mineral. In contrast to beneficiation operations, processing activities often destroy the physical and chemical structure of the incoming ore or mineral feedstock such that the materials leaving the operation do not closely resemble those that entered the operation. Typically, beneficiation wastes are earthen in character, whereas mineral processing wastes are derived from melting or chemical changes.

EPA approached the problem of determining which operations are beneficiation and which (if any) are processing in a step-wise fashion, beginning with relatively straightforward questions and proceeding into more detailed examination of unit operations, as necessary. To locate the beneficiation/processing "line" at a given facility within this mineral commodity sector, EPA reviewed the detailed process flow diagram(s), as well as information on ore type(s), the functional importance of each step in the production sequence, and waste generation points and quantities presented above in this section.

EPA determined that for this specific mineral commodity sector, the beneficiation/processing line occurs between yellowcake production and the conversion/purification processes. EPA identified this point in the process sequence as where beneficiation ends and mineral processing begins because it is here where yellowcake (uranium oxide) is chemically oxidized to uranium dioxide. Therefore, because EPA has determined that all operations following the initial "processing" step in the production sequence are also considered processing operations,

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[14] "Uranium and Uranium Compounds," 1983, <u>Op. Cit.</u>, pp. 523-528.

[15] Clark, D., <u>State-of-the-Art: Uranium Mining, Milling, and Refining Industry</u>. Prepared for EPA, Office of Water Resources Research, Washington D.C., pp. 102-105.

irrespective of whether they involve only techniques otherwise defined as beneficiation, all solid wastes arising from any such operation(s) after the initial mineral processing operation are considered mineral processing wastes, rather than beneficiation wastes. EPA presents the mineral processing waste streams generated after the beneficiation/processing line in section C.2, along with associated information on waste generation rates, characteristics, and management practices for each of these waste streams.

C.   Process Waste Streams

1.   Extraction/Beneficiation Wastes

Wastes and materials generated by uranium mining operations include waste rock, tailings, spent extraction/leaching solutions, particulate emissions, organic vapors, and refuse.[16]

Waste rock and overburden are deposited in waste rock piles or dumps. During the late 1970s, the largest open pit uranium mines produced an average of 40 million metric tons of overburden annually. Underground mines produced an average of 2,000 metric tons per year of waste rock during the same time period. Limited data indicate that waste rock contained higher levels of arsenic, selenium, and vanadium than background levels. Constituents of concern for waste rock and ore piles include low concentrations of radionuclides as well as sulfur-bearing minerals that, under certain conditions, may generate acid and, thus, leach metals.[17]

Most wastes generated by conventional mills are disposed of in tailings impoundments. These wastes, disposed of in the form of a slurry, include tailings (reground and pulped waste rock from the leaching process), gangue (including dissolved base metals), spent beneficiation solutions, and process water bearing carbonate complexes (alkaline leaching), sulfuric acid (acid leaching), sodium, manganese, and iron. Two acid- and alkaline-leach mills were reported to generate approximately 7,400 and 3,200 to 10,900 m^3/day of tailings, respectively. The tailing pond seepage from the acid-leach mill had a mean pH of 1.7 and contained high concentrations of dissolved solids (31,780 ppm), radium-226 (127 ppm), and dissolved metals (including lead, nickel, chromium, arsenic, and selenium). The tailing pond decant from the alkaline-leach mill contained high concentrations of arsenic (4 - 5 ppm), selenium (17 - 20 ppm), vanadium (24 - 27 ppm), uranium (55 - 960 ppm), and radium-226 (30 - 667 ppm).[18] The generation rate for tailing pond seepage was estimated to be 1,800 m^3/day at the facility mentioned above. We used the methodology outlined in Appendix A of this report to estimate a low, medium, and high annual waste generation rate of 17,000 mt/yr, 3,833,500 mt/yr, and 7,650,000 mt/yr, respectively for the tailing pond seepage.

In situ bleed solutions and lixiviant leaching solutions constitute the major wastes directed to lined evaporation ponds. These solutions consist of barren lixiviant and usually have high levels of radium; other contaminants (metals, salts) are limited to what may have been solubilized by the lixiviant. Barium chloride is added to the ponds, which in the presence of radium, forms a barium-radium-sulfate precipitate. This precipitate forms the majority of sludges in the evaporation ponds. These sludges, which may contain metals, sulfates, chlorides, and amines, are either disposed of at an NRC-licensed disposal facility or deposited in the tailings impoundment.

Ion exchange resins are occasionally replaced. Spent resins from *in situ* operations are disposed of at an NRC-licensed disposal facility. Conventional mills typically dispose of the spent resins in the tailings impoundments. The contribution of spent resins to the volume of a tailings impoundment is minimal compared to the volumes of tailings.[19] No information regarding the types of contaminants present in spent ion exchange resins was found.

Waste solutions are generated during acid/alkaline leaching, solvent extraction, stripping, and precipitation. Stripping solution could contain nitrates, chlorides, sulfates, hydroxides or acids. Constituents that could accumulate in the precipitation circuit are primarily anions - sulfates, chlorides, and possibly carbonates. Spent acids from leaching and wash waters from the washing of leached ore solids are generated at an approximate rate of 1,000 gallons per ton of ore processed and are discharged to the tailings ponds. In addition to radionuclides, solvent extraction solutions include phosphoric acids, amines, and ammonium salts. Process water from alkaline leaching is

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[16] U.S. Environmental Protection Agency, <u>Assessment of Environmental Aspects of Uranium Mining and Milling</u>, December 1976, pp. 36-43.

[17] U.S. Environmental Protection Agency, January 1995, <u>Op. Cit.</u>, pp. 30-37.

[18] Werthman P., and K. Bainbridge, 1980, <u>Op. Cit.</u>, pp. 249-250.

[19] U.S. Environmental Protection Agency, January 1995, <u>Op. Cit.</u>, pp. 30-37.

generated at a rate of 250 gallons per ton of ore processed and is discharged to the tailings pond.[20] The supernatant generated from precipitation and dewatering circuits can be recycled to the respective solvent extraction or ion exchange stripping solutions.

Solvent extraction generates the non-uniquely associated wastes listed below. Although no published information regarding waste generation rates or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate low, medium, and high annual waste generation rates (see Exhibit 8).

Waste Acids from Solvent Extraction. We used best engineering judgment to determine that this waste may exhibit the characteristics of toxicity (arsenic, chromium, lead, and selenium) and corrosivity.

Barren Lixiviant. We used best engineering judgment to determine that this waste may exhibit the characteristics of toxicity (arsenic, chromium, lead, and selenium) and corrosivity.

Slimes from Solvent Extraction. We used best engineering judgment to determine that this waste may exhibit the characteristic of toxicity (arsenic, chromium, lead, and selenium).

Waste Solvents. We used best engineering judgment to determine that this waste may exhibit the characteristic of ignitability.

2.   Mineral Processing Wastes

Although no published information regarding waste generation rates or characteristics was found, we used the methodology outlined in Appendix A of this report to estimate low, medium, and high annual waste generation rates (see Exhibit 8).

Production of UO_2

Waste Nitric Acid from the Production of UO_2. Waste nitric acid is produced during dissolution of yellowcake in nitric acid and during back-extraction. We used best engineering judgment to determine that this waste may be partially recycled and may exhibit the characteristic of corrosivity. This waste is classified as a spent material.

Production of UF_4

Waste Calcium Fluoride. Waste calcium fluoride is discharged to sewers. Existing data and engineering judgment suggest that this material does not exhibit any characteristics of hazardous waste. Therefore, the Agency did not evaluate this material further.

Vaporizer Condensate. We used best engineering judgment to determine that this waste may exhibit the characteristic of corrosivity.

Superheater Condensate. We used best engineering judgment to determine that this waste may exhibit the characteristic of corrosivity.

Ames Process

Slag. We used best engineering judgment to determine that this waste may exhibit the characteristic of ignitability. This waste is fully recycled and is classified as a by-product.

Uranium Chips from Ingot Production. We used best engineering judgment to determine that this waste may be recycled and may exhibit the characteristic of ignitability. This waste is classified as a by-product.

D.   Ancillary Hazardous Wastes.

Ancillary hazardous wastes may include vehicular emissions including particulates, sulfur oxides, carbon monoxide, and hydrocarbons. Non-hazardous wastes may include tires from trucks and large machinery, sanitary sewage, and some waste oil and other lubricants.

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[20] Clark, D., Op. Cit, pp. 50 - 51.

EXHIBIT 8

Estimated Waste Generation Rates

Waste Stream	Waste Generation Rate (metric tons/yr)		
	Low	Medium	High
Waste Acids from Solvent Extraction	1,700	9,350	17,000
Barren Lixiviant	0	1,700	17,000
Slimes from Solvent Extraction	1,700	9,350	17,000
Waste Solvents	0	0	1,700
Waste Nitric Acid from Production of UO_2	1,700	2,550	3,400
Vaporizer Condensate	1,700	9,350	17,000
Superheater Condensate	1,700	9,350	17,000
Slag	0	8,500	17,000
Uranium Chips from Ingot Production	1,700	2,550	3,400

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