Extracting uranium from its ores

by D.C. Seidel*

The development of the uranium mining and ore processing industry is unique. In the space of a little less than 10 years it grew from almost nothing to a major hydrometallurgical industry, no other ore-processing operation has developed so quickly. Not only did the industry grow rapidly, but it also became the leader in developing hydrometallurgical operations such as leaching, solid-liquid separation, ion-exchange, and solvent-extraction.

Up to the early 1940s uranium was produced as a byproduct of the vanadium and radium industries and the total world consumption was equivalent to only a few tonnes of uranium each year. By the early 1950s world production had risen to more than 800 tonnes per year, and has continued to increase since. In 1979 more than 50 uranium mills were in operation; and approximately 38 000 tonnes of uranium were produced. Over 65 000 000 tons of feed material were processed: approximately half was new ore, and the remainder was tailings from operations such as the gold mining industry in South Africa.

Until the early 1950s uranium ore came almost entirely from underground mines. In succeeding years the tonnage produced from open-pit mines has steadily increased and more *ore* is now produced from open-pit mines than from underground mines. However, more *uranium* is still produced by underground mines than by open-pit operations, because the ore grade from underground mines is higher.

The choice of an optimum mining system for a given deposit can be very complex. Many factors such as ore depth, deposit size, ore grade, ground conditions, surface topography, etc. must be considered. Each deposit has to be considered individually before a mining plan can be developed. Some underground mines are less than 30m below the surface, and conversely some open-pit mines operate at depths near 150m. Currently one underground mine, Mt. Taylor in the USA, is being developed at a depth of 1000m, and the gold mines in South Africa that produce uranium as a by-product are even deeper.

The size of uranium mines also varies over a wide range Some small, individually owned mines produce less than 50 tons of ore a day, whereas the Rossing open-pit mine in Namibia produces 40 000 tons of ore each day.

* Member of the Agency's Nuclear Materials and Fuel Cycle Section, Division of Nuclear Fuel Cycle

Uranium occurs in a wide variety of geological settings and nearly every type of mining technique has been used. The industry has also developed new technologies to meet special needs. The variability of uranium ore deposits is reflected in the subsequent ore processing technology.

The rapid growth of the uranium milling industry has made the exchange of information on the processing technology particularly important. Both the Agency and its parent United Nations organization have played important roles in this information exchange. The UN-sponsored International Conferences on the Peaceful Uses of Atomic Energy, which were held in Geneva, Switzerland, in 1955 and 1958, produced the first important publications on uranium ore processing. Before these conferences, uranium processing had been classified information. The IAEA has continued to collect and publish technical information on world-wide developments in the uranium milling and refining industry. The publications which are currently available are listed in the table.

Milling operations

After the uranium ore is mined, the next step in the nuclear fuel cycle is to chemically extract the uranium from the ore and produce a partially refined product with a uranium content of at least 65%. This material is normally termed *yellow-cake*. Uranium milling is based primarily on hydrometallurgical operations such as leaching, solvent extraction, and precipitation. Separation based on physical properties, such as specific

IAEA publications on uranium processing

1980	Production of yellow-cake and uranium fluorides (Proceedings of an Advisory Group Meeting – Paris, 5–8 June 1979)
1980	Significance of mineralogy in the development of flowsheets for processing uranium ores (Technical Report Series No 196)
1976	Uranium ore processing (Proceedings of an Advisory Group Meeting – Washington, D C , 24–26 November 1975)
1970	The recovery of uranium (Proceedings of a Symposium – São Paulo, 17–21 August 1970)
1967	Processing of low-grade uranium ores (Proceedings of a Panel – Vienna, 27 June–1 July 1966)

gravity or magnetic susceptibility, is impractical for almost all uranium ores. The yellow-cake is shipped to refining plants where it is purified to produce nuclear-grade uranium compounds.

Acid leaching· Uranium ores vary significantly from deposit to deposit and each mill must be designed to fit the specific characteristics of its ore. The general process, however, is similar for many ores. variations of the acid-leach flowsheet shown in Figure 1 have been used in more than 20 mills. The basic steps in this flowsheet are:

Crushing and grinding;
Leaching;
Solid-liquid separation and washing;
Solvent extraction or ion-exchange,
Yellow-cake precipitation and drying.

The run-of-mine ore, which in some instances may be 25cm or more in diameter, is crushed and then ground to the consistency of fine sand. Since most ores being processed today contain from about 0.02% to 0.2% recoverable uranium, it is necessary to process from 500 to 5000 kg ore for each kilogram of uranium recovered. To produce the same amount of uranium, therefore, mill-size can vary by a factor of 10.

Most uranium mills use wet grinding, and the resulting slurry is fed to a leaching circuit where sulphuric acid is added. Acid consumption does not depend on the uranium content of the ore, but is controlled by the gangue constituents: the carbonate minerals present are often the principal acid consumers. Total acid consumption may vary from 10 kg of H_2SO_4 per tonne of ore to more than 100 kg/tonne. Leaching times vary from a few to more than 24 hours. For some ores the leaching time can be greatly reduced by heating the leach pulp: temperatures in the 40° to 60° C range are used in several mills. With many ores, an oxidant such as manganese dioxide or sodium chlorate has to be added to achieve satisfactory uranium extraction. The oxidant is needed because most ores contain uranium in the reduced, or quadrivalent, form. The reduced uranium is only slightly soluble in the acidic leach solutions; the oxidant provides the driving force to convert the uranium to the hexavalent state which is readily soluble. Leach recoveries normally range from 85% to 95%, and the resulting leach solutions are relatively dilute but complex acidic sulphate solutions containing a wide variety of ions. Metallic ions commonly present include. uranium, iron, aluminium, magnesium, vanadium, calcium, molybdenum, copper, and sometimes selenium. The uranium concentration is normally 1 to 2 g/litre; concentrations of the other ions can vary greatly, depending on the composition of the specific ore being treated.

After leaching, the solids and liquids are separated, and the solids are washed to recover the adhering leach solution. In most mills, the washing operations are

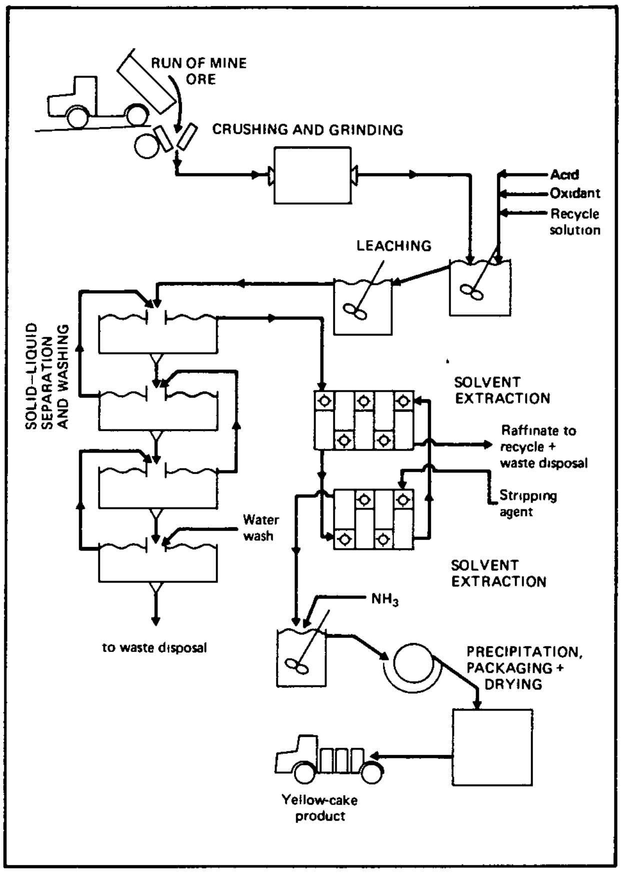


Figure 1. Uranium ore-processing flowsheet.

conducted in countercurrent thickener circuits. Both the thickener techniques and the flocculents developed for use in uranium mills are now widely used in other hydrometallurgical industries. Flocculents are chemical agents that can gather suspended particles into aggregations which settle much faster than the individual particles. The use of flocculents, therefore, reduces the size of the thickeners required for the washing circuit. The flocculent also helps to produce cleaner overflow liquors.

The uranium is separated from the leach solutions by solvent-extraction or ion-exchange. The uranium industry was the first hydrometallurgical industry to make extensive use of these two unit operations. The active agent in the solvent-extraction process is usually an organic amine salt, diluted in kerosene, that can selectively extract the uranium ions into an organic complex which is insoluble in water. The organic phase is separated from the aqueous phase by continuous settling and decantation techniques. The uranium is then stripped from the organic complex by contacting it with an inorganic salt solution, such as sodium chloride or ammonium sulphate. The yellow-cake is precipitated from the strip solution, and the resulting solid is dried and packaged for shipment to a refining plant.

Many modifications of this general flowsheet have been used, the specific process chosen depends upon a combination of factors such as ore characteristics, economics, and environmental considerations

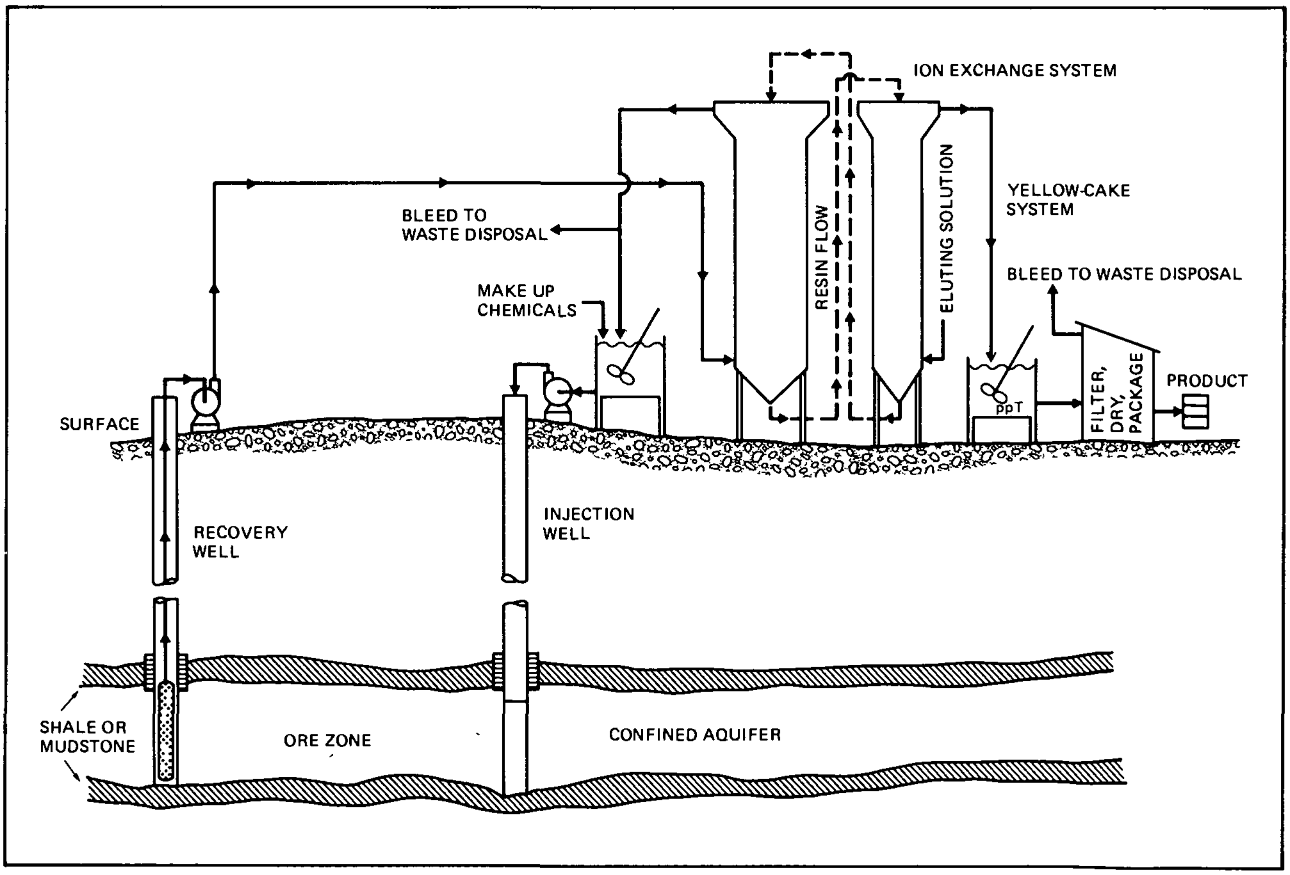
Alkaline leaching. A number of uranium mills use alkaline leaching circuits. This process is used when the limestone content of the ore is high, and, therefore, acid leaching is not economic Alkaline leaching of uranium ores is possible because, under oxidizing conditions, soluble anionic uranium carbonate complexes can form. The most common alkaline leaching solutions are mixtures of sodium carbonate and sodium bicarbonate. To achieve reasonable leaching rates high temperatures are required, and pressurized leaching systems are used in nearly all alkaline leaching plants so that leaching temperatures greater than 100°C can be achieved. Uranium is recovered from the leaching solutions by adding sodium hydroxide to raise the pH. This destroys the anionic complex and the uranium precipitates as a sodium diuranate yellow-cake, which is washed, dried, and packed for shipment.

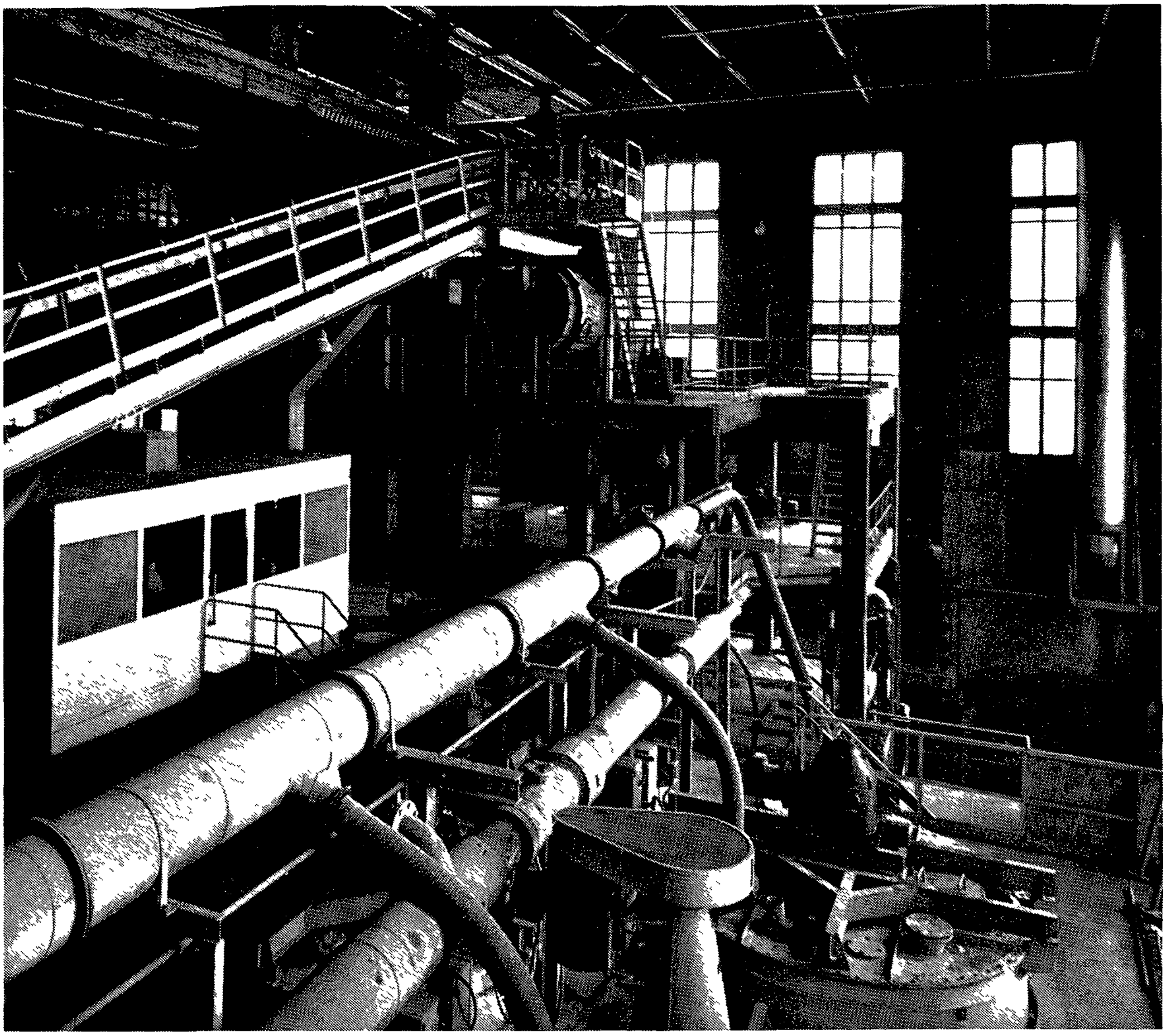
In-situ leaching· This is one of the newest uranium extraction technologies. Most of the industrial-scale development has occurred during the past five years in the south Texas area of the USA. As practised in the USA, the *in-situ* process consists of injecting a suitable leach solution into an ore zone which is below the water table. The leaching solution contains an oxidant together with chemicals that can form uranium complexes and thereby mobilize the uranium. The leach solutions are pumped to the surface where the uranium is recovered by ion-exchange. Figure 2 gives a general illustration of the process.

Nearly all commercial *in-situ* leaching operations have been associated with shallow sandstone aquifers (less than 200m below the surface) confined by low-permeability shale or mudstone strata. Often the relationship between the size, grade, and depth of the deposit has been such that open-pit or underground mining technology was not economic

Both carbonate and acidic leaching solutions have been used. The choice of leaching solution depends on both the chemical and the physical characteristics of the ore horizon. For example, a given leaching agent may adequately mobilize the uranium, but cannot be used because it may have adverse effects on the permeability of the ore horizon. Dilute sulphuric acid solutions are used for acidic systems and most of the alkaline systems use dilute (1 to 3g/l) solutions of ammonium, sodium, or potassium bicarbonate. The cation component is important because it can seriously change the permeability of the ore-bed. In some deposits containing montmorillonite clays the presence of sodium ions has caused the clay to swell and reduce the permeability nearly to zero.

Figure 2. General layout of in-situ leaching operation.





The interior of the ore-processing plant of l'Ecarpière in the Vendée region of France.

In almost every *in-situ* leaching operation oxidants have had to be added to mobilize the uranium. Hydrogen peroxide and oxygen are the most extensively employed because neither introduces any persistent contaminants into the leach system.

The leach solutions are introduced and recovered through a series of injection and recovery wells To obtain good yields, the solution has to be distributed and circulated uniformly throughout the ore-bed. Each design of well-field must take account of many factors specific to the deposit, such as the hydrologic characteristics of the host formation, the size and shape of the ore-body, the desired production rates, etc. Well spacings of 5 to 15m have been common, and a production unit may involve more than 100 wells. In most operations the flow rate to each injection well is controlled and submersible pumps are used to pump the pregnant solutions from the recovery wells.

All the current *in-situ* operations use ion-exchange to recover the uranium from the pregnant leach solutions. Both conventional fixed-bed and continuous ion-exchange systems specifically developed for uranium operations are used. In many operations the uranium is eluted from the loaded resin by contacting it with acidified sodium chloride solution and yellow-cake is precipitated from the resulting eluate. Conventional procedures are then used to filter, dry, and package the yellow-cake.

The major environmental considerations associated with *in-situ* leaching are:

The prevention and control of leach solution excursions during mining,

Restoration of the groundwater conditions in the area after mining has finished.

In general the industry has been able to devise satisfactory methods for controlling and minimizing solution excursions. When leach solutions have deviated from the desired flow pattern, it has been possible to correct the excursions by modification of the injection and recovery pumping procedures.

After leaching has finished the water quality within the affected aquifer has to be restored to standards established by the responsible regulatory agency. Since both the pre-mining water quality and the mineralogical composition within the aquifer can vary considerably from deposit to deposit, restoration procedures are tailored to fit the specific requirements of a given location. A relatively simple washing operation may suffice for some deposits, while significantly more complex combinations of washing and chemical treatment are necessary for other locations.

Research and development

As the uranium industry has matured, research efforts have shifted to optimizing operating techniques and improving environmental compatibility. In recent years further research has also been directed to recovering uranium from non-conventional resources. This research has included new work on uranium recovery from phosphoric acid, copper-leach liquors, low-grade ores, complex high-grade ores, and sea-water. Some developments that have been commercialized in recent years, in addition to those already discussed, include the following:

- Continuous ion-exchange – Several continuous ion-exchange systems are now operating in various parts of the world. Most of the systems are in general based on the countercurrent flow of feed solution and resin in a fluidized system. These systems function with relatively low resin inventories and can treat unclarified leach liquors.
- Semi-autogenous grinding – In this system the ore becomes its own grinding medium. Run-of-mine ore and water are fed directly to the semi-autogenous grinding mill and the product slurry is pumped to the leaching operation. The system can significantly minimize materials handling problems.
- Ore sorting – Although most uranium ores are not amenable to physical beneficiation, radiometric ore-sorting equipment has been successfully used to reject barren rock in several operations. Relatively coarse ore from the mine is passed through the equipment and the non-radioactive pieces are diverted to waste dumps. The technique may be particularly desirable where the haulage distance between the mine and mill is appreciable.
- Belt filtration – Continuous belt filters are being successfully used for washing and dewatering leach residues in a number of mills. The application of this technology is dependent upon the ore characteristics. In general the belt filters are most applicable when the clay content of the ore is relatively low.

The uranium industry has developed this wide variety of mining and processing techniques because uranium ores vary considerably. Processing operations must be designed to fit the specific mineralogical composition and characteristics of the ore being treated. Even within a single mine the processing characteristics of ore from different locations within the mine can vary significantly. Flowsheet-development studies for any specific operation must seek to understand and quantify these inconsistencies and then select a combination of unit operations that will handle the variability economically.

Challenges for the future include the recovery of uranium from more complex resources that often may be lower grade and deeper than deposits currently being processed. Throughout the world research is being directed toward the development of processing technologies that combine both economic and environmental compatibility.