

ALTERNATIVES IN URANIUM EXTRACTION PROCESSES

C. R. EDWARDS

Kilborn (Saskatchewan) Limited
357 Third Avenue South
Saskatoon, Saskatchewan
S7K 1M6

ABSTRACT

Since the first commercial extraction of uranium in the early 1940's, the range of available process alternatives has greatly increased. This paper reviews techniques now in use, and discusses processes under development to reduce extraction cost, improve efficiencies, and ameliorate environmental impacts.

INTRODUCTION

The first techniques developed for the large scale extraction of uranium were kept closely guarded under national security and were not released until the 1955 Geneva Conference for Peaceful Uses of Atomic Energy. In the intervening 33 years, a great deal has been published on uranium extraction, continuously widening the range of extraction process alternatives.

The following review of uranium extraction processes will follow the convenient path, shown in Figure 1, from the raw material source through to a uranium mill concentrate, ready for refining. Geology and mineralogy, which strongly influence the choice of processes, are beyond the scope of this review, but have been discussed previously (1, 2).

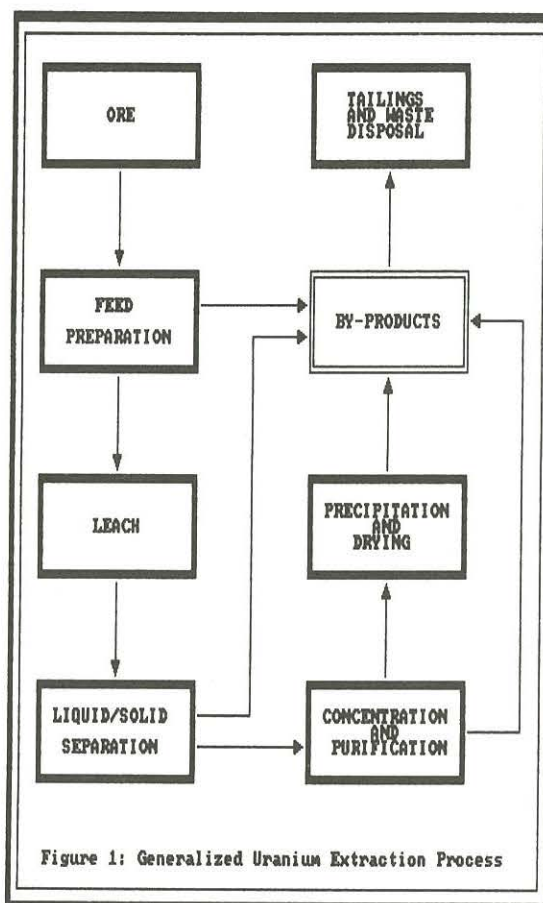
URANIUM SOURCES

Uranium mineralization occurs widely, with deposits (not all economically significant) found in at least 40 countries. At the present time, new supplies of uranium are extracted from a variety of ores, including phosphate deposits, which yield uranium as a by-product of phosphoric acid production. The other touted source, seawater, has enormous reserves but an extremely small uranium concentration, and the most optimistic production costs are about 20 times the current spot price.

FEED PREPARATION

To render the uranium amenable to high recovery by leaching, mined ore must be reduced in size. Originally, a conventional crushing and rod mill - ball mill circuit was used. Currently, semi-autogenous grinding (SAG) or autogenous grinding is being widely adopted when suited to the ore, with crushing, especially fine crushing, being phased out. SAG milling is in use at the Denison Mines Ltd., Elliot Lake operation, the Key Lake Mining Ltd. operation at Key Lake and Queensland Mines Ltd. at Nabarlek. The Eldorado Resources Ltd. Rabbit Lake mill utilizes autogenous grinding. In addition to energy savings, an improved working environment is also realized because of reduced dust generation

and radon release. For fine grinding, the Tower Mill may offer lower capital and operating costs, higher energy efficiency, and a quieter safer operation. (3) In situ leaching avoids all comminution costs.



Efforts at ore preconcentration have been ongoing for some 35 years. (4) Gravity concentration utilized during Phase I of the Amok Ltd., Cluff Lake operation upgraded both uranium and gold in the leach feed. (5) The Palabora Mining Company in South Africa developed a gravity concentration process using Reichert cones and shaking tables to recover byproduct uranium, in uranothorianite, from flotation tailings. Radioactive sorting achieved some success at the Mary Kathleen Mine in Australia, at the Cotter Corp. mine in Colorado, and at South African gold mines treating Witwatersrand conglomerate ores with uranium and gold comingled. Good

results were obtained using radiometric sorting on the Cenex Mine ore processed on a toll basis in the Beaverlodge mill in 1979. The Beaverlodge mill used flotation to remove pyrite from ground ore prior to carbonate leaching to avoid excessive reagent consumption. Frequent efforts to separate arsenic and nickel mineralization from uranium in northern Saskatchewan ores, utilizing radiometric sorting as well as flotation, gravity separation, and screening, have been uniformly unsuccessful. Recent advances in magnetic separation equipment (6, 7) may provide opportunities for uranium feed preconcentration, especially when "hot superconductors" are employed.

LEACHING

Whether acid or alkaline leaching is used, uranium must be oxidized to the hexavalent state before it can be dissolved. The uranium oxidation reaction requires the presence of ferric ion, whatever reagent is used as oxidant.

Acid leaching is the predominant process, with sulphuric acid the reagent of choice. Carbonate leaching, for suitable ores exhibiting excessive acid consumption, is very selective for uranium, and has the added advantage that radium is not solubilized. This process was utilized at Beaverlodge, at several mills in the United States, and at Lodeve, in France, where a two-stage carbonate pressure leach was developed. Carbonate leaching will not significantly attack gangue minerals, however, so comminution must expose the uranium mineralization to the leach solution for uranium extraction to occur. Sulphuric acid leaching may dissolve gangue minerals and thereby extract uranium not liberated by comminution.

With most northern Saskatchewan ores, arsenic and nickel minerals must be solubilized in order to extract uranium. For this and similar severe leaching steps, pressure leaching with air or oxygen as oxidant is often useful. Another severe leach process, pugging with sulphuric acid, has proven useful with ores containing a high clay content (8), and has been applied in Niger. Caro's acid (H_2SO_5) at atmospheric pressure is also an alternative to pressure leaching. Caro's acid may be produced on site by mixing concentrated sulphuric acid and hydrogen peroxide. It has the added benefits of not adding to effluent contamination, and of avoiding the corrosion risk resulting, for example, from the chloride ion contributed by a chlorate oxidant.

For ores with significant sulphide content, especially pyrite, consideration should be given to floating the pyrite and leaching it separately in small high-temperature pressure autoclaves. These autoclaves leach the pyrite and transfer the sulphuric acid, ferric ion and heat to the uranium leach, thus offering significant savings in operating costs. Also, by aggressively leaching the sulphide fraction of the ore, which often contains refractory uranium minerals, this process can be expected to enhance recoveries. Installing the pyrite flotation after the uranium leach can leave the tailings sulphide-free, which is a benefit to long-term waste stabilization. Importing pyrite to a mill site with sulphide-free ore may also provide improved process economics.

In biological leaching, bacteria convert sulphide to sulphuric acid and iron to ferric ion which provides oxidizing capacity. Denison Mines Ltd.'s Elliot Lake operation expects underground biological in-place leaching of low grade ore to contribute 25 percent of their total uranium production in 1990. (9) In this process, efficient and evenly-distributed aeration is critical to high uranium extraction. (10) Genetic engineering techniques may offer improvements in bacterial leaching since, for example, strains of *Thiobacillus ferrooxidans* capable of enhanced growth in the presence of uranium can now be distinguished and selected. (11) In 1977, Agnew Lake Mines in Ontario started a bacterially-assisted heap leach of broken ore left in underground stopes, but it was shut down in 1979 because unsatisfactory uranium recoveries resulted from ore breakage and disposition which were not amenable to trickle leaching. A flooded leaching system, with its costly oxidant delivery and distribution system, was used during final operation but was considered prohibitively expensive.

Vat-heap leaching of cobble ore has been extensively tested by Key Lake Mining Company at the Key Lake mine. (12)

In situ leaching, usually with carbonate/bicarbonate leachant, has been practiced in the United States. Sulphuric acid is not often utilized as the ore pores plug with gypsum. Recoveries are lower than with conventional leaching, so this method is mainly applied to low-grade ores. Most of the United States in situ leaching sites are located in Texas, with a lesser number in Wyoming.

LIQUID-SOLID SEPARATION

After leaching, liquid-solid separation is usually achieved with countercurrent decantation (CCD) thickeners, drum filters, disc filters, or belt filters. Every effort must be made to minimize soluble losses at this stage; lost uranium has a high value since about 75 percent of the direct extraction cost has been expended by this point in the process.

CCD thickeners are well-proven, simple, robust, and smooth operating. High rate thickeners can be used, but they are more prone to upsets from variations in upstream operations. Thickener mechanisms must be protected from potential corrosion from chemicals exiting the leach. The mill area must have a flat topography to site thickeners. CCD thickener operation can be optimized by careful control of flows, precise and efficient flocculant addition, and close monitoring of underflow densities and overflow clarities.

Capital and operating costs are relatively high for drum filters, and they are used less frequently now than previously. The same is true of disc filters, which have an added limitation in that they cannot perform any cake washing.

Belt filters afford space savings and provide a very efficient displacement wash versus, for example, the incomplete displacement wash on drum filters and the repulp wash with disc filters or in a CCD circuit. Belt filters require careful operation and tend to consume more flocculant and filter aid reagents. Their use was pioneered in France and

South Africa.

Clarification of the feed to ion exchange or solvent extraction is generally achieved in downflow pressure sand filters, which are more economical than the formerly common precoat leaf vacuum clarifiers and precoat pressure filters.

CONCENTRATION AND PURIFICATION

The purpose of this process stage is to obtain a uranium solution with higher uranium concentration than the pregnant solution, and with relatively much lower concentrations of impurities such as nickel, molybdenum, vanadium, arsenic, and iron. Either ion exchange (IX) or solvent extraction (SX) is normally used. The chemistry of these two processes is similar, but the extractant is a solid in IX and a liquid in SX. SX is sometimes called "liquid ion exchange" (LIX). This stage may be avoided if the ore is high grade and the leach solution is sufficiently pure, as was the case early at Cluff Lake, and may be the case in future with the Eagle Point ore at the Rabbit Lake operation.

The earliest IX process used quarternary ammonium (strong base) anion-exchange resin, in fixed bed systems, after sulphuric acid leaching. Its first commercial use was at West Rand Consolidated Mines Limited, at Krugersdorp, South Africa, in 1952. Fixed bed IX may still be the system of choice (e.g. the Denison Mines Ltd. expansion early this decade).

The commercial use of SX in uranium milling commenced in the United States in 1956, using alkyl phosphate extractants such as di(2-ethylehexyl) phosphoric acid (D2EHPA). SX had previously been used in uranium refining and in uranium extraction from phosphoric acid. (13) Amine extractants soon proved superior since they were more selective for uranium. Their first commercial application in North America was in 1958 at Eldorado's Port Radium mill, which had previously used aluminum powder to precipitate uranous arsenate and phosphate from clarified pregnant solution. Amine extraction became the standard uranium SX process, using an amine (usually tertiary) in a kerosene diluent with a long chain alcohol (e.g., isodecanol) as the modifier. Solvent extraction using tri-n-octyl phosphine oxide (TOPO) extractant is used to recover by-product uranium from phosphoric acid.

After trials and commercial use of a wide variety of SX contactors, the most common SX equipment presently consists of multi-stage mixer-settlers with countercurrent aqueous and organic flows. Centrifuges and several designs of columns may also be used. (Columns are common in uranium refining operations.)

Early uranium SX mixer-settlers were simple tanks, usually rectangular, (referred to as "conventional" mixer-settlers) which gave excellent uranium recovery. The developmental thrust has been to reduce SX equipment size and solvent losses. Oil industry electrostatic emulsion separation technology was tested by C-E Natco as an aid to solvent recovery from aqueous SX plant streams (14), but has apparently not been commercially applied. Electrostatic assist to organic/aqueous separation is used in the Davy Power Gas/Acres Davy McKee combined mixer-settler (CMS), which is operated in

two uranium SX plants in South Africa. A mixer-settler featuring a low turbidity pump and a stacked settler was developed by Krebs, and has been installed in uranium plants in France, Gabon, South Africa, Canada, and Australia. The Lurgi multitray settler (LMTS) has multiple settling trays in the settler, with mixer emulsion distributed evenly among the trays. The LMTS operates in several uranium SX plants and at the Sasol plant in South Africa, and in an organic chemicals plant in North America. Despite these advances, in certain applications, the conventional mixer-settler is still the equipment of choice.

SX reagent selection must address environmental concerns as well as process efficiencies, as in the 1985 replacement of ammonia stripping with a unique strong acid strip process in the Rabbit Lake mill. (15)

The ELUEX process which combines sequential IX and SX, was developed to avoid the general requirement for expensive and potentially polluting elution reagents such as chloride and nitrate in IX, and the costly and potentially polluting solvent losses in SX. ELUEX uses a concentrated solution of relatively inexpensive sulphuric acid for resin elution, and the acid eluate, a relatively small volume, is the SX feed. Thus IX operating costs are reduced, and the risk of organic pollution from the SX plant is lessened.

Both packed bed IX and SX require virtually solids-free feeds, so plants must bear significant costs to equip and operate liquid-solid separation and solution clarification stages. To obviate these, the "resin-in-pulp" (RIP) process was developed in the United States. Pulp contacts the resin in jigged baskets or agitated vessels. The process had fair success, but abrasion of the resin increased its loss rate. Up-flow columns, such as those developed by Societe Centrale de l'Uranium et des Minerais et Metaux Radioactifs (SCUMRA) in France, are limited to processing non-viscous, very dilute pulps; 5 weight percent solids at SCUMRA. More recently, extensive RIP pilot plant work has been performed in South Africa. The technique appears to be ready for implementation in any new plant. Kilborn feels that a combination of the earlier RIP experience and modern ion exchange and carbon-in-pulp (CIP) technologies could lead to a very effective and economical uranium extraction plant.

To handle solids-containing feeds, several continuous countercurrent ion exchange (CCIX) systems have been developed. The Himsley Column, developed in Canada, utilizes a fluidized bed column with resin transfer from stage to stage. Three Himsley columns, operated in parallel, were installed at Agnew Lake Mines. The rehabilitation of Rio Algom's Stanleigh mill also used Himsley columns. Five Himsley columns, handling 1000 cubic metres per hour of pregnant solution, were installed at the Vaal Reefs South plant in South Africa. A single resin loop, with downflow of pregnant solution, is the main feature of the Higgins Contactor, or Chem-Seps system. At the Bingham Canyon operation in Utah, a Chem-Seps system was installed to recover by-product uranium from copper dump leach solutions. The Cloete-Streat Contactor, essentially a column with stages separated by perforated plates, was further developed in South Africa into the NIMCIX

Contactors, which was put in at Blyvooruitzicht and Chemwes. Rossing, in Namibia uses the Porter CIX system, featuring multiple tanks containing fluidized resin beds and resin transfer by airlift.

A comparison of order-of-magnitude capital and direct operating costs for various uranium concentration and purification circuits is shown in Figure 2. The circuit feed carries 4 to 6 grams per litre uranium, which is typical of mills processing northern Saskatchewan ores. IX is generally more economical when dealing with lower concentration feeds.

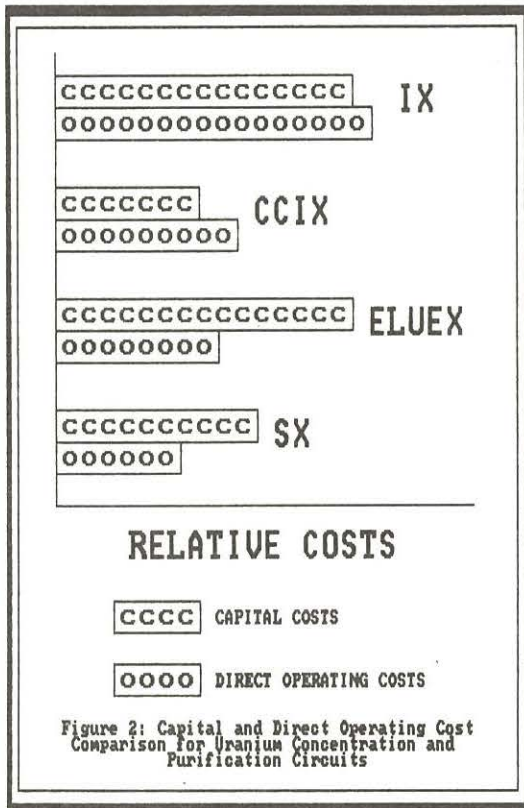


Figure 2: Capital and Direct Operating Cost Comparison for Uranium Concentration and Purification Circuits

PRODUCT PRECIPITATION AND DRYING

Historically, the uranium product was usually removed from solution via an alkaline precipitation with ammonia, caustic soda, or magnesia. The results were amorphous, variably-structured materials, the so-called "diuranates". These were actually a mixture of uranates, polyurantes, uranium hydrolysis products, and precipitated or absorbed impurities. (16)

Today, environmental concerns are as important as process efficiency and economics and product quality. The Rio Algom Panel mill removed nitrate and ammonia from mill effluent by switching to sulphuric acid IX elution, partial lime and magnesia neutralization, and uranium precipitation with magnesia. At Rabbit Lake, Eldorado Resources Ltd. changed their precipitant from ammonia to hydrogen peroxide, as part of the mill expansion for the processing of the Collins Bay ores, in order to

reduce ammonia in effluent below 15 parts per million. A level of 13 parts per million was achieved.

Uranium precipitation with hydrogen peroxide has other advantages such as improved product purity and easier product handling. (15) Further advantages, especially in product particle size growth and minimization of dusting, can be obtained from using a solid-liquid fluidized bed for precipitation, rather than the conventional stirred reactors, in a process developed in France. (17)

Washing of the uranium precipitate is usually carried out in several stages using thickeners, centrifuges, or filters. The efficient washing available with belt filters is being utilized more frequently in this application.

Product drying has been conventionally performed with multiple hearth roasters, which have inherent problems with dusty off-gas and, in ammonia precipitation plants, ammonia gas generation. An attractive alternative is to use indirectly-heated dryers, such as the oil-heated Porcupine dryer at the Eldorado Resources Ltd. Rabbit Lake mill, or the steam-heated Holoflite dryer formerly used in Eldorado's Beaverlodge mill. Another option is pellet extrusion as practiced by Denison Mines Ltd. at Elliot Lake, or belt filtration as at the Amok Ltd. Cluff Lake mill, followed by drying in a horizontal belt Proctor & Schwartz dryer. The latter methods can virtually eliminate dust in the off-gas.

BY-PRODUCTS

By-product recovery should be examined for economic benefit and to maximize the utilization of the resource. Thorium and rare earths were formerly recovered in the Elliot Lake area mills. An yttrium recovery plant, utilizing SX from IX barren, is now operating at Denison Mines Ltd. in Elliot Lake. Molybdenum and vanadium have been recovered in United States mills, and copper has been recovered in the United States and in Australia. Gold was recently recovered from mill tailings by carbon-in-pulp adsorption at the Amok Ltd. Cluff Lake mill (5), with more than 186 kilograms (6000 ounces) produced in 1987. Nickel recovery from mills processing northern Saskatchewan ores has not proven to be economical so far, but with the high nickel prices in mid-1988, this option deserves close study.

TAILINGS AND WASTE DISPOSAL

Tailings and waste disposal has three facets: containment, effluent treatment, and stabilization for decommissioning and abandonment. Difficulties can be lessened by using processes which do not contaminate effluents or produce deleterious wastes. Caro's acid leaching and hydrogen peroxide precipitation are examples. Efforts should be made to maximize the recycle of tailings slurry water and the reuse of mine water and in-circuit solutions in order to minimize the fresh water demand.

Acid formation by bacteria in sulphide-containing tailings may be controlled by removing the sulphides, for example by flotation as discussed

above, or by containing the tailings in a manner that either oxygen or water, or both, do not contact the tailings.

Radon escape to the atmosphere may be controlled by covering the tailings. A water-saturated tailings cover layer of soil or compost about 30 centimetres thick reduces radon emanation to the background levels of the cover materials. (18) A portion of the radium in the ore can be leached from the ore to give low radium tailings, but this results in a high-level radium material to dispose of or store, since radium today has virtually no uses or commercial value. (19) Thiobacillus ferrooxidans bacteria present in uranium tailings have been found to lower the concentration of dissolved radium. (20)

Conventional tailings disposal methods, including the Robinsky thickened tailings coning method and sub-aerial deposition, encounter problems with seepage, dam failure, decommissioning, and long-term environmental protection. The pervious surround tailings disposal method, developed by Geocon Inc. and in use by Eldorado Resources Ltd. at Rabbit Lake, provides a more assured long-term containment since tailings are isolated from groundwater movements and buried or flooded. (21)

Arsenic removal from effluents by precipitation is now understood (22), and arsenic discharges are now well controlled at northern Saskatchewan sites. (21, 23)

Aqueous discharges are treated with barium chloride to produce radium-barium sulphate, which is settled out of suspension. There may be subsequent polishing in sand filters. Handling the radium sludge is difficult, since it is low density, highly radioactive, and toxic. The best method of disposal of the sludge is to thicken it to the extent possible, then admix with neutralized tailings for disposal, with the caveat that the tailings containment method must prevent subsequent leaching or mobilization of the radium.

Control of radium in surface water and mine/mill site runoff using the "ecological engineering" approach is being tested by Boojum Research Ltd. and Eldorado Resources Ltd. in the Rabbit Lake drainage basin. Ecological engineering uses naturally occurring processes to purify water and control the mobilization of precipitated metals from contaminated sediments. At Rabbit Lake, a locally-growing algae, nitella flexilis, will be nurtured, with the intention of having the algae remove radium from surface water and permanently sequester it in lake bottom sediments. (24)

REFERENCES

- (1) "World Uranium: Geology and Resource Potential", Miller Freeman, San Francisco, 1980.
- (2) "Significance of Mineralogy in the Development of Flowsheets for Processing Uranium Ores", International Atomic Energy Agency, Vienna, 1980.
- (3) DAYTON, S.H., "Technology Update: Fine Crushing and Grinding", Engineering and Mining Journal, Vol. 188, No. 2, pp 26-33, 1987, February.
- (4) GRIMES, M.E., "The Technological Future of Canada's Uranium Industry", CIM Bulletin, Vol. 79, No. 888, pp 73-80, 1986, April.
- (5) MELIS, L.A. and ROWSON, J.W., "Operation of a Gold Extraction Circuit for Recovery of Gold from Uranium Mill Tailings at Cluff Lake, Saskatchewan", CIM, Canadian Mineral Processors, 20th Annual Operators Conference, Ottawa, 1988, January.
- (6) NORRGRAN, D.A. and ORLICH, J.N., "Fundamentals of high-intensity magnetic separation as applied to industrial minerals", Minerals and Metallurgical Processing, Vol. 5, No. 1, 1988, February, pp 1-11.
- (7) MATHIEU, G.I., "Historical Evolution of Magnetic Separation", CIM, Canadian Mineral Processors, 20th Annual Operators Conference, Ottawa, 1988, January.
- (8) SEIDEL, D.C., "Stored technology for possible use in uranium ore processing", Proceedings of the Washington Meeting on Uranium Ore Processing, International Atomic Energy Agency, Vienna, 1976.
- (9) ANON., "Heap leaching for uranium", Canadian Mining Journal, Vol. 109, No. 3, pp 29-34, 1988, May.
- (10) HARDCASTLE, S. and SHEIKH, A., "Applying tracer gas techniques to evaluate the air distribution in flood leaching stopes", CIM Bulletin, Vol. 81, No. 913, pp 53-58, 1988, May.
- (11) HOLMES, D.S., LOBOS, J.H., BOPP, L.H., and WELCH, G.C., "Setting up a Genetic System De Novo for studying the Acidophilic Thiobacillus T. ferrooxidans", in Recent Progress in Biohydrometallurgy, Associazione Mineraria Sarda, Iglesias, Italy, 1983, pp 541-554.
- (12) HOLL, N. and ROSNER, B., "Pilot Testing Vat-Heap Leaching Technology on Uraniferous Cobble Ore at Key Lake", in Projects '88, Proceedings of the 18th Annual Meeting of the Hydrometallurgy Section of the Metallurgical Society, CIM, Edmonton, 1988, May.
- (13) MERRITT, R.C., "The Extractive Metallurgy of Uranium", Colorado School of Mines Research Institute, Golden, Colorado, 1971, p 183.
- (14) WARREN, K.W., PRESTRIDGE, F.R., and SINCLAIR, B.A., "Electrostatic Separators May Supplant Mixer-Settlers", Mining Engineering, Vol. 30, No. 4, pp 355-357, 1978, April.
- (15) EDWARDS, C.R., "Hydrogen Peroxide Precipitation of Uranium in the Rabbit Lake Mill", Proceedings of the International Symposium on Crystallization and Precipitation, Pergamon Press, Toronto, 1987, pp 149-157.

- (16) ASHBROOK, A.W., "Basic Uranium Extraction Chemistry", Extractive Metallurgy of Uranium Short Course, University of Toronto, 1978, May, pp 1-46.
- (17) CUER, J.P., LACHAPPELLE, R. and FLOREANCIG, A., "Optimization of Hydrogen Peroxide Usage in Uranium Hydrometallurgy", paper presented at the International Symposium on Crystallization and Precipitation, CIM, Saskatoon, 1987.
- (18) McCORKELL, R.H. and SILVER, M., "Effect of compost and soil covers on radon emanation from uranium tailings", CIM Bulletin, Vol. 80, No. 908, pp 43-45, 1987, December.
- (19) HAQUE, K.E., "The leachability of radium from uranium ores", CIM Bulletin, Vol. 80, No. 908, pp 76-82, 1987, December.
- (20) PEREZ, J., TORMA, A.E., AND ITZKOVITCH, I.J., "Effects of Thiobacillus ferrooxidans on Barium-Radium Sulfate in Uranium Mill Tailings", in Recent Progress in Biohydrometallurgy, Associazione Mineraria Sard, Iglesias, Italy, 1983, pp 643-656.
- (21) PHILLIPS, R.L.J., "The Rabbit Lake Story - Environmental", in Projects '88, Proceedings of the 18th Annual Meeting of the Hydro-metallurgy Section of the Metallurgical Society, CIM, Edmonton, 1988, May.
- (22) KRAUSE, E. AND ETTTEL, V.A., "Solubilities and Stabilities of Ferric Arsenates", Proceedings of the International Symposium on Crystallization and Precipitation, Pergamon Press, Toronto, 1987, pp 195-210.
- (23) NEVEN, M., STEANE, R., and BECKER, J., "Arsenic Management and Control at Key Lake" in Impurity Control and Disposal, proceedings of the 15th Annual Meeting of the Hydro-metallurgy Section of the Metallurgical Society, CIM, Vancouver, 1985, August.
- (24) STRUGNELL, A., Ed, "Novel Solution to Watershed Decommissioning Underway", In Research News, Issue 1, Eldorado Resources Limited, Ottawa, 1988, p 7.