Environmental design of a uranium mill[1]

C.H. Quan, R.J. Ring, S.J. McNaughton[2]
Environment Division, Chemical and Waste Engineering,
Australian Nuclear and Technology Organization (ANSTO),
Lucas Heights Science and Technology Center,
Menai NSW, Australia

Abstract. In the frame work of the Cleaner Technology Project for Uranium Mining and Milling, Australian Nuclear and Technology Organization (ANSTO), Environment Division of ANSTO has carried out a programme of research which seeks to identify, investigate and develop cleaner technologies that have the potential to minimize the environmental impact of uranium mining and milling. This paper describes three design options of a new uranium mill that can meet environmental, technical and economical objectives. The feasibility of such an approach was examined in the laboratory and in a pilot plant study.

1. INTRODUCTION

ANSTO has undertaken many collaborative projects with industry. These projects were concerned with environmental management for uranium mining and milling in Australia. Through this work, a number of technologies have been identified that, if incorporated into a single mill design, could represent Best Practice Technology (BPT), with regards to environmental performance. The feasibility of such an approach was examined and is described in this paper.

The objectives of the study were to design and evaluate a proposed uranium milling circuit for an Australian deposit that would satisfy at least three environmental aims:

- Minimize plant footprint;
- Disposal of tailings underground;
- Maximize water recycle and re-use.

These constraints were focussed on minimizing the impact of an operating uranium mill on the local environment. This approach is a clear example of the changing attitudes in the uranium industry, which has accepted more responsibility for greater environmental awareness during the design stage. The early uranium processing operations were typical of conventional practice, and environmental problems were generally given low priority. There was little or no recycling of process water, acid waste streams were not neutralized and tailing storage and management was not always considered in the broader long term context. Nowadays mill design is no longer a case of putting together known technology in the most economic configuration, but rather the total performance of the mill – environmental, economic and social factors must be addressed and considered at the design stage.

2. CONVENTIONAL URANIUM FLOW SHEET

Uranium is mined by both underground or open pit operations. The ore is subjected to a size reduction process to liberate the mineral particles. A typical grind size is 50 wt% less than 75 μm. In the most common flow sheet, uranium ores are treated by sulfuric acid leaching under oxidizing conditions. Ferric ion and a secondary oxidant are required to achieve rapid and complete oxidation of most uranium minerals (typically uraninite). The selection of suitable leaching conditions requires a balance between uranium recovery and processing costs, which is usually determined by the consumption of reagents and energy. Following leaching, solid-liquid separation step and washing are usually

achieved in a counter current decantation (CCD) circuit. From this step, the tailing slurry is pumped to a retention facility, and the 'pregnant liquor', after clarification, undergoes solvent extraction (SX) for uranium recovery. The strip liquor from the SX process is the feed liquor for a precipitation step in which the uranium is recovered typically as ammonium diuranate. The raffinate is recycled to the washing circuit. The diuranate is washed, dewatered and calcined to produce a high purity product. A simplified mill flow sheet is shown in Fig. 1.
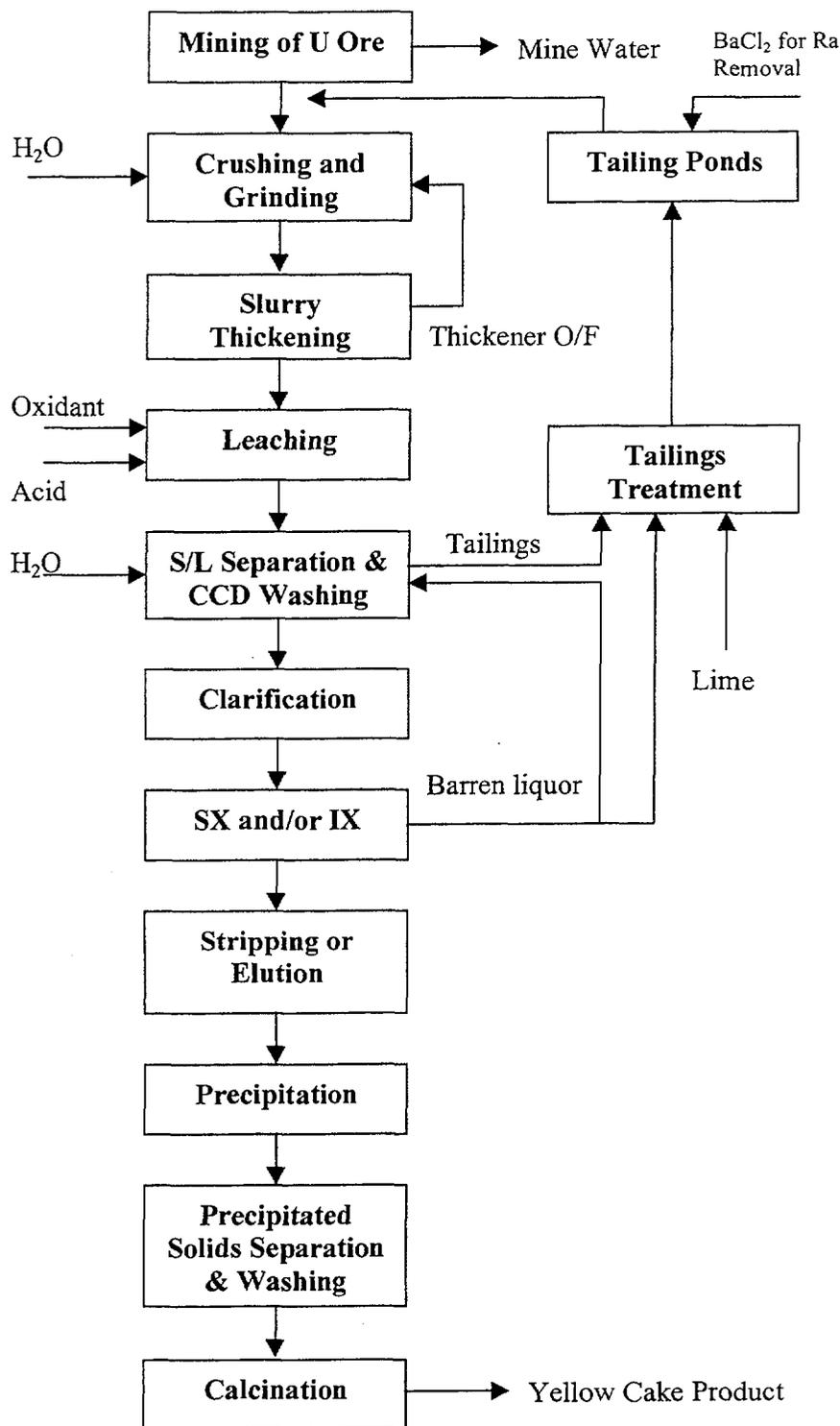
FIG. 1. A conventional acid leaching uranium mill flow sheet.

3. PROPOSED FLOW SHEET OPTIONS

The first design criteria, viz., minimize plant footprint makes a CCD washing circuit unattractive. An alternative to CCD washing is belt filtration and washing. The study criteria to dispose of all waste solids underground also strongly favours an approach whereby the tailings are prepared as a paste. The advantages of disposal of mine tailings as paste are now realized [1]. The paste is total tails thickened to a density where it can still be pumped, but will not segregate into fractions. It may or may not contain additives and has good settling characteristics.

For this design exercise, the option of paste technology has an impact on many aspects of process plant design. The filtration option after leaching has the potential of producing a highly dewatered filter cake that can be used directly to produce paste. Therefore, the simplest approach (option-1) is to replace the CCD circuit with belt filtration and washing and then recover the uranium using SX followed by precipitation. Filtration has usually taken second place to a CCD circuit on the grounds of ease of operation and reliability, even though filtration has the advantages of reducing water usage and increasing the uranium tenor of the pregnant liquor.

Two other less conventional options were also considered:

— The direct precipitation flow sheet (option-2). This flow sheet has a similar 'front end', which includes grinding, leaching and filtration, as the option-1 flow sheet. The 'back end' includes a partial neutralization step in place of the solvent extraction circuit, followed by direct precipitation of the uranium.

— The resin-in-pulp (RIP) or resin-in-leach (RIL) flow sheet (option-3). Instead of separating the leached solids from the pregnant solution, as in both options 1 and 2, a uranium-selective ion exchange resin is added to the leach slurry to recover uranium directly in a RIP process. Alternatively, leaching and RIP are integrated into a single unit operation as a RIL flow sheet.

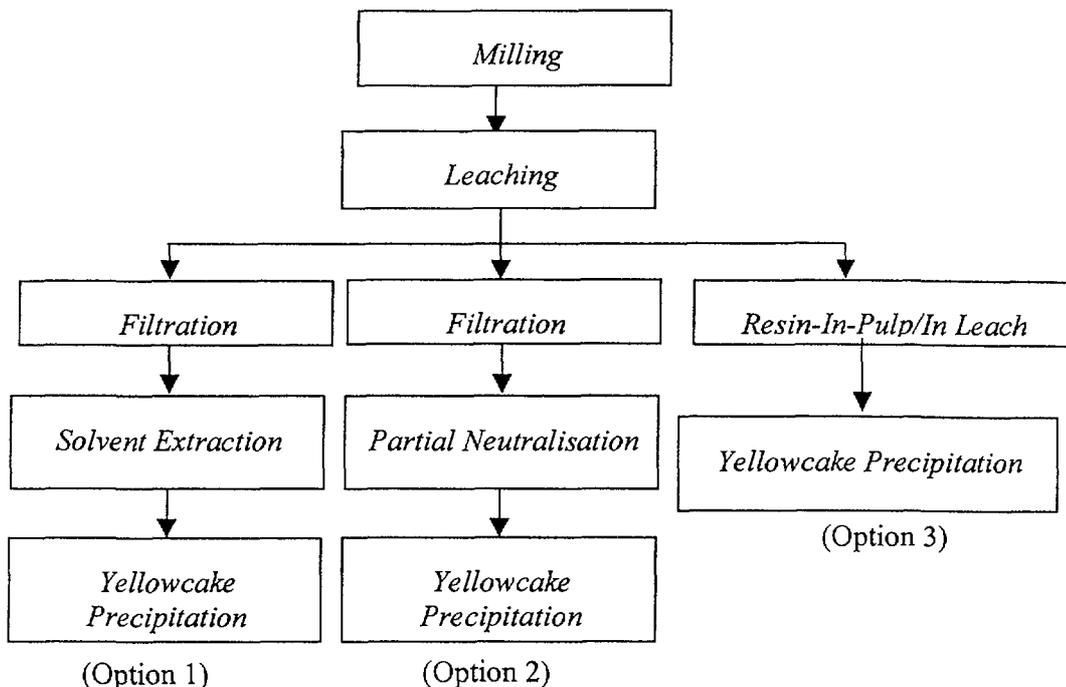A block diagram of the three proposed flowsheet options is shown in Fig. 2.

FIG. 2. Three flow sheet options under consideration.

3.1. Option 1 – The conventional approach

The horizontal belt filter is chosen to replace the multistage CCD circuit in the solid liquid separation step. In a typical design, this filter works by separating (under vacuum) the solids and liquor contained in the uranium slurry. The filtrate drains through a filter cloth transported by a carrier belt. The carrier belt is supported by an air cushion generated by a series of air boxes on either side of a central vacuum box assembly. The air cushion helps to reduce the friction generated by the weight of the materials on the cloth and the belt, and the applied vacuum. The belt filter has the ability to filter large volumes of solids with quite efficient washing. The wash volumes used are comparatively low and produce only minimal dilution of the uranium leach solution. During the late 1960s belt filtration received increasing acceptance in Europe. During the mid 1970s horizontal belt filters were installed in South African and North American uranium mills [2]. The horizontal belt filter was also proposed for the Kintyre mill in the recent feasibility study.

The belt filter also produces much drier tailings, containing 20–25 wt% water, which may be suitable for paste disposal. However, not all tailings can be effectively dewatered on a belt filter, especially the clay-rich ores, because the filtration rate may be too low to be practical. The CCD circuit for this type of ore also produces sludge underflow of very low density. Consequently, this flow sheet option will have application for some ores, but will be limited for clayey ores.

3.2. Option 2 – The direct precipitation flow sheet

In the so-called direct precipitation flow sheet, a partial neutralization step is introduced to effectively replace the SX circuit in the option-1 flow sheet. After filtering the leach slurry, the acid leach liquor is neutralized to a pH condition where iron and other impurities, but not uranium, are selectively removed. The technical feasilbility of the flow sheet is dependent on the circuit configuration and the impurities that are leached with the ore. Although the use of SX is economical for the production of high-grade yellowcake when using a very selective extractant [3], there have been frequent reports of losses of organic to the environment and crud problems associated with the SX operation. One review stated that there was a hidden cost in the solid-liquid separation involved with SX recovery due to the imperfect washing, resulting in soluble uranium losses [4]. Also, the operating cost of treating low-grade ores is proportional to the volumetric feed rate in an SX plant. An attractive feature of the option-2 flow sheet is the elimination of the SX circuit. The performance of the proposed direct precipitation flow sheet was evaluated in bench-scale laboratory experiments, and in a pilot scale study, for two uranium ores. These feasibility studies will be discussed and summarized later in this paper.

3.3. Option 3 – Resin-In-Pulp/Resin-In-Leach flow sheet

The first resin-in-pulp (RIP) process for the recovery of uranium from leach slurry was developed in 1953 in the former USSR [5] with a relatively high losses of the resin. Since then other researchers [2;4;6] have reported various success in developing the RIP/RIL process for uranium hydrometallurgy. Although the ability of ion exchange resin to adsorb uranium from solution has been known for a long time, there were engineering problems associated with the separation, transportation and mixing of the RIP/RIL mixture. These engineering aspects have an impact on resin losses and preventing the commercial implementation of the RIP/RIL process to recover uranium from 'thick' pulps. Major innovations in processing equipment are still taking place.

This flow sheet option appears to be the simplest of all because it eliminates the unit operations of solid-liquid separation and solvent extraction by adding the resin beads directly to the leach pulp, without clarification, to adsorb the uranyl sulfate ions. The uranium-bearing resin beads are then recovered by screening such that the finely ground ore particles will pass through the screen, but the coarse resin will not. In fact, when large throughput of low grade uranium ores are processed, the capital and operating costs of the solid/liquid separation circuit can become significant in relation to the total cost. South African Mintek has undertaken an extensive R&D program to develop RIP

technology for the recovery of gold and uranium [9, 10]. They considered that the significant developments in screening systems for the carbon-in-pulp process could be used for RIP. Different types of screen have been tried for this application, with some types being much more successful.

The application of RIP is attractive to uranium processing. However, it has been demonstrated that ion exchange resins have the potential to minimize the effects of preg-robbing during the leaching of uranium from carbonaceous and other ores. This is the RIL application. The resin beads are added in the leach tank for the adsorption of uranium almost as soon as it is extracted by the acid. A preliminary design concept of RIL was tested in the laboratory using a four stage counter-current circuit to contact an available commercial resin and the leach pulp followed by continuous counter current resin stripping. Based on this flow sheet a simple mass balance revealed an inherent difficulty with the flow sheet. The head grade of the ore was 0.5–0.1% U_3O_8 and given a 20 hour resin cycle time the resin inventory would have to be excessive. An additional concern was the rate at which the resin would have to be recycled through the plant and probable loss of resin due to abrasion. An annual loss of only 5% of the resin would have been prohibitively expensive given the size of the resin inventory.

An alternative to a conventional ion exchange resin is a magnetic ion exchange resin. This type of resin incorporates a magnetized component in the resin structure which allows the resin particles to act as an individual weak magnet. These resins can be tailor-made for specific application and have smaller particle sizes than conventional resins. A simple wet magnetic drum separator can then be used to effectively separate the small resin particles from the leach pulp. The magnetic separation method is generally considered to be a less vigorous or abrasive method (mechanically) when compared to the screening method used for the conventional non-magnetic resin. Therefore, physical degradation of the magnetic resin will be lower than that of sreening on the conventional resin.

ANSTO is currently undertaking a research and development collaborative project with a leading Australian chemicals company to develop a novel magnetic ion exchange resin (MIEX®) and process for the recovery of uranium (and gold) from hydrometallurgical operations. Following dissolution of the uranium in the leaching circuit, the slurry is contacted with the MIEX® resin in the adsorption circuit. The resin is separated from the slurry and advanced counter-currently along the circuit until it is loaded with uranium. The resin is advanced by passing the slurry through a magnetic separator on which the resin is retained and moved on to the next adsorption vessel. The slurry passes through the magnetic separator and back to the process, eventually discharging from the last vessel to the tailings impoundment.

The MIEX® resin has very small particle size of around 200–400 μm. It provides a high surface area allowing rapid adsorption kinetics. Equilibrium loadings of up to 20 g of U per litre of wet settled resin can be obtained. Recent tests have shown that the time required to achieve 50% of the equilibrium loading, t_{50}, for the MIEX® resin is only a few minutes.
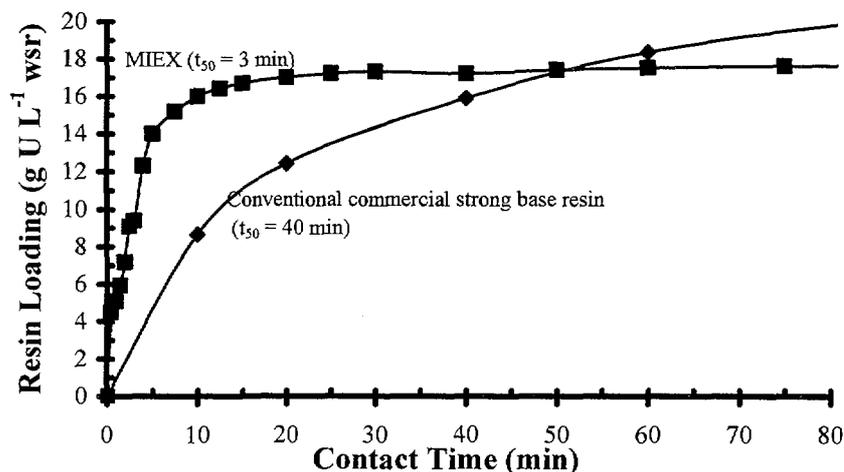

FIG. 3. Comparison of resins for uranium loading kinetics.

Figure 3 shows a loading time comparison between the MIEX® resin and a conventional strong base commercial resin. The required t_{50} loading time is about one tenth of that required for the conventional non-magnetic commercial resin.

The application of MIEX® and magnetic separating equipment is attractive to uranium processing using RIP. This because (i) the resin inventory would be less than that required by the RIL process; (ii) the elimination of expensive conventional solid-liquid separation and (iii) the fast loading kinetics of the resin which can be translated to fewer adsorption stages. All these benefits will result in smaller plant footprint and minimize water usage in the process. The design of resin-pulp mixture agitation and separation, and the pilot scale study of the MIEX® RIP process are currently taking place at ANSTO.

The development of a RIP uranium process in the Western World was initially driven by the poor filterability of some ores in the USA [8]. Various RIP systems were used in three Wyoming uranium mills to produce uranium from sandstones ores, and the operating personnel in these mills concluded that the continuous RIP process offered substantial benefits in their situation [11]. However, a major impetus to the further development of the RIP technology resulted from its adorption for gold processing applications. For a variety reasons, the use of ion exchange technology for gold processing was overtaken by the development of CIP/CIL technology. The role of ion exchange was also superseded by the development of SX technology to process high concentration uranium pregnant liquor.

4. FEASIBILITY STUDY

We have identified that the two proposed flow sheets (options 2 and 3) warrant consideration. The application of RIP in the option-3 flow sheet has been undertaken to further assess the MIEX® resin approach. The more readily applicable in the feasibility study is the direct precipitation (option-2) flow sheet. The flow sheet was studied for two Australian uranium ores separately in the laboratory and in the pilot scale experiments. A brief discussion of the performance of the flow sheet from a hydrometallurgical perspective is presented below.

4.1. Laboratory study

Two ores were tested in the laboratory using the direct precipitation flow sheet. The influence of pH and reagent selection on the performance of the iron precipitation, the iron cake releach and the uranium precipitation stages of the proposed flow sheet has been examined. Emphasis was placed on selectivity towards uranium and the ease of handling of the solid phases produced in the work. The sulfuric acid leaching conditions were similar for both ground ores at 40°C, pH 1.8, 55 wt% solids and under oxidizing condition (controlled ORP with oxidant addition) for 24 h. Uranium extraction of 98–99% was readily achieved.

The leach residue was filtered and washed on a Buchner funnel using an industrial belt cloth type. The filtrate was treated with an oxidant to oxidize the ferrous ion before adding limestone to pH 4.0. This partial neutralization step adequately removed iron, thorium and some of the aluminium and silica. In this step, some of the uranium also reported to the solids. Subsequently the neutralized solids (iron cakes) were releached in sulfuric acid to recover uranium, and the residue was combined with the primary leach filter cake to make into a paste product for tails disposal. In practice, the releach liquor could also be recycled to combine with the feed solution to the iron removal circuit.

After iron removal, the final liquor containing a few mg L^{-1} of Fe was achieved. This liquor, after clarification, was precipitated with hydrogen peroxide and sodium hydroxide (to pH 3.8) to produce a uranium peroxide product. The remaining uranium in the supernatant liquor represented a loss of ~0.1%. The precipitate was readily filtered, washed and dried to give a uranium concentrate product containing about 22 wt% moisture. Further calcination of the oven-dried precipitate to 600°C produced a final uranium product, which satisfied available converter specifications. The main issue

with this circuit concerns the impact of recycling the process water and the consequent build up of cations, which have the potential to contaminate the yellowcake product. A process model was used to evaluate steady state concentrations of all species in process water and a synthetic solution was then prepared to assess the impact on circuit performance. However, the impact of these cations on the properties of the paste tailings remains unknown.

4.2. Pilot plant study

An upgraded uranium ore product (from a medium grade using gravity concentration and radiometric sorting) was used as the feed material in the pilot plant. The process flow sheet used in the pilot plant was divided into three main circuits – leaching, iron precipitation and uranium precipitation. The pilot plant was successfully operated continuously over seven campaigns for a total of 42 days. During this period a range of plant operating conditions were tested. The objectives were to verify the technical feasibility of the proposed direct precipitation flow sheet under continuous operating conditions and provide data necessary for a commercial plant design.

The ore was first wet ground in a closed circuit ball mill with a 500 μm vibratory screen. The ball mill was only operated to grind enough ore to last for six days duration of each pilot plant campaign. The screen undersize was stored as slurry at 56 wt% solids in a 4500 L stirred tank from which the feed to the leach circuit was drawn. The leach circuit consisted of a cascade of stirred tanks to give a leach residence time of 14–25 h. The slurry in the tank was heated to the required leaching temperature of 45°C by means of steam and/or electric heaters. Sulfuric acid and an oxidant were added to the tanks to maintain the target leaching conditions. Uranium dissolution after 24 h generally exceeded 98% at 45°C and pH 2.0.

After leaching, the primary leach liquor was oxidized with hydrogen peroxide to oxidize all the ferrous ion before entering the iron circuit. Lime was added to the tanks to control the pH for iron precipitation. Iron concentration in the supernatant liquor was reduced to 2 mg L^{-1} at pH ~4.0. However, the iron sludge still contained up to 2% U_3O_8. This uranium was recovered by releaching the iron precipitate. There was no dissolution of ferric iron during the releach and therefore the releach filtrate was returned to the iron circuit feed. The washed releach filter cake was blended with the primary leach filter cake to be disposed of as tailings. This represented ~2% of the solid tailings produced in the whole process.

The iron circuit filtrate was passed through a clarifying filter to remove any suspended solids before entering the uranium precipitation circuit. Uranium peroxide was precipitated with the addition of hydrogen peroxide and the pH was controlled to the set point using sodium hydroxide. Stage recovery of more than 99.9% was achieved for the uranium. The uranium peroxide precipitate settled very easily in a thickener underflow with densities of ~65 wt% solids. The underflow solids were filtered and calcined at 250°C for 1 h to produce a product that contained 94% U_3O_8 and met the converter specification.

This bench scale investigation and the successful pilot plant operation have proved the technical feasibility of the direct precipitation flow sheet for processing two Australian uranium ores. Further optimization of the operating conditions such as the distribution of reagents and water management within each circuit as well as adopting the paste technology for tailing disposal will make this process option commercially and environmentally attractive.

5. CONCLUSION

New approaches to minimize environmental impacts for uranium mill design will, in future, receive wider attention by the industry. The environmental and technical constraints of minimizing plant footprint, water usage and disposal of tailings as paste were identified as important criteria in the design of a new uranium mill. Options for meeting these criteria are available and the feasibility of these approaches were assessed in a mill design case study.

On the grounds of minimizing water usage, the belt filtration system can replace the CCD circuit or be incorporated into a smaller CCD circuit. The highly dewatered filter cake tailings can be converted to paste for underground disposal. This option can be easily implemented into the conventional uranium hydrometallurgical plant.

The direct precipitation of uranium from the pregnant liquor makes the unit operation of solvent extraction redundant. The direct precipitation flow sheet was successfully tested at bench scale and pilot plant operation. The proposed uranium mill has a smaller footprint than the conventional design, utilizes almost complete water recycle, and allows for disposal of all waste as paste tailings.

The application of resin beads directly to the leach pulp in the RIP/RIL flow sheet has been considered to have several advantages over both the conventional and the direct precipitation flow sheets. The major advantages are the elimination of the solid liquid separation for the leached ore and the fast kinetics of the resin beads for uranium loading. The RIL process also has the potential to minimize the effects of preg-robbing during the leaching of uranium from carbonaceous ores. However, the major problems that prevented the implementation of RIP or RIL to uranium hydrometallurgical plant in the Western world are attributed to the difficulty in the effective separation of the resin from the leach pulp and the physical degradation of the resin beads at an acceptable rate. These are the driving forces for the development of the MIEX® resin. The magnetic resin-in-pulp process will meet all the environmental design criteria for a new uranium mill and as such, it warrants further development. ANSTO will continue to research and monitor developments of cleaner technologies in uranium processing and waste management.

REFERENCES

[1]   *Australian Center for Geomechanics Seminar on "Paste Technology 2000"*, 13–14 April, Perth (2000).

[2]   STREAT, M., NADEN, D., Ion exchange in uranium extraction. In: *Ion exchange and sorption processes in hydrometallurgy*. (STREAT, M. AND NADEN, D., CHICHESTER, Eds.) West Sussex, England: Wiley, (1987).

[3]   INTERNATIONAL ATOMIC ENERGY AGENCY, VIENNA, Technical Reports Series No. 359, (1993).

[4]   PROCEEDINGS OF THE FIFTH INTERNATIONAL SYMPOSIUM OF URANIUM AND NUCLEAR ENERGY, held by the Uranium Institute, London, 2–4 September 1980. Guildford, Westbury House, (1981).

[5]   HOLLIS, R.F., MCARTHUR, C. K., "The resin-in-pulp process for the recovery of uranium", *Proceedings of the Second U. N. Conference on the Peaceful Uses of Atomic Energy, Geneva,* vol. 8, (1955).

[6]   LASKORIN, B.N. *et al.*, "A filtration free method of processing uranium ores", translated from *Atomnaya Energiya*, vol. 43, no. 6, (1977).

[7]   READ, F.O., "Development of a resin-in-pulp process for the extraction of uranium from acid-leached pulps", *J. S. Afr. Inst. Min. Metall.*, vol. 60, (1959).

[8]   CLOETE, F.L.D., "The Relix process for the resin-in-pulp recovery of uranium", *J. S. Afr. Inst. Min. Metall.*, vol. 81, (1981).

[9]   FORD, M.A., "The engineering of a resin-in-pulp contactor for the recovery of gold and uranium from high-density slurries", *XVth CMMI Congress. Johannesburg, South African Institute of Mining and Metallurgy (South Africa)*, vol. 2, (1994).

[10]   FLEMING, C.A., "The potential role of anionic exchange resins in the gold industry", *EPD Congress 1998*, (Mishrs, B., Ed.) Warrendale, Pennsylvania, TMS: (1998).

[11]   SIMONSEN, H.A., BOYDELL, D.W., JAMES, H.E., "The impact of new technology on the economics of uranium production from low-grade ores", paper presented at the 5th *International Symposium of the Uranium Society, London* (1980).