

Reprint

of a Paper Presented
at a Technical Conference

of

THE INSTITUTION OF ENGINEERS, AUSTRALIA

3 CONCLUDING REMARKS

The recovery of fine coal from washery effluent streams is not only desirable from resource conservation, plant efficiency and environmental points of view but also represents an extremely attractive financial proposition. An economic analysis (Swanson et al., 1977a) has shown that high Discounted Cash Flow rates of return (Peters and Timmerhaus, 1968), and associated short pay back periods are available at relatively low capital investments. The high operating costs incurred by using an expensive reagent are more than offset by the low level of expenditure needed for plant construction. The key to the economic study is valuing the feed to the plant at nil cost. This nil cost feed assumption can be justified because the mining and treatment cost of this discarded material is included as part of the production cost of the currently saleable material.

4 ACKNOWLEDGEMENTS

The authors would like to thank the Broken Hill Proprietary Company Limited for permission to publish this work and to acknowledge the help and co-operation of personnel from BHP Collieries. This work was partially supported by grants from the Australian Government under their Industrial Research and Development Incentives Scheme.

5 REFERENCES

ARMSTRONG, L.W., SWANSON, A.R., and NICOL, S.K., 1978. Selective Agglomeration of Fine Coal Refuse, BHP Tech. Bull., 22 (1), May 1978, p 37.

BEHRENBECK, H. -J., PLATE, W., and SIMONIS, W., 1974, Die Selektive Agglomeration Kohle-Mineralstoffkollektives in feinsten Steinkohlenschlamm. Aufbereit. - Tech., 15 (9), p 495.

BENSLEY, C.N., SWANSON, A.R. and NICOL, S.K., 1977. The Effect of Emulsification on the Selective Agglomeration of Fine Coal, Int. J. Miner. Process., 4, p 173.

BOGENSCHNEIDER, B., BEHRENBECK, H.-J., and KUBITZA, K.-H., 1976. Die Aufbereitung feinsten Steinkohlenschlamme durch die Selektive Agglomeration. Gluckauf, 112 (23), p 1314.

CAPIES, C.E., McILHINNEY, A.E., McKEEVER, R.E., and MESSER, L., 1976. Application of Spherical Agglomeration to Coal Preparation, in Partridge, A.C. (Ed.), Proceedings of the Seventh International Coal Preparation Congress, Sydney, Australia, H.2.

JOINT COAL BOARD, 1978. Thirty-First Annual Report, 1977-78.

LEMKE, K., 1954. The Cleaning and Dewatering of Slurries by the Convertol Process. in Int. Coal Prep. Congr., 2nd, Essen, Germany, Paper A IV 2.

PERROT, G. and KINNEY, S.P., 1921. The Use of Oil in Cleaning Coal. Chem. Met. Engng., 25 (5), p 182.

PETERS, M.S., and TIMMERHAUS, K.D., 1968. Plant Design and Economics for Chemical Engineers, McGraw-Hill, pp 238-242.

NAGATA, S., 1975. Mixing - Principles and Applications, Halsted Press, N.Y.

SWANSON, A.R., NICOL, S.K., and BENSLEY, C.N., 1977a. Selective Agglomeration: A Solution to Problems in the Efficient Treatment of Fine Coal. Chemeca 77, 5th Australian Conference on Chemical Engineering, 1977, p 304.

SWANSON, A.R., BENSLEY, C.N., and NICOL, S.K., 1977b. Some Fundamental Aspects of the Selective Agglomeration of Fine Coal. Proceedings 2nd Int. Symp. on Agglomeration Atlanta, Ga, p 939.

VERSCHUUR, E. and DAVIS G.R., 1976. The Shell Pelletising Separator. Key to a Novel Process for Dewatering and De-ashing Slurries of Coal Fines. in Partridge, A.C. (Ed.). Proceedings of the Seventh International Coal Preparation Congress, Sydney, Australia, H.1.

Alternative Leaching Processes for Uranium Ores

R.J. RING

Research Scientist, Australian Atomic Energy Commission

SUMMARY The substantial increase in the demand for and price of uranium has stimulated research into the recovery of uranium from low grade and refractory ores and the exploitation of small orebodies. Economic processing of these ores requires new or improved leaching technology which can also be applied to conventional ores. Strong acid curing, pressure leaching and ferric sulphate leaching have been developed to improve the recovery of uranium from refractory ores. Leaching in nitric and hydrochloric acids has been studied as a method of reducing the long-term environmental impact of tailings by extracting radium and other radionuclides from the ore during milling. In the USA, many low grade and/or small deposits are being profitably exploited by in-situ or heap leaching.

Laboratory studies have been carried out to compare the extraction of uranium from Australian ores by conventional leaching in sulphuric acid with that obtained using hydrochloric acid and acidified ferric sulphate solutions. Leaching with hydrochloric acid achieved high extractions of radium-226 but the extraction of uranium was reduced considerably. The use of acidified ferric sulphate solution reduced acid consumption by 20-40 per cent without any detrimental effect on uranium extraction. The ferric ion, which is reduced during leaching, can be reoxidised and recycled after the addition of acid makeup. Hydrogen peroxide was found to be an effective oxidant in conventional sulphuric acid leaching. It is more expensive than alternative oxidants, but it is non-polluting, lesser quantities are required and acid consumption is reduced.

1 INTRODUCTION

Uranium is extracted from its ores by leaching in sulphuric acid or sodium carbonate-bicarbonate solution. Acid leaching accounts for over 80 per cent of the world's uranium production. It is more effective than alkaline leaching which is mainly used when the host rock is strongly alkaline.

Uraninite, the principal ore mineral of uranium, is readily dissolved at low temperatures and acid concentrations provided that oxidising conditions are maintained to convert uranium to the soluble uranyl form. However, more refractory minerals require severe leaching conditions to release the uranium. The most common leaching process is the dilute acid route by which ore as a 50-60 wt % slurry is leached at pH 1.0-2.0 for 10-36 h at 30-80°C in a mechanically agitated tank or pachuca. In alkaline leaching, ore is leached as a finely ground slurry in a solution containing 25-60 g l⁻¹ Na₂CO₃ and 5-25 g l⁻¹ NaHCO₃, but elevated temperatures (80-120°C) are necessary to obtain acceptable extraction rates.

The substantial increase in the demand for and price of uranium has stimulated research into the recovery of uranium from low grade and refractory ore and the exploitation of small orebodies. Economic processing of these ores requires new or improved leaching technology which can also be applied to conventional ores. This paper briefly reviews recent developments in leaching practice and summarises AAEC work on the applicability of some non-conventional processes to Australian ores.

2 OVERSEAS DEVELOPMENTS IN LEACHING TECHNOLOGY

2.1 Strong Acid Leaching

Strong acid leaching (SAL) involves impregnating

coarsely ground dry ore with a small volume of concentrated sulphuric acid (sufficient to wet the ore) and curing at 65-100°C for 12-24 h. The uranium solubilised during the curing stage can be extracted from the ore by any of the following methods: deep bed percolation through the cured ore in a storage silo; washing the ore as a shallow bed on a belt or pan filter; or slurrying and solid-liquid separation by conventional methods (Skelton and Scowen, 1977).

The leaching conditions of the SAL process are much more severe than for dilute acid slurry leaching. They are attractive for refractory ores which require concentrated acid to achieve uranium extraction. In addition, no oxidant is required as the hot concentrated acid is a sufficiently strong oxidising agent. The need for grinding is reduced as SAL extracts uranium from ore at much larger particle sizes; this also simplifies the solid-liquid separation step. The quantity of water required for washing the coarse ore is less than for a fine pulp, which also makes the process particularly suitable for applications in arid regions (Skelton and Scowen, 1977). The biggest disadvantage of SAL is that it requires almost dry ore for the leaching step which can be achieved only by dry grinding or drying after wet milling.

Pechiney Ugine Kuhlmann was responsible for the design and construction of a SAL milling plant at Arlit in the Niger Republic (Boutonnet, 1975). The acid consumption under conventional leaching conditions is 150 kg t⁻¹ ore with a water requirement of 1000 l t⁻¹ ore. The SAL process requires an acid consumption of 55 kg t⁻¹ ore when water is restricted to 50 l t⁻¹ ore. The acid impregnation and curing steps are carried out in a rotating horizontal drum. The ore is then disintegrated in a revolving tube loaded with pebbles and transferred to stirred tanks for repulping.

A similar process has been proposed for a mill at Akouta, also in the Niger Republic, and is scheduled to start up this year. Unlike the Arlit mill, curing will be carried out on a continuous, rubber conveyor belt, following the practice of the fertilizer industry. A vacuum belt-filter will be used for washing and liquid-solid separation.

The United Kingdom Atomic Energy Authority (UKAEA) has also conducted laboratory tests of a SAL process using conglomerate and sandstone ores ground to about minus 1 mm. Uranium extractions and acid consumptions were comparable to those obtained in conventional leaching but reaction times were significantly shorter. Skelton and Scowen (1977) claimed that capital and operating costs would be of the order of 25 per cent lower than those for a conventional plant. The first commercial plant using the UKAEA process will treat a copper ore at a mill near Santiago, Chile (Parkinson, 1978).

Ores from the Alligator Rivers region are not amenable to SAL as the gangue contains chlorite which consumes acid rapidly under conditions of high temperature and strong acid concentration (Alfredson et al., 1975; Skelton and Scowen, 1977).

2.2 Ferric Sulphate Leaching

Ferric sulphate leaching is carried out with a higher concentration of ferric ion than is normally used in conventional dilute acid leaching. Ferric ion is reduced during leaching but can be regenerated by chemical or bacterial oxidation and recycled, after addition of a small quantity of makeup acid.

Tests on South African ores showed that leaching at 55°C with an iron concentration of 7 g l⁻¹ achieved a uranium extraction of 93 per cent compared with the 80-85 per cent obtained by conventional leaching (about 2 g l⁻¹ iron) using manganese dioxide as oxidant (James, 1976). A process using this technique has been installed at the Buffelsfontein gold/uranium plant (SAMEJ, 1977).

The UKAEA and the Warren Spring Laboratory have also developed a ferric sulphate leaching process in pilot plant trials. The main advantages of the process were higher extraction rates, because of the high ferric ion concentration (12 g l⁻¹ at pH 1.2) and a smaller acid requirement compared with conventional leaching (Derry et al., 1977).

2.3 Pressure Leaching

A process for the pressure leaching of South African pyritic ores at elevated temperatures, with air as oxidant, was successfully demonstrated in the 1950s. Under these conditions the pyrite decomposed to ferric sulphate and sulphuric acid. This method of treatment was not adopted at that time because of the high capital cost. Because of recent increases in the prices of uranium and acid, this technique has been reassessed. A demonstration plant was constructed comprising a 20 m³ capacity, four-compartment, mechanically agitated autoclave. Results showed that greater extractions of uranium were obtained at comparable operating costs to conventional leaching, although capital costs were higher. It is expected that pressure leaching will soon be incorporated into some mill circuits (James, 1976; James et al., 1978).

In the USSR, an autoclave fitted with an airlift column for pulp circulation is being successfully used to process refractory and complex low-grade uranium ores. Improved extraction rates of uranium

were obtained with lower consumptions of sulphuric acid (Skorovarov et al., 1976).

A new pressure leaching system which allows operation at much higher temperatures with extremely short residence times has been developed recently in Germany (NF, 1977). The system employs a plug-flow "tube digester". The slurry is introduced into a central inner tube whose first section is preheated by a countercurrent flow of hot slurry in the surrounding outer tube. The tail end is heated by a heat exchanger using steam or fused salts. Advantages claimed for this system over conventional autoclaves are improved heat transfer coefficients, virtually no moving parts, faster reaction times, and rapid startup and shutdown.

2.4 Leaching Processes to Recover Uranium and Radium

The tailings residue produced by sulphuric acid leaching contains about 70 per cent of the radioactivity originally in the ore. The most significant daughter product of uranium is the potentially hazardous radium-226 which, as a member of the alkaline earth family, is readily incorporated into bone structure. Radium is also important as a source of radon which acts as a vehicle for dispersal of its short-lived alpha-emitting daughters.

In acid leaching mills, almost all of the radium remains in the tailings which must be properly impounded to control radium and radon releases. The long-term environmental impact of tailings would be reduced if radium was removed from the ore during processing. Tests by the US Bureau of Mines and the Canada Centre for Mineral and Energy Technology have shown that leaching with hydrochloric acid gives high extractions of both uranium and radium (Borrowman and Brooks, 1975; Saint-Martin, 1977). Leaching with nitric acid results in increased extractions of uranium and low residual radium in the tailings (Ryon et al., 1977). Both methods are expensive because of high acid costs, although only limited attention was directed at optimising leaching conditions.

2.5 In Situ Leaching

In situ leaching involves the injection of solutions through an orebody (solution mining), or through broken rock in underground mines (stope leaching) or through an ore pile that has been removed from the mine (heap leaching). The latter two approaches may be enhanced by bacterial action. These techniques are receiving wide attention in the United States for the recovery of uranium from small and low grade deposits.

Solution mining has been used to exploit copper, evaporites, gold and uranium deposits in the United States, Canada and USSR (Bhappu, 1976; Skorovarov et al., 1976). For amenable orebodies, solution mining has the advantages over conventional mining and milling of low initial capital investment, short lead times, low manpower requirements and (in terms of surface disturbance, tailings storage and radon release) less environmental impact (Hancock, 1977). The disadvantages are the difficulty in controlling and predicting ground water hydrology, ensuring containment of leach solutions in the orebody, restoring the original groundwater conditions after cessation of mining and monitoring the whole operation (Rouse, 1974).

The following criteria determine the suitability of an orebody to solution mining (Hancock, 1977):

- (i) The orebody must be permeable, otherwise fracturing may be necessary.
- (ii) The orebody should be a horizontal bed underlain by a relatively impermeable stratum.
- (iii) The orebody must be below the static water table.
- (iv) The direction and velocity of water flow must be known.

Leaching solutions are injected through and withdrawn from boreholes or wells to control the flow of leachant. The spacing of wells is a vital factor. Both acid and alkaline leaching solutions have been used, but the latter is more common. An oxidant such as oxygen or hydrogen peroxide is also required.

At present, there are 15 or more solution mining test programs in progress on unconsolidated sedimentary deposits in the Western United States. The Beverley deposit in South Australia is similar and could be exploited by solution mining (Slee, 1978).

Types of heap leaching include leaching of as mined or crushed low-grade ore piles on areas sealed with plastic sheeting or bitumen pads, and leaching of average grade crushed ores from small deposits in vats (Michel, 1976). In all cases, ore is placed in a controlled manner and then sprayed with dilute sulphuric acid; the run-off solution is then collected and treated to recover uranium or recycled. Stope leaching is essentially the same as heap leaching except that is carried out in an underground mine as a very simple operation.

4 EXPERIMENTAL STUDIES

Experimental studies have been carried out to determine the suitability of hydrochloric acid and ferric sulphate as leachants for Australian uranium ores and a program is in progress to assess the potential of hydrogen peroxide as an oxidant in sulphuric acid leaching.

4.1 Hydrochloric Acid Leaching

The efficiency of uranium and radium extraction using hydrochloric and sulphuric acids was compared under typical plant conditions:

pH	: 0.7-2.0
Redox potential	: -475 mV
Temperature	: 33-55°C
Duration of leaching	: 14 h
Slurry density	: 10-55 wt %

Under all conditions, leaching with hydrochloric acid resulted in 30-40 per cent lower acid consumptions, but also 3-4 per cent lower uranium extractions, than were obtained with sulphuric acid (Figure 1). As the cost of hydrochloric acid is about four times that of sulphuric acid, the use of hydrochloric acid could not be economically justified. With hydrochloric acid, high extractions (85-95 per cent) of radium-226 were obtained during leaching and washing operations (Ring and Rapisarda, 1977).

4.2 Ferric Sulphate Leaching

The effect of leaching with acidified ferric sulphate on uranium extraction and acid consumption was determined for Nabarlek and Ranger ores. Figure 2 shows that additions of ferric ion within the range 5-15 g l⁻¹ reduced acid consumption by 20-40 per cent compared with conventional leaching at

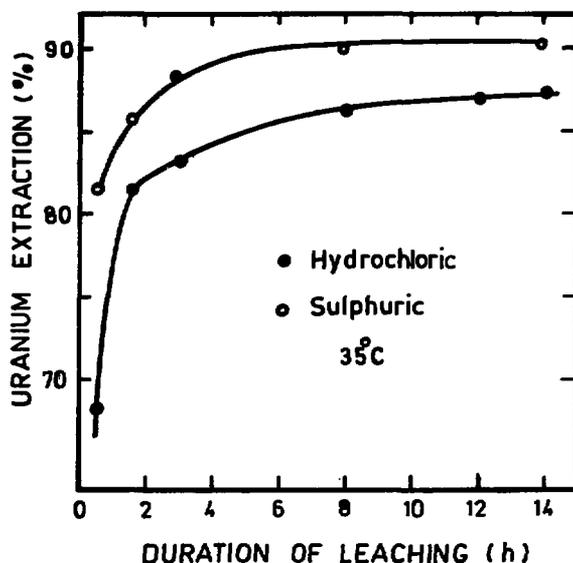


Figure 1 Comparison of leaching data for hydrochloric and sulphuric acids at pH 1.0 and slurry density 55 wt %

35-40°C and the same pH, where redox potential was maintained at -475 mV by additions of pyrolusite. For concentrations of 10-15 g l⁻¹ Fe³⁺, the final extraction was virtually the same as that obtained in conventional leaching, although the initial rate of extraction was increased. The effect of an increase in temperature was the same as with conventional leaching; a slight increase in uranium extraction was obtained at the expense of a substantial rise in acid consumption.

The decrease in acid consumption at 35-40°C is greater than the amount of acid that would react with the normal addition of pyrolusite. The results in Table 1 show that ferric sulphate leaching dissolves less gangue than conventional leaching. The decrease in iron dissolution ranges from about 1.5 to 4.0 g l⁻¹, which would result in an acid saving of at least 3.5-8.5 kg t⁻¹ ore. As one of the major acid consuming gangue minerals in the ores is chlorite, an iron-aluminium-magnesium silicate, the observed reductions in the dissolution of magnesium and aluminium would be expected to accompany the dissolution of iron.

Work is under way to determine the most effective method of reoxidation of ferrous to ferric ion, which will require some acid and increase acid consumption by about 4-5 kg t⁻¹ ore.

4.3 Hydrogen Peroxide as an Oxidant in Sulphuric Acid Leaching

Pyrolusite (primarily MnO₂) is the oxidant for all proposed mills in the Alligator Rivers region. The disadvantage of using pyrolusite is the high concentration of manganous ion in the leach liquor and ultimately in the waste effluent. Neutralisation of the effluent is not a completely effective method for precipitating manganese and about 100 mg l⁻¹ remains at pH 8 (Levins et al., 1977). Sodium chlorate is commonly used in overseas mills, but, under the system of water management proposed for Australian mills, chloride ion would build up in the recycled process water from the tailings retention system. Excessive chloride levels would result

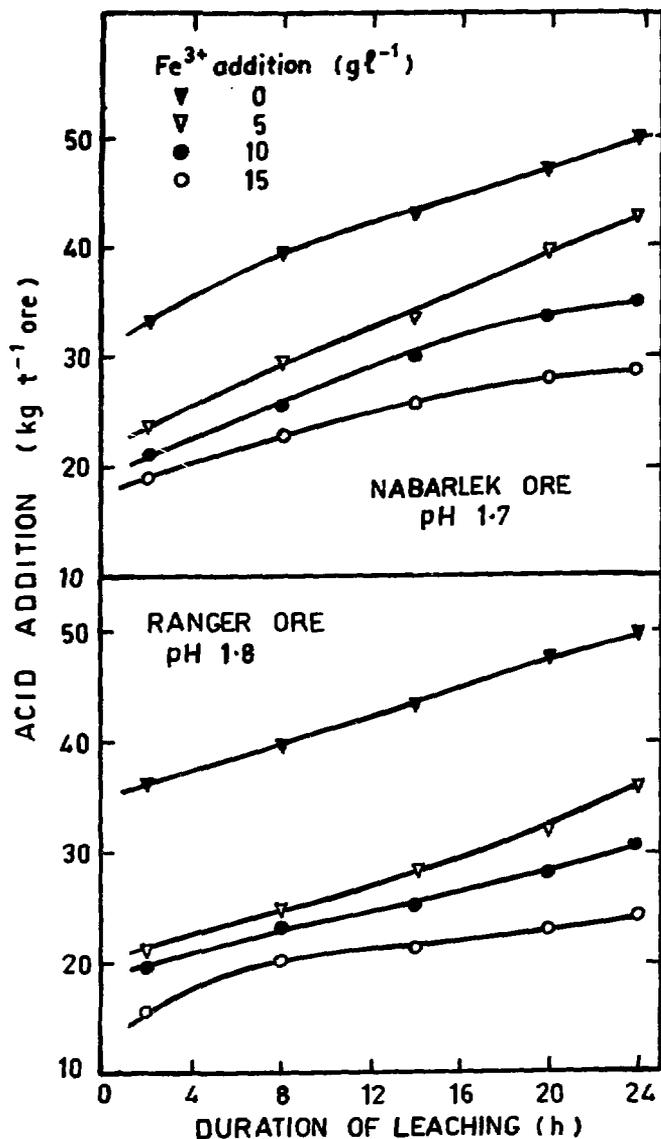


Figure 2 Effect of ferric ion concentration on acid addition

in a decrease in the efficiency of the solvent extraction operation. Hydrogen peroxide is an attractive oxidant on environmental grounds, forming water rather than manganous ions on reduction. Its main disadvantage is its high cost compared to pyrolusite.

Leaching experiments were carried out on Ranger and Nabarlek ores to assess the potential of hydrogen peroxide as an alternative oxidant. Almost identical uranium extractions were obtained with both oxidants at the same redox potential. Figure 3 shows that peroxide additions were 2.2 to 2.7 times less than pyrolusite (compared to a theoretical value of 3.2) and the acid consumption was 10 to 20 per cent lower. The reduction in acid consumption should also result in an equivalent decrease in lime requirements for neutralisation. With these additional savings in reagent costs, hydrogen peroxide may prove to be competitive with pyrolusite. These promising results are being investigated further, with particular emphasis on determining those factors which influence the utilisation of peroxide.

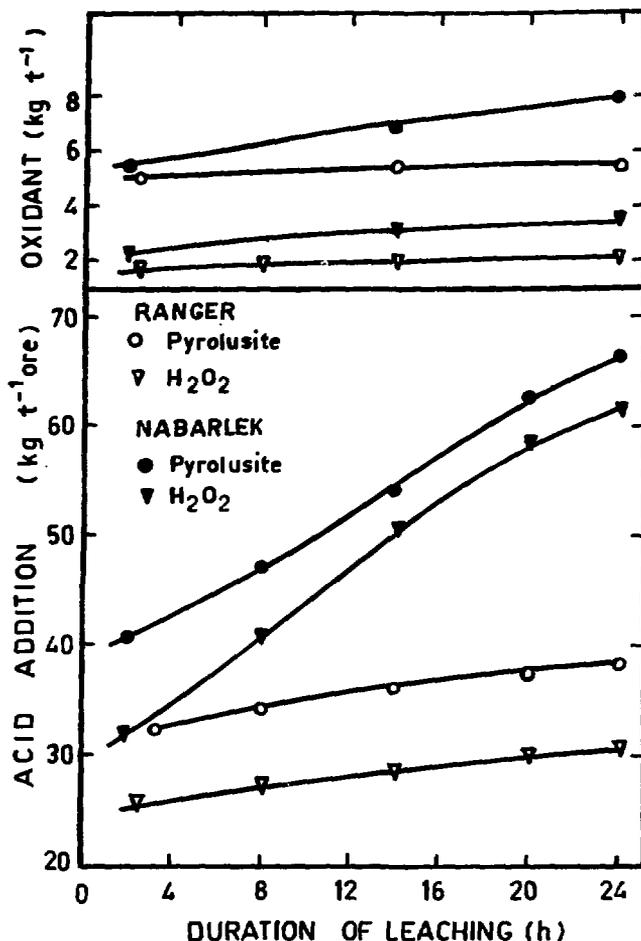


Figure 3 Consumption of reagents for Ranger and Nabarlek ores under typical leaching conditions

TABLE 1
COMPOSITIONS OF LEACH LIQUORS FROM RANGER ORE*

	Conventional Leaching	Ferric Sulphate Leaching	
	Acid addition (kg t ⁻¹ ore)	48.7	35.7
Pyrolusite addition (kg t ⁻¹ ore)	6.3	0	0
Addition of Fe ³⁺ (g l ⁻¹)	0	5	10
Component	Concentration (mg l ⁻¹)		
Al	3,020	2,580	2,140
Ca	410	140	170
Fe	4,200	7,600	9,800
K	270	220	68
Mg	3,000	2,600	2,100
Mn	3,800	n.d.	63
P	226	67	97

*Leached for 24 h, pH 1.8 and 35°C
n.d. - not determined

5 CONCLUSIONS

Although present generation uranium mills mostly use the basic sulphuric acid and carbonate leaching processes developed in the 1950s, several promising leaching processes have been developed during the 1970s. These processes, which will enable economic treatment of refractory and lowgrade ores and the exploitation of small orebodies, can also be applied to reduce the costs of processing conventional ores. In particular, the use of acidified ferric sulphate solution, which can be recycled after regeneration, appears to have potential in reducing reagent consumptions for Australian ores.

Hydrogen peroxide is an effective oxidant in the acid leaching of uranium ores and is attractive on environmental grounds. It is more expensive than pyrolusite but lesser quantities are required and acid consumption is also lower.

6 ACKNOWLEDGEMENTS

The author gratefully acknowledges the assistance of Mr. G.P. Shaw in carrying out the experimental work, the chemical analyses by the AAEC's Uranium Analysis Service and Analytical Chemistry Section and the cooperation of Ranger Uranium Mines Pty Ltd, and Queensland Mines Ltd, in providing ore samples.

7 REFERENCES

- ALFREDSON, P.G., HENLEY, K.T. and RYAN, R.K. (1975). Leaching of Ranger and Nabarlek ores. Extractive Metallurgy Symposium, Melbourne. AIMM.
- BHAPPU, R.B. (1976). In situ extraction and leaching technology. In Economics of Mineral Engineering. Mining Journal Books Ltd, London. pp 90-124.
- BORROWMAN, S.R. and BROOKS, P.T. (1975). Radium removal from uranium ores and mill tailings. US Bureau of Mines Report RI-8099.
- BOUTONNET, G. (1975). Uranium hydrometallurgy prospects. Nucl. Eng. Int. Vol. 20, Feb. pp 100-102.
- DERRY, R., GARRETT, K.H., LEROUX, N.W. and SMITH, S.E. (1977). Bacterially assisted plant process for leaching uranium ores. International Symposium on the Geology, Mining and Extractive Processing of Uranium, London. IMM.
- HANCOCK, B.A. (1977). Uranium in situ leaching: its advantages, practice, problems and computer simulation. AIME Annual Meeting, Atlanta. Preprint 77-AS-66.
- JAMES, H.E. (1976). Recent trends in research and development work on the processing of uranium ore in South Africa. Proceedings of an Advisory Group Meeting on Uranium Ore Processing, IAEA, Vienna.
- JAMES, H.E., BOYDELL, D.W. and SIMONSEN, H.A. (1978). South African uranium industry plans for expansion. Nucl. Eng. Int. Vol. 23, Nov. pp 42-45.
- LEVINS, D.M., RYAN, R.K., STRONG, K.P. and ALFREDSON, P.G. (1977). Improving pollution control in uranium mining and milling. 5th Australian Conference on Chemical Engineering. Inst. Chem. Eng. Aust.
- MICHEL, P. (1976). Processing of low grade uranium ores. Proceedings of an Advisory Group Meeting on Uranium Ore Processing. IAEA, Vienna.
- NF (1977). A new pressure leaching process. Nuclear Fuel. Vol. 2, No. 6, p 20.
- PARKINSON, G. (1978). Cu/U ore-leaching route cuts pollution, trims costs. Chem. Engng. Vol. 85, No. 10, Apr. pp 54-55.
- RING, R.J. and RAPISARDA, A. (1977). Leaching of uranium ores with hydrochloric acid. Extractive Metallurgy Symposium, Sydney. AIMM.
- ROUSE, J.V. (1974). Environmental aspects of in situ mining and dump leaching. Proc. Solution Mining Symposium, 103rd AIME Annual Meeting, Dallas. AIME, New York.
- RYON, A.D., HURST, F.J. and SEELEY, F.G. (1977). Nitric acid leaching of radium and other significant radionuclides from uranium ores and tailings. Oak Ridge National Laboratory Report. ORNL/TM-5944.
- SAINT-MARTIN, N. (1977). Hydrochloric acid leaching of an Elliot Lake uranium ore - a preliminary study. Canada Centre for Mineral and Energy Technology Report ERP/MSL 77-38(TR).
- SAMEJ (1977). Bacterial oxidation to raise uranium extraction rate. S. Afr. Min. Eng. J. Vol. 88, No. 4127, pp 61-63.
- SKELTON, R.J. and SCOWEN, P.A. (1977). Improvements in processes and equipment for the uranium industry and their effect on plant costs. International Symposium on the Geology, Mining and Extractive Processing of Uranium, London. IMM.
- SKOROVAROV, D.D. et al. (1976). Processing of low grade uranium ores in the USSR. Proceedings of an Advisory Group Meeting on Uranium Ore Processing. IAEA, Vienna (AAEC-LIB/TRANS-621)
- SLEE, J. (ed.) (1978). Australian Mines Handbook 1977-78. Minex Services and the National Miner, Perth, pp 81-91.