


1. **INTRODUCTION**

The recent discovery of extensive deposits containing uranium mineralisation in a shallow calcrete environment in Western Australia has directed attention to the possible application of carbonate leaching as an alternative to the acid leaching process used at all plants operated to date in Australia.

Only sketchy information on mineralisation is available for publication at this stage, but the ores are of secondary origin and apparently contain carnotite and other oxidised minerals, with uranium/vanadium ratios ranging from 1:1 to 10:1. The mineralisation is associated with calcite and pyrite is absent. One published report has indicated an average grade of 3 lb U₃O₈/long ton* (Liddy 1972).

This paper reviews the standard practice in Canada and the United States with special references to the Beaverlodge plant in Canada, with which the author was associated some years ago. Apart from the question of its application to carbonate-bearing ores, carbonate leaching could have special significance in the West Australian environment because of its closed-circuit operation. This minimises the fresh-water intake requirements and reduces pollution problems as a negligible quantity of dissolved chemicals is discharged from the plant.

2. **THE SELECTION OF CARBONATE LEACHING**

The presence of carbonate minerals in sufficient quantity to cause acid consumptions of more than 150-200 lb/ton is likely to be the deciding factor in favour of using a carbonate leach. This is equivalent to a calcite content in the ore of 7%-9% (Gow and Ritcey 1969).

Much higher acid consumptions (~250-350 lb/ton) may be acceptable where a high vanadium content warrants its recovery in addition to the uranium. Vanadium cannot be efficiently recovered by a sodium carbonate leach, except after salt roasting which produces water-soluble sodium vanadate and sodium uranyl vanadate. A high calcium carbonate content in the ore interferes with the effectiveness of salt roasting (Merritt 1971).

Modern practice, adopted in four American mills recovering both uranium and vanadium from carnotite ores with U/V ratios of between 1:3 and 1:5, is to use high acid concentrations in two-stage countercurrent leaching circuits.

* As other data in this paper are derived from Canadian or American sources, the term 'ton' refers to the short ton of 2,000 lb and "$" refers to the American or Canadian dollar.
Recoveries of the order of 95% of the uranium and 75% of the vanadium are achieved, with both products being of approximately equal value. Recovery of vanadium from carnotite ores has not been a prime consideration in the design of plants in the United States where the U/V ratio has been 1:1 or higher in uranium content.

3. CHEMISTRY OF CARBONATE LEACHING PROCESS

The basis of the process is the formation of the stable 'uranyl tricarbonate' complex ion, in which form the uranium passes into solution. To be able to dissolve in carbonate solution, the uranium must be present in the hexavalent (uranyl) state and it is necessary, therefore, first to oxidise tetravalent (uranous) minerals.

The dissolution may be represented by the following equations:

(a) In the case of oxidised minerals - such as carnotite, \( \text{K}_2\text{O} \cdot \text{2UO}_3 \cdot \text{V}_2\text{O}_5 \)

\[
\text{UO}_3^- + 3\text{CO}_3^{2-} + \text{H}_2\text{O} = [\text{UO}_2(\text{CO}_3)_3]^{4-} + 2\text{OH}^- 
\]

(b) In the case of primary minerals - such as uraninite, \( (\text{UO}_2)_n\text{UO}_3 \)

\[
\text{UO}_2^- + 2\text{O}_2^- + 3\text{CO}_3^{2-} + \text{H}_2\text{O} = [\text{UO}_2(\text{CO}_3)_3]^{4-} + 2\text{OH}^- 
\]

The dissolution reaction produces hydroxyl ion and is reversible. For maximum dissolution, the hydroxyl ion must be removed and this is normally achieved by neutralisation with bicarbonate ion.

\[
\text{HCO}_3^- + \text{OH}^- = \text{CO}_3^{2-} + \text{H}_2\text{O} 
\]

Precipitation is achieved by first neutralising the excess bicarbonate ion and adding sufficient caustic soda to precipitate sodium diuranate, essentially reversing equation (1) above:

\[
2[\text{UO}_2(\text{CO}_3)_3]^{4-} + 6\text{OH}^- + 2\text{Na}^+ = \text{Na}_2\text{U}_2\text{O}_7 + 6\text{CO}_3^{2-} + 3\text{H}_2\text{O} 
\]

This occurs at a pH of approximately 11. It should be noted that precipitation may also be achieved by acidifying to pH 6 and this has been used commercially on liquors containing both vanadium and uranium. Several other precipitation methods have been investigated. Hydrogen reduction appears attractive, but requires high temperatures and pressures to achieve satisfactory precipitation rates.

Ion exchange processes have been developed for the selective recovery of uranium from carbonate leach solutions. Solvent extraction has not proved economically attractive, but resin-in-pulp extraction (with a quaternary ammonium resin) is used at one plant.

4. FACTORS AFFECTING LEACHING RATE

4.1 Oxidation

Under carbonate leaching conditions, effective oxidation of tetravalent uranium can be achieved by molecular oxygen. The rate of oxidation is proportional to the square root of the oxygen partial pressure and can be increased, therefore, by operating with oxygen-enriched air or under high total pressure conditions.

Although more rapid oxidation and improved recoveries can be achieved under alkaline conditions with chemical oxidants (e.g., potassium permanganate) or with air in the presence of an oxidation catalyst (e.g., cupric-ammonia complex), economic conditions generally favour the use of air or oxygen, with relatively long leaching times (Merritt 1971).

4.2 Temperature

Elevated temperatures are necessary to achieve acceptable reaction rates which almost double for each ten-degree rise in temperature between 60°C and 100°C. It must be noted that oxygen solubility (i.e., partial pressure) falls with increasing temperature under constant pressure conditions and, therefore, a combination of elevated temperature and high pressure gives the highest dissolution rate. Temperatures over 70°C must be used to achieve acceptable air oxidation rates for tetravalent uranium minerals (Forward et al. 1953).

4.3 Reagent Concentration

Leach solutions contain a mixture of sodium carbonate and bicarbonate, each of which dissolves uranium. The rate of dissolution increases with increasing reagent concentration. Some bicarbonate is necessary to prevent re-precipitation of dissolved uranium, but excess bicarbonate consumes caustic
soda in the precipitation stage. The carbonate concentration is dictated by economic considerations such as soluble losses. Normal concentrations (in circuit feed) are 30 - 60 g/litre Na₂CO₃ and 5 - 15 g/litre NaHCO₃.

4.4 Particle Size

The rate of chemical reaction is controlled by the specific surface area available. In carbonate leaching, a high specific surface area is necessary to achieve acceptable leaching rates and grinding to 70% - 80% passing 200 mesh is common. A few sandstone ores, where the uranium is present in interstitial cementing material, give good extractions at comparatively coarse grinds (Stephens and MacDonald 1956).

5. ELDORADO BEAVERLODGE OPERATION

5.1 Introduction

The Eldorado Nuclear mill at Beaverlodge is the only Canadian operation using an alkaline leaching process (Harding et al. 1960, Thumaes and Colborne 1964, Colborne 1963, Marshall 1962). It has a semi-isolated location, north of Lake Athabasca in the far north of Saskatchewan. The processing plant has been in continuous operation since 1953 when a 500 ton/day pressure leaching circuit was started up. It was enlarged to 750 ton/day in 1955 and 2,000 ton/day capacity in 1957 by the addition of atmospheric leach pachucas. The autoclave section was shut down in 1963 and the plant is currently operated on a reduced tonnage of approximately 900 ton/day.

The current flow-sheet utilises autogenous grinding in carbonate solution, flotation to remove pyrite, atmospheric carbonate leaching, liquid-solid separation by two stages of filtration, precipitation of the product with caustic soda and re-generation of the barren liquor. The small quantity of pyrite concentrate is acid-leached in a batch system. A flow-sheet is shown in Figure 1. Recovery has averaged approximately 90% of the U₃O₈.

5.2 Ore

Uranium occurs as the mineral pitchblende in a series of vein-type deposits in association with calcite, chlorite and haematite. Calcite content averages in excess of 5%. Pyrite and chalcopyrite are present with an average sulphur content of 0.5%, but ranging up to several per cent in some sections. The ore is very hard with a Bond Work Index of 20. The average grade of current reserves is 0.24% U₃O₈.

5.3 Ore Sorting

Because of the nature of the orebodies - fracture fillings associated
with a major fault system - there is a sharp demarcation between barren
country rock and the mineralised vein material. This feature permits
upgrading by electronic ore sorting (Colborne 1963).

The ore sorting plant has been shut down since 1964 partly due to a
change in run-of-mine ore sizing, and partly due to the planned cut-back in
production resulting in adequate capacity to process the entire mine output.
Run-of-mine ore is crushed to a maximum size of about 6" underground and is
screened at 3" ahead of the coarse ore bin.

The oversize (3 - 6"), which constitutes about 35% of the ore feed,
passes to 4 K and H Ore Sorters, where approximately half is rejected. Each
sorter handles 20 tons of rock per hour. Thus, 17% of the feed is rejected
as coarse waste with a loss of 2% of the uranium value. The sorting units
result in a net operating cost saving of about 20 cents per ton of ore mined.

5.4 **Comminution**

Crushing was formerly by a conventional two-stage circuit to approximat-
ely 1/2-inch sizing. The crushing plant is now largely by-passed and run-of-
mine ore is fed directly to a 19' x 12' Nordberg semi-autogenous mill with
central peripheral discharge. The run-of-mine ore is too fine for good auto-
genous grinding and it has been necessary to add a light charge of 6" balls to
the mill to prevent the build-up of small rock (Lendrom 1970).

The pump from the autogenous mill is classified on a stationary sloping
B - Z screen with 35 mesh deck, the oversize material being re-circulated.
The minus 35 mesh ore is cycloned to remove minus 200 mesh material before
passing to two conventional ball mills, operating in parallel in closed
circuit with rake classifiers. This secondary grinding reduces the ore to 70%
passing 200 mesh which is necessary for good extraction.

It is of particular interest to note that all grinding is done in the
mill-leaching solution with a mean S.G. of 1.13 and temperature about 40°C.
This results in equipment capacities considerably below those required for
grinding in a water media (Harding et al. 1960).

5.5 **Flotation**

To decrease reagent consumption, pyrite is removed from the carbonate
pulp by flotation prior to leaching. Approximately 90% of the pyrite content
is removed to give a leach circuit feed assaying 0.06% S. Essentially, all
the sulphur passing through the pachucas reacts with sodium carbonate to
produce sulphate and bicarbonate, consuming 3.3 pounds of soda ash per pound
of sulphur (Thunaes and Colborne 1964).

Isopropyl xanthate is used as a collector. A frother has been found to
be unnecessary. The rougher concentrate is subjected to three stages of
cleaning to give a product assaying 25 - 30% S. The concentrate, after thick-
ening and wash filtration, is subjected to acid leaching. Uranium is precip-
itated from the acid pregnant solution with magnesium hydroxide and the impure
precipitate returned to the alkaline leaching circuit.

Operation of the flotation-acid leach section costs 25 - 30 cents/ton.
By eliminating an average of 0.50% sulphide sulphur, the reagent saving has
been $1.80 per ton for a net saving of about $1.50 per ton.

5.6 **Leaching**

The sulphide flotation tailings slurry is thickened to 50 - 55% solids
before entering the pachuca circuit. Thickening is achieved by a combination
of cyclones and thickeners, the latter operating on the cyclone overflow only.
Flocculants are added to the thickener feed.

There are four parallel banks of six pachucas per bank. Each pachuca is
13 feet in diameter and approximately 50 feet high, with a 60-degree cone
bottom. When first installed, agitation was achieved by a central air lift,
with oxidising air introduced through eight separate diffusers. The pachucas
have recently been modified to mechanical agitation, with gaseous oxygen being
fed through two diffusers. Heat is provided by steam coils. No chemical
oxidents are used in the leaching circuit.

Temperature is held above 80°C. Retention time is approximately 96 hours.
The change from the use of air as a means both of oxidation and of agitation,
has resulted in a major reduction of heat losses and improved extractions on
refractory ores.

5.7 **Filtration**

On leaving the pachuca circuit, the leached pump passes to the filtration
circuit via a concentric pipe heat exchanger which reduces the pulp temperature
from 80°C to 50°C and transfers heat to the residue wash water. The leached
residues are separated by two-stage filtration utilising string discharge drum
filters. Washing on the first stage is with fresh leach liquor, whilst re-
pulping and second-stage washing use hot water. Soluble losses average 1% of
the uranium feed.

5.8 **Steam Stripping and Lime Addition**

After clarification, part of the pregnant solution passes through steam
stripping and lime addition before precipitation with caustic soda. The primary purpose of these units is to remove bicarbonate ion from the solution prior to precipitation and thereby reduce the consumption of caustic soda in precipitation. A secondary objective of the steam-stripping plant is to remove bicarbonate ion from the solution prior to precipitation and thereby reduce the consumption of caustic soda in precipitation. By removing water at this point, additional water can be introduced at the second-stage filter wash, thereby reducing dissolved uranium losses.

The steam-stripping process is essentially two-stage evaporation with the second-stage steam going to the pachuca heating coils at 10 - 20 psig. The capacity of the plant is 350 tons evaporated water per day. Two - three lb NaOH per ton of ore are saved by the 350 tons/day reduction in pregnant solution volume. In addition, approximately 14,000 lb per day of bicarbonate are converted to carbonate, saving 4 lb sodium hydroxide per ton of ore. Net savings attributed to the plant amount to 45 - 50 cents per ton.

The lime addition plant reduces the sodium bicarbonate content of the liquor from 12 - 14 g/litre to 3 - 5 g/litre by reaction with lime. (The bicarbonate level must not be reduced below 2 g/litre or premature uranium precipitation may occur.) Calcium carbonate is precipitated according to the reaction:

\[ 2 \text{NaHCO}_3 + \text{Ca(OH)}_2 = \text{CaCO}_3 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \]

and is removed by settlement in a thickener, the overflow passing to precipitation. The lime sludge is fed into the pachuca leaching circuit. The lime plant results in a net saving of 50 cents/ton.

A major advantage of the steam stripping and lime plant is that they have reduced the caustic addition requirements, bringing it into balance with the sodium ion removed from the circuit in the yellow cake and as the minor solution loss occurring with the washed tailings. Thus a solution bleed is no longer necessary to maintain a balance.

5.9 Precipitation

Pregnant solution is precipitated with caustic soda. Sufficient caustic is added to ensure an excess of 6 g/litre and the temperature is held at about 50°C. Precipitation takes place in a series of six agitators. Retention time is 10 - 12 hours. Pregnant solution entering the circuit contains an average of 2 - 3 g/litre U_3O_8. Barren solution after precipitation averages 0.1 g/litre. A 'reseeding cone' is included in the circuit to recycle fine precipitate to the head of the precipitation tanks. This results in a coarser particle size, and improved filtration.

The yellow cake slurry is filtered in standard filter presses. The cake discharged from the presses is re-pulped and pumped into a steam-heated twin-screw Holoflite drier. The average composition of the drummed precipitate is:

- U_3O_8: 72 - 77%
- H_2O: 2 - 4%
- V_2O_5: 0.5 - 0.7%
- SO_4^2-: 0.4 - 0.5%
- Cl^-: 0.02 - 0.05%

5.10 Solution Regeneration

The carbonate process is a closed-circuit operation. It is, therefore, necessary to maintain close control on water and chemical balances. The advantages of the steam-stripping and lime unit operations in removing water and controlling sodium hydroxide addition have already been pointed out.

Carbonation of the caustic barren solution is achieved by blowing flue gas from the boilers and power-house installation through two packed towers. The barren solution flows countercurrent to the gases through the towers, converting 6 g/litre caustic soda content to about 3 g/litre sodium bicarbonate.

Sulphate ion generated by the oxidation of pyrite has built up to very high levels (50 - 60 g/litre, sodium sulphate) without adversely affecting leaching rates or product quality. Sulphate ion level is controlled by solution losses with the tailings and by removal in the yellow cake (Clegg and Foley 1958).

5.11 Corrosion

Corrosion proved to be an unexpected major problem as alkaline sodium sulphate-carbonate-bicarbonate solutions had not been considered corrosive to plain carbon steel from which the process tanks were fabricated. Severe pitting corrosion was found beneath caked solids at the froth line and below the pulp surface in leaching vessels after a relatively short period of operation (Colborne et al. 1961). Undoubtedly, the major pitting was due to differential aeration cells (soil-type corrosion) being set up under caked solids. Their activity was probably greatly enhanced by the high solution
conductivity, the presence of oxygen consumers in the deposited solids and the cementing action of iron oxides produced by the corrosion.

However, it was established that the mud deposits are not required to initiate corrosion, but arise subsequently, aggravating the situation. Severe corrosion was shown to take place in clear solutions at pHs of 9.5 and less, but is insignificant when the pH is over 9.7. Arising from this, action was taken to operate at a minimum pH of 9.5 in the leaching circuit and this has greatly reduced corrosion. Additionally, a programme of repair and protection was undertaken. Epoxy tank linings have been found to perform very satisfactorily.

5.12 Reagent Consumption
Sodium hydroxide consumption has been reduced to 10 lb/ton with 7 - 8 lb/ton of lime. These are the only reagents used in the carbonate-leaching section of the plant (Ross and Guglielmin 1968).

Reagent consumption in the acid circuit is:

<table>
<thead>
<tr>
<th></th>
<th>lb/ton of</th>
<th>lb/ton of '</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentrate</td>
<td>Mill Feed</td>
</tr>
<tr>
<td>Sulphuric Acid</td>
<td>100</td>
<td>2</td>
</tr>
<tr>
<td>Sodium Chlorate</td>
<td>3</td>
<td>0.06</td>
</tr>
<tr>
<td>Magnesium Hydroxide</td>
<td>15</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Overall power consumption is 30 - 35 kWh/ton and water usage 550 gallons/ton, with no re-cycling of tailings pond water.

6. COMPARISON OF ALKALINE LEACHING PLANTS
There are three alkaline leach plants operating in the United States (1970 data):
- Moab Mill (Atlas Corporation) - 900 ton/day (plus 400 ton/day acid circuit).
- Cotter Corporation Mill - 400 ton/day.
- United Nuclear-Homestake Mill - 3,500 ton/day.

Detailed descriptions of these three plants are given by Merritt (1971).

A comparison of practice at the four plants follows:

One plant (Cotter) operates on hydrothermal vein-type ore similar to the Beaverlodge ore. The other two operate on sandstone ores where the uranium occurs in association with vanadium as coatings and interstitial filling in the sandstone and, thus, a relatively-coarse grind (to 65 mesh) is adequate to liberate the uranium for dissolution. Crushing and grinding practices tend to be conventional, except for the Beaverlodge autogenous mill.

All plants, except the United-Homestake plant, provide facilities for the flotation of sulphides before leaching. All plants grind and float in leach solution. Leaching is by autoclaves in the Moab and United-Homestake plant, and by pachucas in the Cotter Mill. Increased capacity has been added to the United-Homestake autoclaves by adding pachucas and to the Cotter pachucas by adding autoclaves. Generally speaking, autoclaves operated at 50 - 80 psig and 95° - 120°C give a slightly improved recovery in about 20% of the leaching time required by pachucas operating at 70° - 80°C. Beaverlodge experience indicates a net cost saving in favour of pachucas of about 45 cents per ton of ore based on the technology of the mid-1950s (Thumaes and Colborne 1964). Advances in pressure-leaching techniques could alter this assessment.

In all cases, air or oxygen has been used as the oxidant. The Moab Mill uses a copper-ammonium complex as an oxidation catalyst and this was formerly used at the United-Homestake Mill when processing refractory ore. The addition of three pachucas provided additional air and residence time to achieve the same results as the catalyst. From this, it would appear that the use of the copper-ammonium catalyst results in a 10% - 20% reduction in leaching time. The copper-ammonium catalyst is not effective in atmospheric leaching due to the rapid volatilisation of ammonia from the solution.

Various combinations of filters and thickeners are used for separating and washing the leached residue. The problem of slimes has resulted in the use of Esperanza classifiers at the Moab Mill to separate a sand fraction from the slime fraction, followed by resin-in-pulp recovery of the uranium values. All other plants employ caustic soda precipitation. The Moab Mill resin-in-pulp process uses a strong base anionic resin, Dowex 21K.

In two of the American mills, yellow cake is re-processed to give a purer product. At the Cotter Corporation Mill where the caustic-precipitated product is too high in sodium content, the yellow cake is dissolved in sulphuric acid and re-precipitated with ammonia. At the United-Homestake Mill, the yellow cake is roasted with soda ash to solubilise the vanadium content which is removed by water leaching.

7. CARBONATE LEACHING COSTS
It is somewhat difficult to draw reliable conclusions on the subject of
costs from the sketchy and varied information available. The following
general remarks are offered as a guide:

(a) The capital cost of a carbonate leach plant is likely to be about
10% - 20% higher than an acid leach plant of the same capacity
(Ross and Guglielmin 1968).

(b) The capital cost of two carbonate leach plants built in 1958 were -
1,500 ton/day - $6,000.00 per ton/day capacity.
(Homestake)
200 ton/day - $9,000.00 per ton/day capacity.
(Cotter)
To arrive at a 1972 costing basis, these capital costs should be
increased by 40% - 50%.

(c) Beaverlodge milling costs in 1960 were $4.80 per ton or $1.22 per
pound of U₃O₈ produced (Harding et al. 1960).
The breakdown of these costs was as follows:

<table>
<thead>
<tr>
<th>Item</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Labour</td>
<td>26.5%</td>
</tr>
<tr>
<td>Supplies</td>
<td>16.3%</td>
</tr>
<tr>
<td>Reagents</td>
<td>30.7%</td>
</tr>
<tr>
<td>Power</td>
<td>9.3%</td>
</tr>
<tr>
<td>Air</td>
<td>3.7%</td>
</tr>
<tr>
<td>Process and Building Heat</td>
<td>11.7%</td>
</tr>
<tr>
<td>Other Distributables</td>
<td>1.8%</td>
</tr>
</tbody>
</table>

8. ACKNOWLEDGEMENTS

The carbonate leaching process at Beaverlodge has been refined over the
years by the team work of many skilled engineers, with whom the author was
proud to be associated for a period. In particular, thanks are due to Mr.
G.F. Colborne, of Eldorado Nuclear Ltd., whose critical reading of the manu-
script has been greatly appreciated.

9. REFERENCES


Colborne, G.F., Allan, A.R., Thunaes A., (1961) - Crash repair program to
control serious pitting corrosion on process tanks. Corrosion, 17

Min. and Met. Bull. 56 (616) 684-68.