

# Pressure leaching of uranium-bearing Witwatersrand ores\*

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## SYNOPSIS

Since 1955 extensive pressure-leaching testwork has been conducted by Anglo American Research Laboratories (AARL) in laboratory-scale batch autoclaves. In 1958 a small continuous pilot-plant of 45 kg of solids per hour was operated by AARL. In 1974, when high uranium prices were anticipated, Anglo American, encouraged by successful commercial-scale autoclave operations as practised by Outokumpu, Sherritt Gordon, and Impala Platinum, decided to install a continuous pilot plant at Western Deep Levels. At that time the proposed pilot plant was considered to be of prototype size. The project was funded by members of the Nuclear Fuels Corporation (Nufcor).

Since its commissioning in February 1977, the pilot plant at Western Deep Levels, which can treat between 10 and 20 tons of dry solids per hour, has been used to test ores from four different mines. The paper compares the uranium extractions and pyrite oxidation obtained in laboratory batch autoclaves with those obtained in the continuous pilot plant. In general, differences in uranium extraction are not great and can be explained; the differences in pyrite oxidation are less well understood. The effect on plant design of the evolution of carbon dioxide during leaching is discussed.

Evaluation of the equipment and materials of construction would have been almost impossible in a small-scale batch autoclave. It is doubtful whether such results would have generated the necessary confidence to permit decisions to install a commercial-size plant. The development and performance of the multistage pumps, instrumentation, shaft seals, and shaft-seal water treatment are discussed.

It is concluded that the operation of a large-scale continuous pressure-leaching pilot plant to supplement laboratory batch autoclave tests has been a necessary part of the development of this process.

## SAMEVATTING

Daar is sedert 1955 uitgebreide drukloogtoetse deur die Anglo American se navorsingslaboratorium in laboratoriumskaallotoutoklawe uitgevoer. Anglo American se navorsingslaboratorium het in 1958 'n klein deurlopende proefaanleg van 45 kg vaste stowwe per uur bedryf. In 1974, toe hoë uraanpryse verwag is, het Anglo American, aangemoedig deur die suksesvolle outaklaafbewerkings op kommersiële skaal soos deur Outokumpu, Sherritt Gordon en Impala Platinum toegepas, besluit om 'n deurlopende proefaanleg by Western Deep Levels te installeer. In daardie stadium is daar gereken dat die voorgestelde proefaanleg die grootte van 'n prototipe sou hê. Die projek is deur lede van die Kernbrandstofkorporasie gefundeer.

Sedert sy inbedryfstelling in Februarie 1977 is die proefaanleg by Western Deep Levels, wat tussen 10 en 20 ton droë vaste stowwe per uur kan behandel, gebruik om erte afkomstig van vier verskillende myne te toets. Die referaat vergelyk die uraanekstraksie en piriëtoksidasie wat in laboratoriumlotoutoklawe verkry is, met dié wat in die deurlopende proefaanleg verkry is. Die verskille in die uraanekstraksie is in die algemeen nie groot nie en kan verklaar word; die verskille in die piriëtoksidasie word nie so goed begryp nie. Die uitwerking van die afgee van koolstofdioksied tydens die logging op die ontwerp van die aanleg word bespreek.

Die evaluering van die toerusting en konstruksiemateriale sou feitlik onmoontlik gewees het in 'n kleinskaalse lotoutoklaaf. Dit is te betwyfel of sulke resultate die nodige vertroue sou geskep het vir die besluit om 'n aanleg van kommersiële grootte te installeer. Die ontwikkeling en werkverrigting van die veeltrappompe, instrumentasie, asafdigtings en die waterbehandeling van asafdigtings word bespreek.

Die gevolgtrekking word gemaak dat die bedryf van 'n grootskaalse proefaanleg vir deurlopende druklogging ter aanvulling van die laboratoriumlotoutoklaaf-toetse 'n noodsaaklike deel van die ontwikkeling van hierdie proses was.

## Introduction

In the plants of the Anglo American Group, uranium leaching is conducted in air-agitated pachucas at temperatures between 50 and 60°C. Leaching efficiencies in this system range from 80 to 85 per cent of the uranium contained in the ore. The remaining 15 to 20 per cent represents uranium contained in the more refractory minerals such as brannerite and euxenite. The financial benefits to be derived from improvements in this recovery at current uranium prices are obvious.

As far back as 1955 Anglo American Research Laboratories (AARL) had started testwork on leaching at higher temperatures and pressures aimed at improving the recovery of uranium from more refractory minerals.

In 1958, a small single-stage continuous pilot plant with a capacity of 45 kg of dry solids per hour was operated at AARL<sup>1, 2</sup>. The autoclave in that plant was

1,8 m high and 0,3 m in diameter. It was agitated by air and steam. The following are the most important findings from that work.

1. When the tests were operated in the batch mode, extractions of 94 per cent of the uranium in a sample of Witwatersrand ore could be achieved in 115 minutes at an air flowrate of 0,25 m<sup>3</sup>/min, a temperature of 160°C, and a total gas pressure of 1360 kPa. Owing to short circuiting, this extraction would be reduced to 82 per cent when the unit was operated continuously, with a mean solids retention time of 115 minutes.
2. An initial pH value of above 5 would cause slow initial oxidation of pyrite as a result of the formation of a surface film on the pyrite.
3. 316L stainless steel would be a suitable material of construction under the required process conditions.
4. Minimum oxygen partial pressures of 300 kPa would be required for the attainment of high uranium extractions.
5. The overall heat-transfer coefficient for slurry-to-slurry heat exchange in stainless-steel pipes is

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880 kcal/h.m<sup>2</sup>.°C at slurry velocities of about 1 m/s.

6. A highly corrosion-resistant reddish-brown film would form in regions of low turbulence, e.g. on reactor walls.
7. A 'semi-scale' pilot plant would be necessary before a full-scale plant could be designed.

In the period between 1958 and 1974, although AARL continued pressure-leaching testwork in laboratory batch autoclaves, the effort was reduced because of the low uranium prices.

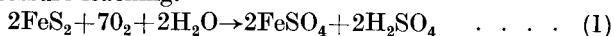
By 1974, higher uranium prices were anticipated. Encouraged by the successful use of horizontal multi-compartment, mechanically agitated autoclaves by such companies as Sherritt Gordon, Outokumpu, and Impala Platinum, it was decided to pilot test uranium pressure leaching in this type of leaching vessel. The large volumes of air required to keep the slurry in suspension were now unnecessary, and pure oxygen could be used as the oxidant.

The choice of pilot-plant size is always difficult. A plant to treat, say, 1 ton of solids per hour would have been relatively inexpensive. In addition, the amount of test ore to be transported to the pilot plant would be less compared with that for a larger pilot plant. However, it was believed that metallurgical results and equipment performance from any plant other than a prototype would not provide the confidence necessary for the construction of a full-scale installation. Consequently, an autoclave similar in size to those used by Sherritt Gordon and Impala Platinum was selected, with an internal diameter of 2,6 m and a length of 11,7 m. The unit and its ancillaries were to provide a mean retention time of 2 hours for a continuous flow of slurry containing 20 t of solids per hour in a slurry of 60 per cent solids by mass. Western Deep Levels was selected as the site for the pilot plant.

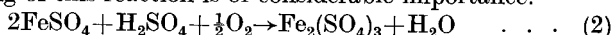
The value of being able to correlate the metallurgical results from such a pilot plant with results from a laboratory batch autoclave was appreciated. It was therefore planned that all the ores leached in the continuous pilot plant would also be tested in a 2-litre laboratory autoclave.

### Chemistry of Pressure Leaching

Reactions (1) to (4) are believed to take place during pressure leaching.



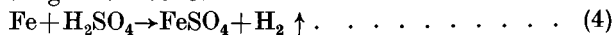
This exothermic reaction represents the oxidation of pyrite to produce the soluble iron and acid necessary for the dissolution of uranium. The amount of sulphide sulphur in the pyrite that is oxidized largely defines the amount of oxygen consumed during pressure leaching. As oxygen is the reagent of highest cost, an understanding of this reaction is of considerable importance.



Here the oxygen is playing the role of oxidant in transforming ferrous iron to the ferric form, a role normally taken by manganese dioxide or sodium chlorate in the conventional acid-leaching of uranium. Laboratory testwork has shown, as the equation would suggest, that higher partial pressures of oxygen favour higher ratios of ferric to ferrous iron.

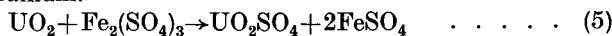


At higher temperatures (between 170 and 225°C), reaction (3) proceeds fairly rapidly. Ferric iron, which is required for the dissolution of the tetravalent uranium, is removed from solution by the reaction. The precipitated iron salts are believed to be the cause of the deterioration in filtration characteristics of the slurry from the pressure leach that occurs at temperatures in the region of 200°C.



An additional source of dissolved iron is steel from the crushing and grinding plants. Small but measureable quantities of hydrogen have been found in the vent gas.

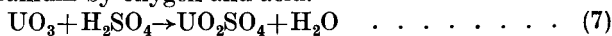
Reactions (5), (6), and (7) represent the dissolution of uranium.



In pressure leaching, as in conventional leaching, the oxidation of tetravalent uranium by ferric iron is assumed to be the main vehicle of dissolution. Hence, maximization of the ferric iron and of the ferric to ferrous ratio is considered important in pressure, as in conventional, leaching.

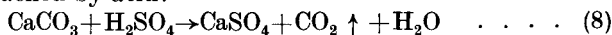


Gray<sup>3</sup> also proposed the dissolution of tetravalent uranium by oxygen and acid.



Hexavalent uranium will dissolve in the presence of sulphuric acid alone.

Acid-consuming gangue, including the carbonates, is leached by acid:



As well as its significance as an acid consumer, this reaction is important in pressure leaching because of the evolution of carbon dioxide. The presence of carbon dioxide reduces the partial pressure of oxygen, necessitating a gas bleed. The vent gas contains oxygen, which, if not recovered, can represent a significant additional cost. Reaction (8), by consuming acid, increases the pH value. At a pH value above 5, the formation of iron oxide can prevent the oxidation of pyrite to sulphuric acid, and thus slow down the complete chain of reactions (1) to (7) that constitute uranium pressure leaching. Therefore, with most ores, the continuous addition of from 5 to 7 kg of sulphuric acid per ton of ore treated is necessary to prevent the formation of iron oxide.

### Laboratory Autoclave

The 2-litre laboratory autoclave used in the tests illustrated in Figs. 3 and 4 is made of titanium. It has twin impellers, both axial flow, rotating at 600 r/min, which is equivalent to an impeller-tip speed of 1,9 m/s. Oxygen is injected just below the level of the slurry-gas interface. There is provision for the venting of gas from the vapour phase above the slurry. An electric heating jacket is used for temperature control.

The test procedure involves the making up from the test ore of a slurry containing 60 per cent solids by mass. The autoclave is then heated up to the required starting temperature, which takes about 30 minutes. Fresh acid is added, and the oxygen purge is commenced to rapidly bring the total pressure to a level equivalent to the required partial pressure of oxygen.

Samples containing about 40 g of dry solids are then withdrawn from the autoclave at intervals of 30, 60, 90, and 120 minutes. These samples of slurry are filtered and washed. The solids are analysed for uranium and for sulphide sulphur, and the solution for uranium, free sulphuric acid, and other important constituents. In the solution analysis, allowance is made for the vapour lost during flashing when the high-temperature slurry is withdrawn from the autoclave.

### Pilot Plant

Fig. 1 shows the various components of the 20 t/h pilot plant at Western Deep Levels. A feed pachuca with a solids capacity of 450 t feeds six 75 mm by 75 mm Hydroseal pumps in series, the last-stage pump being fitted with a Voith variable-speed coupling. The pump discharge passes through a mass flow system, the set point of which controls the variable-speed pump.

The incoming alkaline slurry, which has a solids content of 55 to 60 per cent by mass, is preheated to a temperature of 100 to 110°C by hot, acidic slurry leaving the autoclave. The heat-exchanger is a 38,5 m<sup>2</sup> Alfa-Laval spiral, manufactured from Avesta 254 SLX stainless steel.

The four-compartment mild-steel autoclave is lined

with lead and acid-proof bricks. Each compartment is agitated by a single four-bladed, radial-flow impeller. The gearboxes are PTE MH20 Philadelphia units fitted with 30 kW motors. The shaft speed is 155 r/min, which is equivalent to an impeller-tip speed of 6 m/s. Shaft speeds can be varied between 84 r/min and 230 r/min by gear changes in the Philadelphia gearbox. As the power drawn is directly proportional to the speed to the third power, the changing of gears offers a very wide power range for the testing of different mixer systems. The slurry cascades over brick vee-notches between compartments, which are designed to maintain a slurry level of about 75 mm higher in the preceding compartment; 70 to 80 per cent of the total autoclave capacity is occupied by slurry.

Steam, oxygen, and concentrated sulphuric acid are injected into the autoclave below the gas-slurry interface. Although most of the steam and oxygen are added to the first compartment, they can be added to any of the compartments. Acid is added only to the first compartment. The temperature is controlled by manually operated, direct steam injection to maintain the first compartment at the desired temperature, usually between 150 and 160°C. The total pressure of 1250 and 1350 kPa in the gas phase is automatically controlled

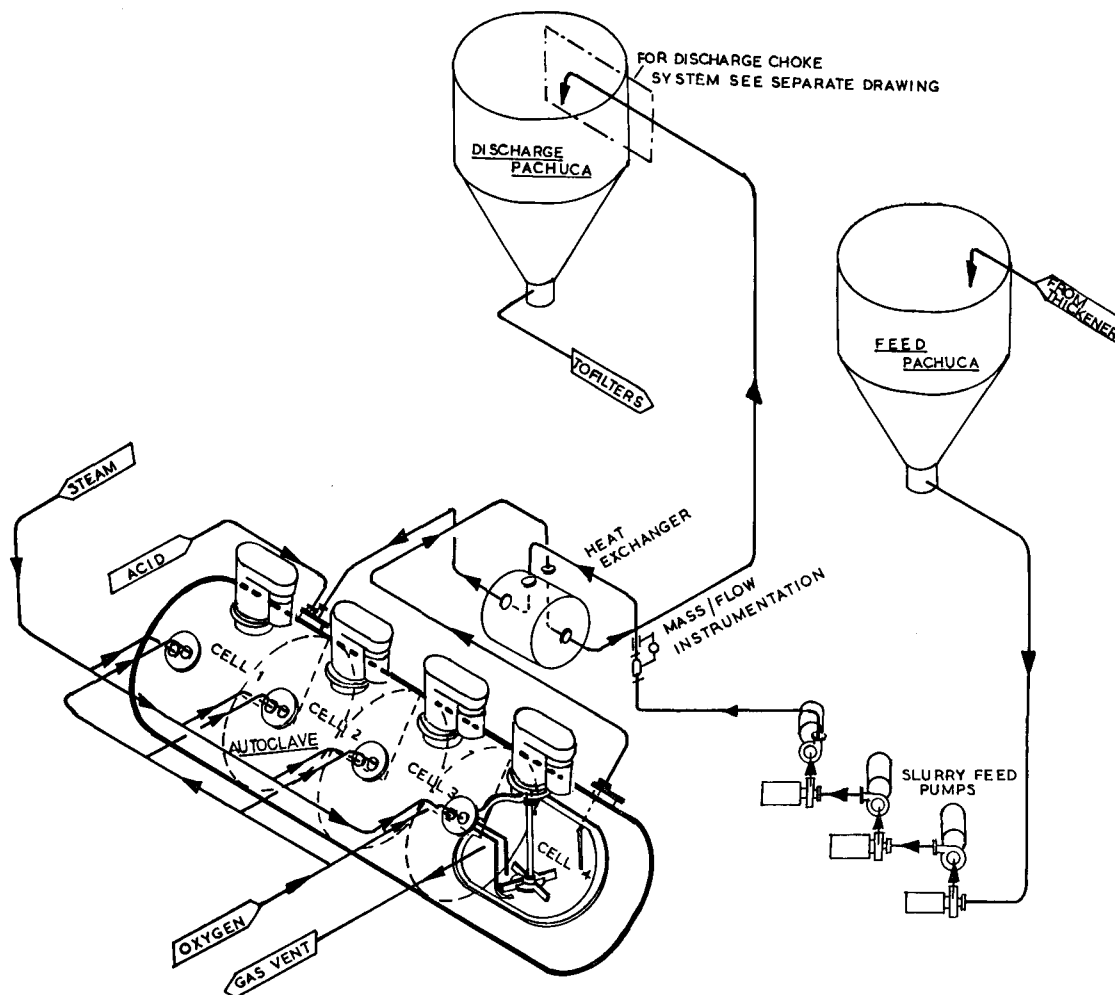


Fig. 1—The 20 t/h pilot plant at Western Deep Levels

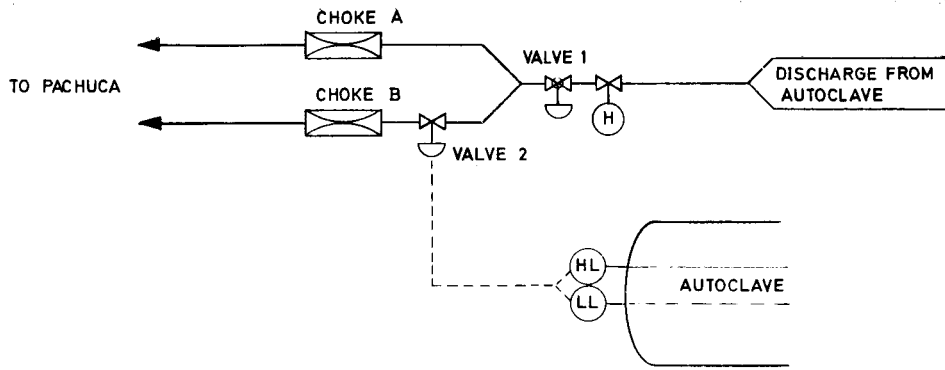


Fig. 2—The discharge choke system (valve 1 is a remote-controlled isolating plug valve, and valve 2 a Saunders on/off control from autoclave level)

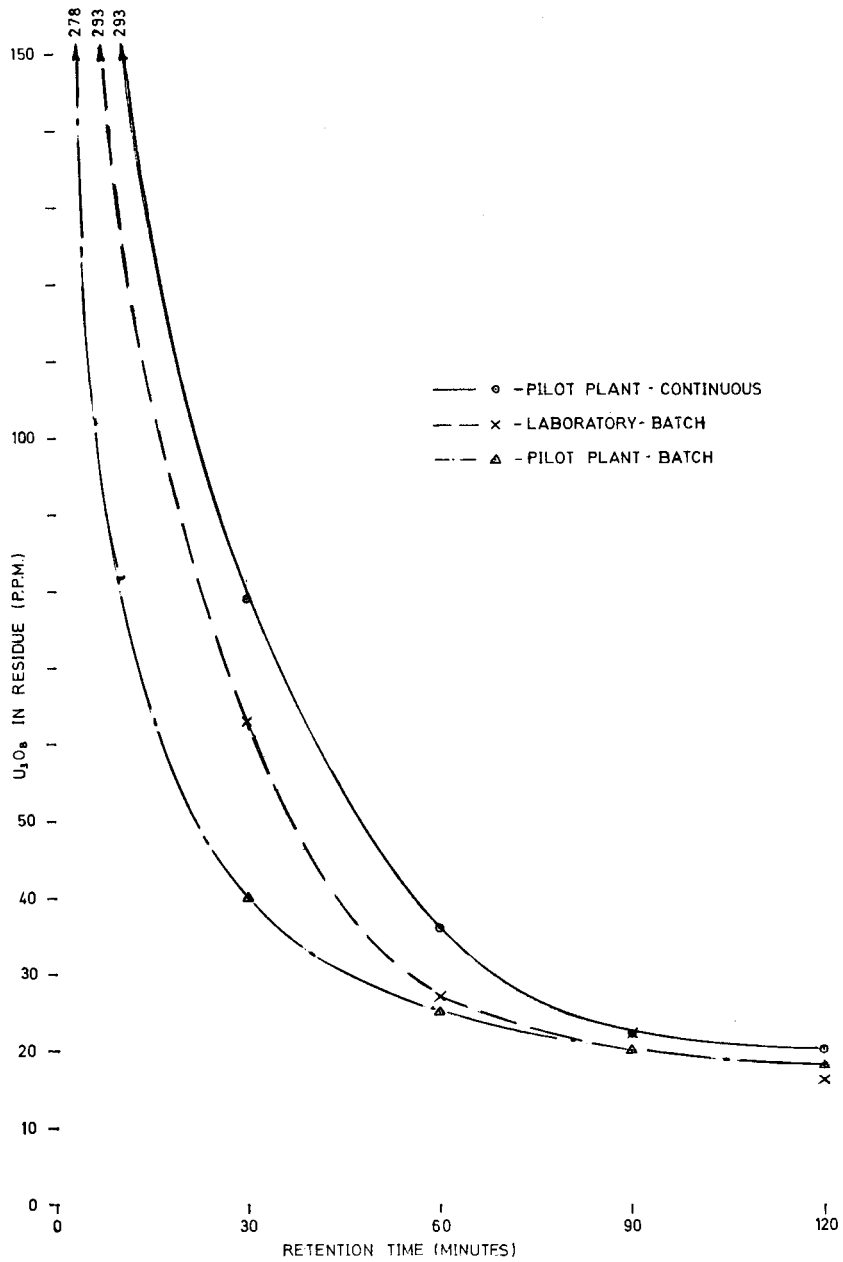


Fig. 3—Uranium in residue versus retention time in leach (the values on the graphs are the head grades in p.p.m.)

by the oxygen flowrate. A prior knowledge of the oxygen purity, which is maintained by a gas-phase vent, thus ensures the desired partial pressure of oxygen. A more sophisticated control system would probably be used on a commercial scale.

Slurry leaving the autoclave at 170 to 180°C passes through the spiral heat-exchanger, where it is cooled to between 70 and 80°C. Depressurization to atmospheric pressure and the control of the autoclave slurry level are achieved by the use of two ceramic orifices and a control valve as shown in Fig. 2. The principle is that described in a paper on material selection for the Moa Bay nickel-cobalt plant<sup>4</sup>. Chokes made from Carborundum Refrax with orifices between 12 and 18 mm in diameter were selected so that 80 per cent of the flow passes through choke A. The Saunders valve in series with choke B operates on/off, actuated by high- and low-level signals

from a bubble-tube level-measuring device in the last autoclave compartment. Thus, on average, 20 per cent of the slurry flow passes through choke B.

Since commissioning, all the piping and other components that are subjected to temperatures above 120°C, which were originally of 316L stainless steel, have been replaced by 2RK65, a stainless steel containing 20 per cent chromium, 25 per cent nickel, and 4,5 per cent molybdenum.

### Comparison of Results

The results from tests on a gold-plant residue from a mine in the Klerksdorp area are illustrated in Figs. 3 and 4. Extensive laboratory batch autoclave tests on this ore had been conducted by AARL and by the research laboratories of Sherritt Gordon Mines in Canada. During these tests, the temperature had been varied

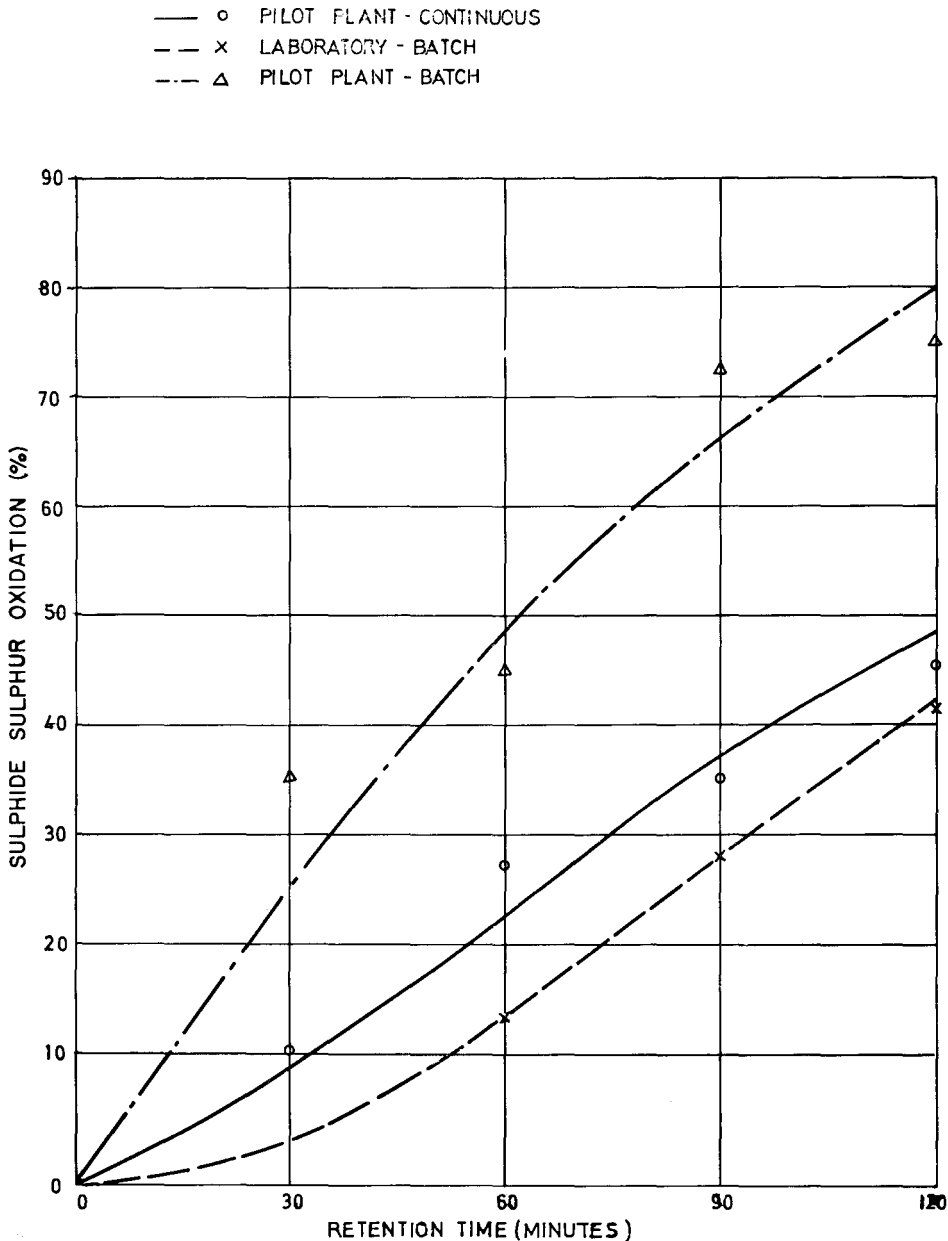


Fig. 4—Oxidation of sulphide sulphur versus retention time in leach



task owing to the large number of interacting variables. For this reason, it is also difficult to draw firm conclusions when comparing batch and continuous operation.

However, the pattern of results on uranium extraction shown in Fig. 3 was maintained over the four different ores that have now been tested in the pilot plant. Uranium residue values in the continuous pilot-plant tests are always higher (lower extraction) than the laboratory batch results and the pilot-plant batch results after 30 and 60 minutes. The residue values converge rapidly and are almost identical after 120 minutes.

The retention-time distribution of the solids in the pilot plant operated in the continuous mode was studied by the Isotopes and Radiation Division of the Atomic Energy Board. In their report<sup>5</sup>, Smith and Hills concluded that the contents of the vessel were well mixed in all four compartments and that no short circuiting or stagnancy occurred. Estimates of effective volume showed a dead volume of about 10% was present in the vessel<sup>7</sup>.

By regular sampling of the slurry in each compartment following the addition of a small quantity of irradiated ore to the main slurry feed stream, they determined the retention-time distribution of the solids in that compartment. A similar measurement gave the retention-time distribution of the solids in the final discharge from the autoclave (Fig. 5). As would be expected from theory, their results showed that a significant proportion of the solids leave each compartment in less than the mean retention time, and that the spread of this distribution decreases as the number of stages increases. This finding would explain the higher values of uranium in solids in continuous operation after a nominal retention time of 30 minutes (first compartment), compared with the values in the batch tests. However, as shown in Fig. 5, even after four stages of continuous leaching, a high proportion of the solids leaving the autoclave have still experienced less than

the mean retention time of 120 minutes, and thus the uranium in the solids would still be expected to be higher than in the batch tests, which is not the case.

The improved rate of uranium extraction in the batch pilot-plant tests compared with batch laboratory tests can possibly be explained by the higher levels of free acid (see Table I) that prevailed in the former.

#### *Oxidation of Sulphide Sulphur*

The oxidation of pyrite and other metal sulphides has been extensively investigated in laboratory-scale batch equipment<sup>3, 6-9</sup>. Among the many factors shown to be significant to the kinetics are the following:

- (1) the design of the nozzle supplying oxygen to the impeller and of the impeller itself, which both affect the size of the oxygen bubbles<sup>9</sup>,
- (2) the surface area of the pyrite<sup>7</sup>,
- (3) the partial pressure of oxygen<sup>7</sup>,
- (4) the reaction temperature<sup>6-9</sup>.

The much slower oxidation of sulphide sulphur in the laboratory batch test compared with the pilot-plant batch test is partly explained by the different modes of oxygen addition. In the pilot plant, oxygen is injected beneath the radial-flow impeller, which must result in good dispersion and small oxygen bubbles. In the laboratory autoclave, the impellers are of the axial-flow type and oxygen is injected just below the surface of the slurry. In addition, the partial pressure of oxygen and the reaction temperature were somewhat higher in the pilot-plant batch test, both of which would increase the rate of sulphur oxidation.

The difference between the sulphur-oxidation rates in the batch pilot-plant tests and the continuous pilot-plant tests can be partly explained by the retention-time distribution in continuous operation, which has already been discussed. However, this difference should be diminishing after four stages of continuous operation (120 minutes) if a difference in retention time is the only cause. It is possible that, as oxygen is added mainly

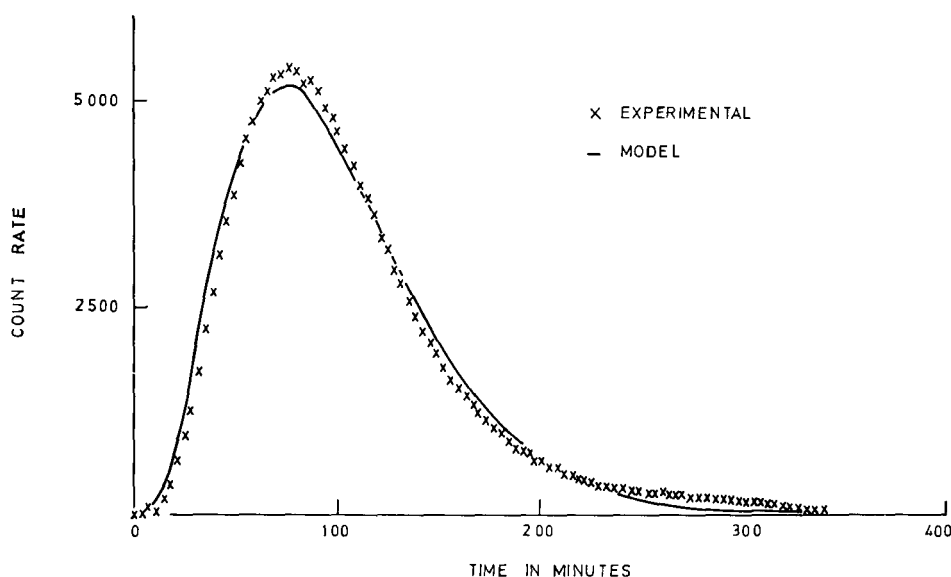


Fig. 5—Response obtained by on-line detector at the output of the vessel (solids tracer)

in the first compartment in the continuous mode of operation, there is a gradient of oxygen partial pressure reducing towards the discharge end of the autoclave, resulting in lower sulphur oxidation rates at that end. Further work will be required to establish this.

The lower sulphur oxidation rate that was experienced in the continuous pilot-plant test had a positive economic implication for the pressure-leaching process. The low sulphur oxidation requires less oxygen, which is one of the major working costs of the process, and generates less sulphuric acid, which would consume lime for neutralization prior to being discharged from the plant.

### Development of Equipment

Before meaningful metallurgical testwork could be undertaken on the pilot plant, there was an eight-month period of intensive equipment development, during which many modifications and changes in materials of construction were made. To a much lesser extent this development is still continuing. The following major alterations were made.

- (a) After a short period of operation, it was apparent that 316L stainless steel was totally unacceptable for pipes and autoclave internals, where the acid tenors were up to 15 g/l and the temperatures above 120°C. Nearly all such parts have been replaced with either 2RK65 or 904L stainless steel. These steels have so far proved much superior to 316L but may not necessarily be selected for a full-scale plant. Chloride levels of 200 to 250 p.p.m. in the plant water fed to the pilot plant are believed to have caused the stress-corrosion cracking in the 316L stainless steel. Presumably much lower levels of chloride existed in the Rand Water Board water used in the 1958 testwork mentioned earlier.
- (b) The most serious wear occurred on the impellers of the agitators; impellers of 904L stainless steel, titanium, and Carborundum Refrax have since been used with varying degrees of success.
- (c) Frequent failures of the agitator-shaft seals occurred before gland-seal water treatment was introduced. It was established that filtration, softening, and cooling of this water are essential.
- (d) Leaks at flanges on the nozzles through which the agitator shafts and dip pipes pass were a regular occurrence. The gasket system has now been re-designed.
- (e) Chokes in the bubble tube used for measurement of the levels were solved by the installation of a water purge in a concentric outer tube, which prevents solids choking the end of the inner air tube.

### Conclusions

There is no doubt in the opinion of the writers that the operation of a large-scale continuous pilot plant was essential in the development of pressure leaching for the extraction of uranium from Witwatersrand ores.

Metallurgically, it is confirmed that the uranium extractions obtained in the laboratory can be reproduced in continuous operation. The consumption of reagents and utilities is now reasonably well defined, as is the retention time and therefore the autoclave size required to produce a given uranium extraction.

Without the pilot plant, realistic assessments of materials of construction could not have been made. A full-scale project could not have borne the cost in lost production of the time that has been spent on mechanical development in the pilot plant.

Finally, provided the full-scale project using pressure leaching is successful, the pilot plant will have proved an invaluable training ground for both operating and maintenance manpower.

### Acknowledgements

Without the perseverance of the Management and Staff of AARL in the study of pressure leaching over a number of years, the process would not have reached continuous pilot-plant stage. Much of the credit for the progress on the pressure-leaching pilot plant to date is attributable to the willing co-operation given by both operating and maintenance staff at Western Deep Levels Gold Mine.

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