

AUSTRALIAN ATOMIC ENERGY COMMISSION
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LUCAS HEIGHTS

BACTERIAL LEACHING OF URANIUM ORES – A REVIEW

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R. T. LOWSON

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ABSTRACT

The bacterial leaching of uranium ores involves the bacterially catalysed oxidation of associated pyrite to sulphuric acid and Fe^{3+} by autotrophic bacteria and the leaching of the uranium by the resulting acidic, oxidising solution. Industrial application has been limited to *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans* at pH 2 to 3, and examples of these are described. The bacterial catalysis can be improved with nutrients or prevented with poisons. The kinetics of leaching are controlled by the bed depth, particle size, percolation rate, mineralogy and temperature. Current work is aimed at quantitatively defining the parameters controlling the kinetics and extending the method to alkaline conditions with other autotrophic bacteria.

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BACTERIA; CHEMICAL REACTION KINETICS; COUNTER CURRENT;
ECONOMICS; IRON SULFATES; LEACHING; OXIDATION; PH VALUE;
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URANIUM ORES

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1. INTRODUCTION

Bacterial leaching has been practised for over one hundred years (Moss and Andersen 1968) and probably goes back to the 17th century (Taylor & Whelan 1943). However, its application to treatment of pyritic uranium ores did not commence until the 1950s when it was observed that the Urgeirica uranium treatment plant in Portugal was not achieving the expected yield of uranium. The error was traced to substantial leaching by rain water of the stockpile between initial sampling and treatment. The National Chemical Laboratory (NCL) Teddington, UK, acting as consultant to the mine operators, established that the reaction was catalysed by autotrophic bacteria (Cameron 1963).

The bacteria oxidised the pyrite in the ore to ferric sulphate and sulphuric acid, and the resulting acidic oxidising solution solubilised the uranium. Initially, work was directed towards preventing the reaction but it soon became clear that the process could be applied economically on an industrial scale to ores with grades in the range 0.5 to 1.5 kg U₃O₈ Mg⁻¹. These grades are rejected by geiger-counter sorters. The first industrial heaps, built at Urgeirica in 1952-53, were fully described by Cameron (1963). A research program was initiated and reported by Byrne (1957), Wells (1957), Miller, Napier & Wells (1963) and Audsley & Daborn (1963a, b). The method was independently developed in Canada in the early 1960s and became the standard method for recovering the remaining uranium in the Stanrock mine with a production cost of \$US1.58/kg U₃O₈ (McGregor 1966). Since then, the method has been studied in Argentina, France, Russia, Spain, South Africa, the United States and Yugoslavia.

The International Atomic Energy Agency (IAEA) has set up a co-ordinated research program on the bacterial leaching of uranium ores. The first meeting was held at Hacettepe University, Ankara, Turkey, 11-15 December 1972. The aim of the program is to co-ordinate research and disseminate the results to participating members (IAEA 1973).

Overshadowing the application of this technique to the recovery of uranium from pyritic uranium ores, is the very extensive application to the recovery of copper and, to a lesser extent, other heavy metals (Pings 1968). Historically, the method was first developed for copper recovery, and the technology for this metal is more advanced than for any other element.

Although this report is centered around the recovery of uranium, reference will also be made to the bacterial leaching of copper where the theory or application overlap. Accordingly, this report is limited to reviewing the laboratory and industrial experience gained in developing the

bacterial leaching of uranium ores. The discussion includes a description of the bacteria, the conditions under which they live, and the application of the method to the industrial recovery of uranium. Also discussed are possibilities for future research and development of the process.

2. THE MECHANISM

Industrial bacterial leaching of ores has been limited to autotrophic bacteria in acidic media. However, there is every indication that the method can be extended to cover a far wider range of bacterial species (Silverman & Ehrlich 1964), and there is now a specific case of copper ores being efficiently leached by fungi of the *Penicillium* species (Wenberg, Erbsch & Volin 1971). Biological mineral recovery is, in many cases, complementary to the problems of mine drainage which has been found to support many varieties of heterotrophic bacteria, algae, yeast and protozoa. There is no limitation on pH since alkaline mine drainage has been reported to support mineral oxidising autotrophic bacteria (Lundgren, Vestal & Tabita 1970). Thus, it seems likely that a catalytic biological species can be found for almost any mineral environment.

In a general review of microbial formation and degradation of minerals, Silverman & Ehrlich (1964) reported only one instance of bacterial action on uranium. Unfortunately this was the reduction



since any uranium recovery process requires the formation of a U(VI) soluble complex, reaction (1) is of no use. The reaction was catalysed by the species *Micrococcus latilyticus* which can also catalyse a number of reduction processes.

The natural and industrial bacterial leaching of uranium ores is currently limited to pyritic ores. In these circumstances, autotrophic bacteria will oxidise the pyrite to sulphate and ferric iron. The orebody progressively becomes more acidic and oxidising until it reaches the conditions for oxidation and solution of the uranium; this process is discussed in detail.

2.1 The Autotrophic Bacteria

The autotrophic bacteria are a group of structurally unrelated species of the *Pseudomonadales* order whose common feature is that they can derive their growth energy from the solubilisation of inorganic compounds (chemolithotrophy) or from light adsorption (photolithotrophy). It is the former which are responsible for mineral transformation. The species are subdivided into the obligate which are obliged to derive their carbon only from carbon dioxide, and the facultative which have the faculty for deriving carbon from carbon dioxide or organic compounds. The species are also divided into groups based on the

source of inorganic electron donors. A more exact definition of this type of bacteria has eluded microbiologists to date (Kelly 1971).

Table 1 lists the principal autotrophic bacteria capable of sulphur and iron oxidation; it has been compiled from data published by Bergey (1957) and Lundgren, Vestal & Tabita (1970). However, these data should be treated with caution since there is now evidence that the measurements were made on mixed cultures (Ralph 1975). At the present time, only the first four species of the table have been reported in industrial applications. Their oxidation ability is limited to those reactions listed. Thus *Thiobacillus ferrooxidans* will oxidise thiosulphate to sulphate but cannot oxidise sulphides or elemental sulphur. Some initial investigations have been made into bacterial leaching under alkaline conditions by Marjanovic (IAEA 1972, preprint 10) and Czegledi et al. (IAEA 1972, preprint 5) and the results suggest that the method is applicable to these media.

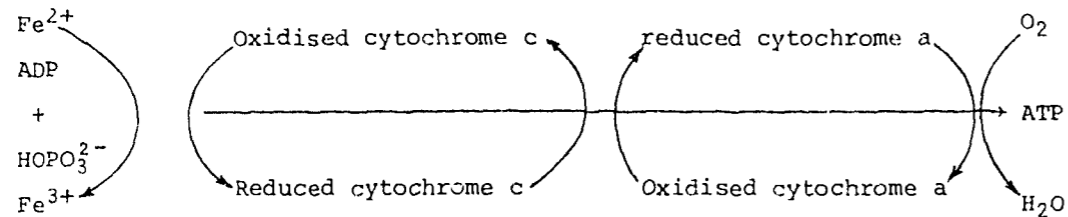
The structure of these bacteria is now known (see Figure 1). They consist of rod shaped bodies, approximately 1.4 μm long and 0.4 μm diameter. They have an outer membrane of lipopolysaccharide and lipoprotein, a middle rigid layer, and an inner layer known as the cytoplasmic membrane. This laminate is the container for the cytoplasm which is made up of a nucleus, ribosomes, dense bodies probably mesosomes, and polyhedral bodies.

The autotrophic bacteria have a unique mode of carbon fixation. This is via the Calvin cycle (Figure 2) in which carbon dioxide reacts with ribulose-1, 5-diphosphate to form 3-phospho-glycerate. A cyclic series of reactions then occurs during which some of the products are absorbed by the living system for growth and reproduction, while the remainder form the reactant ribulose-1, 5-diphosphate. Each reaction is driven by a catalyst known as an enzyme. These are globular masses of protein to which is attached an active group known as the co-enzyme.

The co-enzyme takes part in the overall reaction causing a hydrogenation, or phosphorylation, etc., and is dehydrogenated or dephosphorylated in the process. In the Calvin cycle, nicotinamide adenine dinucleotide (NAD^+/NADH) is a common hydrogenating co-enzyme while adenosine triphosphate (ATP/ADP) is a common phosphorylating co-enzyme (Figure 3). The reacted enzyme then enters a regenerative system whose mechanism is still imperfectly understood, but which may be considered as a series of biochemical cogs called cytochromes, through which electron transport can occur. These cytochromes are protein masses to which is attached a porphyrin group of which hemin is a typical example (Figure 4). These porphyrins complex both ferrous and ferric

iron and provide the pathway for electron transport. The sequence of reactions is still largely theoretical for many systems and the identification of the particular cytochromes involved is often unknown.

The regenerative system requires a driving force; for the chemoautotrophic bacteria the energy is obtained from mineral oxidation. This has allowed Lundgren, Vestal & Tabita (1970) to propose the following system for the regeneration of ATP from ADP



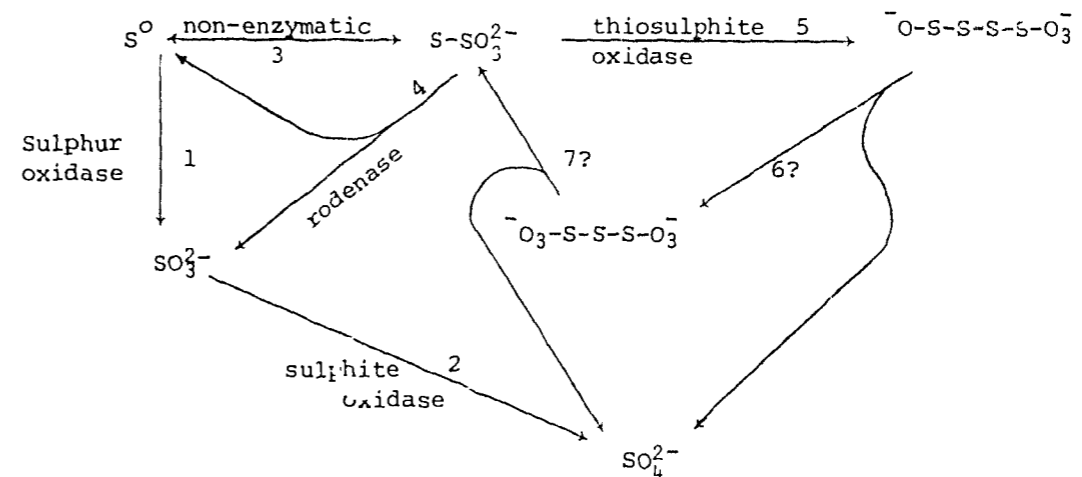
However, it is considered that this description is still incomplete in that there are several biochemical cogs missing in the initial stages. From studies of ^{59}Fe uptake, Lundgren, Vestal & Tabita (1970) suggested that a suitable oxygen-bonded complex of ferrous iron is adsorbed onto the cell wall and is temporarily bound to the cell by an SO_4^{2-} group. The bound Fe^{2+} will then oxidise to Fe^{3+} , releasing an electron to an electron-deficient sulphate group. The electron is then transferred to the cytochrome system by some as yet undetermined mechanism. The Fe^{3+} is excreted by the cell as either $\text{Fe}(\text{OH})_3$ or $\text{Fe}_2(\text{SO}_4)_3$.

There is also an energy paradox. Part of the Calvin cycle requires the presence of the reduced form of the co-enzyme nicotinamide adenine dinucleotide (NADH). This has a redox potential of -0.320 V for the couple NADH/NAD^+ (Table 2). However, the redox potential for $\text{Fe}^{2+}/\text{Fe}^{3+}$ is $+0.77$ V. Hence, under normal conditions, NAD^+ could not be reduced by ferrous iron. Exactly how the in vivo cell achieves this is probably one of the most fascinating problems in the field of autotrophic biochemistry (Lees 1962). Solution of this problem and an exact description of the enzyme systems may open the way to the tailoring of autotrophic bacteria to a far wider range of minerals than is presently known.

2.1.1 Sulphur as an alternative energy source

Thiobacillus ferrooxidans will also feed on sulphur instead of iron as the energy source. The ability to oxidise iron is retained by sulphur grown cells and vice versa although it is generally concluded that, while the ability to oxidise reduced iron and sulphur compounds is an inherent characteristic of these bacteria, the two mechanisms are located at different sites.

From studies with *Thiobacillus thiooxidans* it has been found that these bacteria excrete wetting agents, allowing the bacteria to bond onto sulphur crystals. One of these wetting agents is known to be phosphatidylinositol (Figure 5) (Schaeffer and Umbreit 1962). This suggests that the cell envelope membrane plays an important part in the initial stages of sulphur oxidation. The exact pathway of sulphur oxidation is even less well defined than that of iron oxidation. Lundgren, Vestal & Tabita (1970) have drawn up the following scheme:



Enzymatic action is known for reactions 1, 2, 4 and 5. Reaction 3 occurs non-enzymatically and reactions 6 and 7 are only postulated to occur.

2.1.2 Bacterial nutrients and inhibitors

Bacteria require an energy source (in this case from the solubilisation of inorganic minerals), a carbon source (which may be CO_2 , HCO_2^- , mineral carbonates or organic carbon), and sources of N, P, S, Ca, Mg and K. In addition trace levels of Zn, Co, Fe, Mo and other elements are essential for growth. Growth will not occur unless all the major and minor nutrients are present. A standard laboratory solution is Silverman 9K (Silverman and Lundgren, 1959) listed in Table 3. This solution provides the major nutrients in a solution of tap water. The tap water is the source of the minor nutrients and if it is replaced by distilled water then growth cannot be guaranteed.

The use of nutrients is generally considered to promote bacterial growth (Pings 1968), but is not economically justified on an industrial scale. However McCreehy, Harrison and Gow (1969) used the Silverman 9K solution as the leaching solution in a proposed continuous bacterial leaching process and, because of a rapid and concentrated leaching process, they claimed the method was economically viable. In comparison, industrial testing at the Milliken

mine, while obtaining an increased yield through the use of Silverman 9K nutrient, showed that the cost was not economically justified, and at the neighbouring Stanrock and Denison mines, the use of nutrient showed no appreciable increase in uranium recovery (McGregor 1969, Anon 1967).

Goren's patent (Goren 1966) recommended the use of nitrates or ammonium salts to provide a nitrogen concentration of up to 0.02 g l⁻¹ together with other salts of cobalt, magnesium, manganese, phosphorus and potassium or any other salt of an element essential for bacterial growth if these elements are absent under the local conditions.

Audsley and Daborn (1963a) used a nutrient of 3.0 g l⁻¹ potassium phosphate in a series of laboratory experiments and obtained a lower extraction rate. They attributed this to the precipitation of ferric and uranyl phosphate in their experimental columns. Harrison, Gow and Hughson (1966) found also that the uranium extraction rate was not improved by the addition of trace amounts of nutrients such as ammonia or phosphate. However, the iron concentration was critical. The addition of iron as ferrous sulphate will be discussed in detail later.

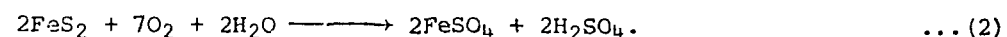
Bacteria are very sensitive to sudden changes in chemical environment. However, they can be slowly acclimatised to tolerate extreme conditions, probably via a mechanism of selection from a mixed population. Table 4 lists the developed tolerances reported by Pings (1968) and Goren (1966). Gow (IAEA 1972, preprint 8) reported that organic liquids commonly used for solvent extraction have an adverse effect on the rate of bacterial oxidation of iron. There are several commercial bacteriacides mostly based on organic chloride such as chlorohexidene hydrochloride.

Chemolithotrophs can be inhibited by light. Malouf and Prater (1961) reported that direct sunlight would render bacteria inactive but not destroy them. In open ponds, this would be effective down to a depth of 0.6 m. Bacteria are very sensitive to ultraviolet light and a short exposure to an intense radiation will completely sterilise a culture

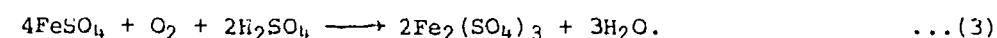
2.2 Optimal Chemical Conditions

The prime requirement for bacterially assisted leaching of uranium ores by *Thiobacillus* and *Ferrobacillus* is the presence of pyrite. However, since the bacteria are only catalysts in the reaction sequence and can be acclimatised to a particular environment, the optimum chemical conditions can be defined without reference to the bacterial action.

The initial reaction in the aerial, wet oxidation of pyrite is

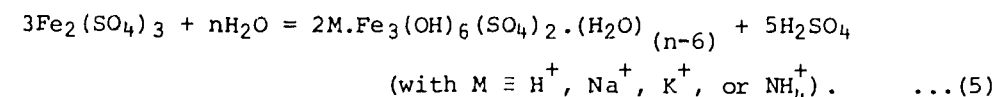
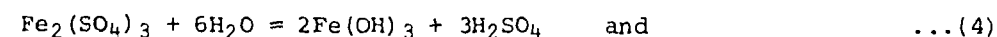


The ferrous sulphate oxidises to ferric sulphate under slightly acid or alkaline conditions according to

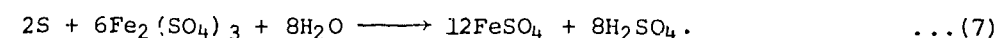
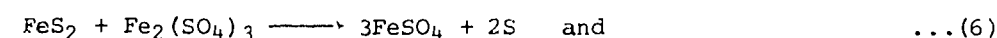


Reactions (2) and (3) can be bacterially assisted by *Thio* and *Ferro* bacillae.

At this stage the pH will be in the range 4-7 and consequently the ferric iron will tend to precipitate out as ferric hydroxide or basic ferric sulphate according to reactions (4) and (5):

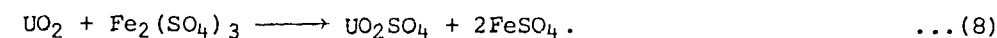


In mine drainage waters, the acid drains away leaving a precipitate known as 'yellow boy'. When the acid is retained within a leaching heap, there is a progressive rise in acidity. Above pH 2.8, the ferric iron redissolves. The solubilised ferric sulphate will attack the remaining pyrite:



Reactions (3), (6) and (7) form an autocatalytic sequence. The acid produced by reaction (7) lowers the pH to around 2. This tends to inhibit reaction (3) which is favoured by alkaline or slightly acid conditions and *Thio* or *Ferro* bacillae are required to keep the sequence working at a significant rate.

With the production of soluble ferric iron, solubilisation of the uranium minerals can now occur by



In order to achieve optimum leaching conditions the following steps should be taken:

1. *Rapid production of Fe²⁺*

Under natural conditions, this will occur by reaction (2). The rate can be increased by bacterial activity; but this still requires a rather long initiation period. The alternative is to add ferrous sulphate directly. This may make the whole process uneconomical on an industrial scale.

2. *Rapid production of Fe³⁺*

This only occurs by reaction (3). Initially it will readily occur by aerial oxidation at neutral pH and the reaction can be catalysed by bacteria. Again, an alternative is to add ferric sulphate, but the same objection applies as in the case of adding ferrous sulphate.

3. *Rapid production of acid*

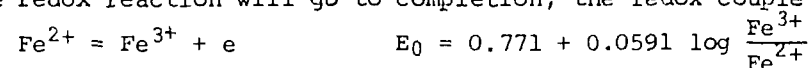
This occurs by reactions (2), (4), (5) and (7). Only reaction (2) is

bacterially catalysed although the sulphur from reaction (4) could be oxidised by another bacterial route. The alternative would be to add acid directly. This may be feasible if the leach heap is being operated in conjunction with a conventional treatment plant which has acid waste liquors. Once the heap has reached the autocatalytic stage, its heap liquors can be recirculated after the uranium has been extracted.

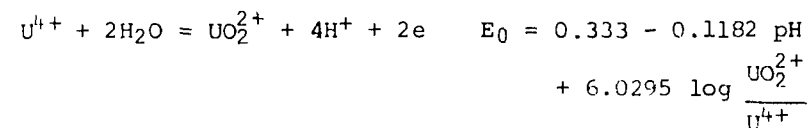
4. Maintenance of an acid oxidising medium

This requires catalysis of reaction (3) which may be achieved by *Thiobacillus ferrooxidans*, *Ferrobacillus ferrooxidans* or metallic catalysts such as copper.

The dissolution of the uranium mineral will depend on the chemistry of the particular mineral. Optimisation may be achieved by mixing different orebodies. The redox reaction will go to completion, the redox couple being



and



$$\log K = \log \frac{[\text{Fe}^{2+}]^2}{[\text{Fe}^{3+}]^2} \times \frac{[\text{UO}_2^{2+}]}{[\text{U}^{4+}]} = 22.8 \text{ at pH } 2 .$$

Hence the method is expected to give high uranium yields. The stability of the system can be investigated by constructing a potential-pH diagram for the materials.

Figure 6 is the potential-pH diagram for the iron-uranium-water system at 25°C. The temperature effect on the position and slope of lines will be insignificant for the range of temperature under which bacteria are normally found. The diagram was compiled from Pourbaix's atlas of potential-pH diagrams (Pourbaix 1966). The limiting concentrations for ionic species to precipitate under given conditions of pH and potential has been set at 10⁻³M, which is a typical concentration for an industrial heap. The greer portion of the diagram represents the area for potential and pH under which heaps normally operate. The diagram shows that up to pH 6.5, UO₂ in the presence of Fe²⁺ will tend to dissolve as UO₂²⁺. The actual solubilisation of UO₂ is insensitive to pH in the acidic range and below pH 1.8, UO₂ is unstable as a solid species. The most sensitive part of the system is the hydrolysis of Fe³⁺ to Fe(OH)₃. This can only be guaranteed not to occur below pH 2.75. Above this pH, hydrolysis becomes progressively more likely with increasing pH and Fe³⁺ concentration. In industrial applications, this reaction could be

controlled by occasionally purging the system of excess iron.

2.3 Catalytic Influence of Bacteria

Although the catalytic influence of bacteria on the oxidation of pyrite has been known since 1926 (Li & Parr 1926), its presence is not a prime requirement for reactions (2) to (8). The beneficial presence of bacteria in promoting uranium solubilisation was first shown by Miller, Napier and Wells (1963) and quantitatively evaluated by their co-workers Audsley and Daborn (1963a). Their experiments were carried out on the Portugese Bica ore to which 2% pyrite had been added. The ore already contained 1% pyrite and in its natural state supported the bacteria *Thiobacillus thiooxidans* and *Ferrobacillus ferrooxidans*.

In these experiments, sterilised or unsterilised ore was leached with sterilised or unsterilised water, and with or without inoculation with a bacterial culture. The ore was sterilised by filling a packed column with alcohol and allowing to stand before washing free with sterile water. The bacterial culture was a mixture of *Ferrobacillus ferrooxidans* and *Thiobacillus thiooxidans*. The percentage extractions after twenty weeks are listed in Table 5.

Unfortunately, the sterilisation techniques were not completely effective and, after ten weeks' operation, the sterilised columns were found to contain viable oxidising bacteria. However, the general trend is significant and it can be considered that bacteria promote uranium extraction in pyritic ores. It can also be concluded that the most efficient are those which grew in the orebody rather than in an added culture. This is due to the slow acclimatisation to specific chemical conditions.

2.4 Kinetics

The kinetics of batch liquid phase oxidation of ferrous sulphate by *Thiobacillus ferrooxidans* was reported by Lacey and Lawson (1970). They concluded that there was a single rate equation governing the oxidation. Marjanovic (IAEA 1972, preprint 9) reported some initial kinetic work for the same species. Three stages were identified, (i) an initial lag stage, (ii) a logarithmic development stage and (iii) a final stationary stage. Caglar (IAEA 1972, preprint 8) reported some studies also on this species and he concluded from the results that it is the oxygen and carbon dioxide supply that is rate limiting. Keenan (1969) reported that the overall reaction rate for uranium beneficiation was a function of the ferric and hydrogen ion concentrations.

The only quantitative treatment of the kinetics of uranium heap leaching is that of Cordero et al. (1966). In the cases where there is efficient

extraction, the curves are hyperbolic and described by the general equation

$$y = \frac{t}{(A + Bt)} \quad \dots(9)$$

where y = % U extracted, t = time (weeks), and A and B are constants.

This can be rearranged to give the linear equation

$$\frac{t}{y} = A + Bt \quad \dots(10)$$

Values for A and B depend on the particular ore. A is usually between 0.01 and 0.03 and B between 0.01 and 1.0. Extrapolation of the results for a particular ore to plant scale give a very good correlation.

The overall kinetics of a heap will either be controlled by the rate of oxidation of the ore-pyrite mixture or by the rate of diffusion of solutions within the ore lumps. The choice depends on a number of interrelated physical factors including bed depth and particle size, percolation rate and mineralogy of the ore. Ore oxidation will tend to become rate determining for a deep bed, fine particle size, slow watering rate and shales, and it tends to become solution diffusion rate determining for a shallow bed, coarse particle size, high watering rate and sandstones.

2.4.1 Bed depth and particle size

Audsley and Daborn (1963b) studied the effect of bed depth with Bica ore to which 2% pyrite had been added for extraction with recirculated water (Table 6). They showed that independent of the particle size in the range less than 13 mm to less than 3 mm, the leaching rate tended to a maximum for a 0.5 metre bed.

They also showed that, independent of bed depth, the optimum leaching rate was obtained with ore crushed to less than 6 mm, although the effect of particle size on the leaching rate diminished as the depth of the bed was increased. These results agree with those of Gow et al. (1971) who showed that progressive crushing of the Elliot Lake ore from 200 mm to 10 mm increased the extraction rate. In fact, Harrison et al. (1966) recommended that this ore be crushed to at least 2mm.

However, the optimum particle size is also dependent on the rock matrix. Cordero et al. (1966) showed that sandstones needed to be crushed more than granites or shales (Table 7). This was explained as being due to the different uranium distribution that occurs in each type of rock. Miller, Napier and Wells (1963) pointed out that ores in which the uranium is locked into a refractory mineral and is only released by fine grinding will also be difficult to leach.

If the ore is crushed to a very fine particle size, the extraction rate

is controlled by the rate of oxygen diffusion into the heap. This will effectively inhibit practical uranium recovery, as found with the Witwatersrand slimes. These tailings from the Witwatersrand gold mines are an inert silica slime of particle size less than 0.25 mm containing up to 3% sulphur as pyrites and between 0.05 and 0.2 kg U_3O_8 Mg^{-1} (Lloyd 1971). While these slimes were chemically ideal for promoting bacterial oxidation of the pyrite, in practice, uranium solubilisation was found to be limited to within 10 cm of the surface. This was traced to the fine particle size which led to small voidage, thus limiting the rate of oxygen diffusion. The proposed solution to the problem was either continuous removal of the top 10 cm of the slime or injection of air into the dams.

2.4.2 Percolation rate

A detailed study of the effect of percolation rate, with all other parameters constant, was made by Audsley and Daborn (1963a) using the Bica ore with 2% pyrite addition: Their results are summarised in Figure 7 which shows the per cent U_3O_8 extracted after 10 weeks. There was a slow increase to an optimum rate past which there was a very rapid decrease in extraction. This effect will depend on the type of ore. Cordero et al. (1966) found that altering the percolation rate from 34 $cm^3 week^{-1} kg^{-1}$ to 340 $cm^3 week^{-1} kg^{-1}$ only increased the extraction from 55.7% U to 59.0% U from a shale ore.

The industrial heaps have tended to be operated in this range. The copper sulphide heap at Rum Jungle was operated at a percolation rate of 35 $cm^3 week^{-1} kg^{-1}$ (Andersen and Allman 1968). Western Nuclear in the USA operated a heap at a percolation rate of between 40-60 $cm^3 week^{-1} kg^{-1}$ (Merritt 1971 p. 116). At this low percolation rate, the heaps were operating with ore oxidation as the rate controlling step.

In comparison, some laboratory work has been operated at very high percolation rates. Gow et al. (1971) operated their columns between 8.4 to 14 $l week^{-1} kg^{-1}$. Likewise Cecchetto et al. (1964) operated their columns at 4.5 $l week^{-1} kg^{-1}$ and Alexandre and Michel-Briand (1967) operated at 0.7 $l week^{-1} kg^{-1}$. In these last three cases, it was assumed that the percolation rate had no influence on the extraction rate. It is quite likely that the rate controlling step was no longer the oxidation of the ore and hence the kinetics of the laboratory experiment would not correlate directly with the industrial situation.

2.4.3 Mineralogy

A wide variety of ores have now been tested for natural leaching with and without the presence of bacteria. These are listed in Tables 8a, b and c.

Because there is a lack of conformity in reporting the mineral composition, it was necessary to divide the table into three parts to cover the different methods of description.

The bacterial leaching of specific ores was reported by Haralambous (IAEA 1972, preprint 4), Bhurat, Dwiredy, Jayaram and Dar (IAEA 1972, preprint 7) and Kulshrestha, Jayaram and Dar (IAEA 1972, preprint 6) and Gonzales and Sedano (1973). They suggest that the following mineral features have some influence on the kinetics - uranium mineralisation, basicity, pyrite concentration, sulphur concentration, phosphorus concentration and iron concentration.

Uranium mineralisation

Because of its reactivity, uranium occurs in several hundred minerals of which however, only a few are of commercial importance. These may be divided into two classes: primary, the oxides such as uraninite, UO_2 , and black oxides; and secondary, which are chemically combined such as autunite $Ca(UO_2)_2(PO_4)_2 \cdot 10-12H_2O$

The influence of type of mineralisation is not clear. Miller, Napier and Wells (1963) suggested that the refractory minerals such as brannerite would be difficult to treat. However, the Elliot Lake ore which is principally of this mineral has been bacterially leached successfully (McGregor 1968).

There has been no definitive study of the influence of type of mineralisation on bacterial leaching.

Basicity

The basicity of the ore determines the method of leaching (acid or carbonate) and the growth of a particular bacterial species to catalyse the formation of acid. It is usually a direct function of the amount of calcium and magnesium carbonate present.

To isolate this effect from the other influences, Miller, Napier and Wells (1963) and Audsley and Daborn (1963b) studied a number of ores to which pyrite had been added to bring the total pyrite concentration up to 10%. These ores were then leached with recirculated water and it is probable that the pyrite oxidation was bacterially catalysed in all cases, although this was not stated. The results are illustrated by Figure 8. It can be seen that, for each ore, there is a time lag before the onset of effective leaching. When leaching started to occur, the water would become progressively more acid according to the autocatalytic sequence of reactions (2) to (8). The period of this time lag is directly related to the basicity of the ore as shown by Table 9. The time lag is due to the neutralisation of the acid consuming

constituents in the host rock. Not until these have been neutralised can the liquors solubilise the uranium.

In the case of the Umtali ore, the time lag was greater than 60 weeks. This was probably because the ore was too basic to allow oxidation of pyrite without the aid of suitable bacteria. Since the ore mixture was artificial rather than natural, it would have been necessary to inoculate the mixture with a suitable alkaline, pyrite oxidising bacteria such as *Thiobacillus neopolitanus*.

A similar situation was reported by Cordero et al. (1966) with the La Virgen ore which is quite basic and on which the addition of up to 10% pyrite had no beneficial effect at all.

Mouret and Pottier (1961) also studied the extraction rate with recirculated water from a range of ores to which 3% pyrite had been added. The presence of bacteria was not reported and no allowance was made for pyrite already in the ore. No time lags were observed with their systems but their extraction rate progressively decreased with increasing calcium carbonate concentration in the ore. However, when they leached the ores with 0.01 N sulphuric acid, with no pyrite addition, there was a very definite time lag which was directly related to the basicity of the ore.

As an alternative to adding pyrite, the highly basic ores can be leached with sodium carbonate solution. This also applies to bituminous ores (Mouret and Pottier 1961). The process has not been applied to heap leaching but it does occur naturally in the Ambrosia Lake area of New Mexico. The mine drainage waters around this area have been found to contain 0.002 to 0.012 $g\ l^{-1}U_3O_8$ probably as the anionic uranyl tricarbonate complex. This has been successfully recovered at a rate of 90 kg $U_3O_8\ day^{-1}$ by the Kerr-McGee and United Nuclear-Homestake Partners companies (Merritt 1971).

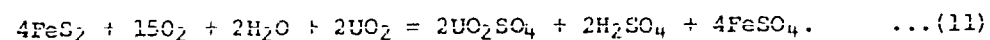
The effect of different liquid media has been reported also by Merino and Saez (1973), Cordero, Villarrubia and Hernandez (1973) and Hernandez, Cordero and Villarrubia (1973).

Pyrite

Acid leaching is promoted by the presence of pyrite which can be oxidised to provide additional acid and an oxidising agent in the form of ferric iron. Addition of pyrite to a crushed ore has been shown to be beneficial (Miller, Napier and Wells 1963, Audsley and Daborn 1963b). This is illustrated by Figure 9 which shows uranium extracted after (15 + L) weeks versus per cent total pyrite. L is the time lag before effective leaching starts and, by including it in the time term, the influence of the calcite is removed. For

these acid or neutral ores, there is a direct correlation between the amount of pyrite added and the percentage uranium extracted. Similar conclusions can be drawn from the results of Cordero et al. (1966).

The theoretical amount of pyrite required to solubilise the uranium is only twice the mol per cent of UO_2 present since the overall reaction is



Hence the need for pyrite in excess of this quantity will be due to consumption of acid by the host rock.

Sulphur

There is only one reported case of the use of sulphur as a leaching agent (Audsley and Daborn 1963a) and this was with Bica ore with 2% added pyrite. The addition was found to be beneficial and *Thiobacillus thiooxidans* was detected in the experimental column. Extraction was also faster with a column treated with a low-phosphate nutrient. Hence it was concluded that oxidation of the sulphur was mainly due to biological influence.

Phosphorus

The reported work on the influence of phosphorus is inconclusive. It appears to depend on whether the phosphorus is present in the uranium mineralisation or the host rock, and whether the system is under bacterial control. Mouret and Pottier (1961) experienced considerable difficulty in leaching an ore in which the uranium was present as a phosphate. Leaching with water, leaching with water after adding 3% pyrite were quite ineffective while leaching with sodium carbonate solution was only marginally better. After 100 days, 30% extraction was obtained with a solution of $2 \text{ g Fe}^{3+} \ell^{-1}$ at pH 2.

Cordero et al. (1966) reported similar difficulties when leaching phosphoric ores with sulphuric acid. This was attributed to reprecipitation of insoluble phosphates in lower parts of the bed, in extreme cases causing complete obstruction. In contrast, when using pyrite as the leaching agent, the phosphoric ores were readily leached, probably because the pyrite was being bacterially oxidised and the soluble phosphates were acting as nutrients. Audsley and Daborn (1963b) found that the addition of a low-phosphate nutrient to the water leaching of the Bica ore + 2% pyrite was beneficial because bacteria were present.

Iron

No investigations have been reported on the influence of iron oxides in the host rock on the uranium extraction rate. This is surprising since the concentration of soluble iron and the ferrous/ferric ratio play an important part in the extraction.

Mouret and Pottier (1961) leached a number of ores with ferric sulphate solution at pH 2. Not surprisingly, very good extraction rates were obtained after only a few weeks with acidic ores. The extraction rate was reduced with a calcitic ore and was low with a phosphoric ore. As this is a rather expensive method of leaching, an alternative is to use ferrous sulphate. Miller, Napier and Wells (1963), and Audsley and Daborn (1963b) who investigated this for a variety of pyritic and basic ores, showed that ferrous sulphate addition was beneficial in all cases. Figure 10 shows the percentage uranium extracted after 15 weeks versus percentage ferrous sulphate added. However, Cordero et al. (1966) showed that, in certain cases, the addition of too much ferrous sulphate to a pyritic ore reduced the extraction rate (Table 10). The reason for this was not fully elucidated.

Initially, the uranium extraction is favoured by a high ferric ion ratio. However, the autocatalytic sequence may cause excess formation of ferric iron which, in the latter stages of extraction, may lead to an undesirably high Fe^{3+}/U_3O_8 ratio which limits the extraction rate.

2.4.4 Temperature

When the reaction sequence is catalysed by bacteria there is a marked temperature effect with an optimum extraction rate occurring between 30° and 40° C. This is the optimum temperature range for bacteria. Miller, Napier and Wells (1963) showed that raising the temperature from 10° to 30° C increased the amount of uranium extracted after 10 weeks, from 2 to 80% for the Urgeirica ore. Subsequently, Audsley and Daborn (1963a) identified the optimum conditions as 35° C, beyond which the rate of uranium extraction decreased.

A more detailed study by Gow et al. (1971) on Elliot Lake ore led them to conclude that there were two rate constants (Figure 11). The first was for the first week with an activation constant of 20 kJ mol^{-1} . This low activation energy suggests a diffusion controlled mechanism which is to be expected since their percolation rate was very high. However, there appears to have been another rate constant for all subsequent time with an activation energy of 40 kJ mol^{-1} which suggests the presence of a chemically controlled mechanism such as ore oxidation.

In his review on bacterial leaching, Pings (1968) set the optimum operating temperature at 35° C and reported that neither freezing nor heating would ensure a 100% death. This temperature dependence can be the controlling economic factor for using this method for uranium recovery. At the Stanrock mine where the remaining uranium in the worked out areas of an underground mine was being recovered by bacterial leaching, it was found to be economical

to heat the mine intake ventilation during the winter months. This added \$CAN1 per kg U_3O_8 to the operating costs.

Mouret (1971) reported that 10 years of research had been carried out in France into bacterial leaching but the work was abandoned because the average temperature of the country was too low. Successful heaps have usually been operated in the tropics and this makes Australia's Northern Territory ideal. The surface water temperatures can reach $38^{\circ}C$ and very rarely drop below $25^{\circ}C$. The normal air temperature is in the range $30^{\circ}C$ - $35^{\circ}C$ with no gross fluctuations.

Brierley and Murr (1973) have described a chemoautotrophic bacteria of the *Sulfolobus* type capable of oxidising sulphur or ferrous iron between 45° and $70^{\circ}C$.

3. LABORATORY TESTING

There are several laboratory testing methods ranging from the simple, which are fast but provide little information, to the complex, which are more expensive, slower, prone to breakdown, but provide more detailed information.

The simplest is the shake flask, which consists of adding a measured quantity of crushed ore to a flask containing leaching solution, bacterial nutrient if required, and a bacterial culture, again if required. The flask is then vigorously shaken to ensure adequate aeration. The method allows rapid testing of a large number of ores over a wide range of conditions. Unfortunately, there is little control over the conditions once the experiment starts, but it will highlight those areas where the more detailed work would be most rewarding.

The batch reactor is a more effective method. It consists of a stirred reactor with provision for adding and withdrawing liquid, controlled aeration, controlled heating and cooling and a controlled light source. Probes can be incorporated to monitor solution potential, pH and dissolved oxygen. An automatic sampling system attached to an autoanalyser could also be incorporated.

However, the most popular method is the leach column. A typical system is described by Gow et al. (1971). The ore is packed into a vertical pipe of plastic, concrete or glazed earthenware. The dimensions of the pipe can vary from 0.1 to 1 m dia. and 0.5 to 4 m high. The base of the pipe has a perforated plate to support the ore and it sits in a sump to collect the effluent. A pump, or air-lift percolator, pumps the sump liquors to the top of the column or to a head tank. Air can be bubbled into the sump solution and acids or nutrients added to the sump. Various probes and a sampling system can be incorporated depending on the refinement desired. In practice,

a number of columns are operated in parallel to reduce the experimental time.

A relatively fast counter-current decantation system can be readily set up with six large flasks. Initially, crushed ore and solution is added to each flask, briefly agitated and allowed to settle. After 24 hours, the supernatant solution is separated and advanced to the next flask. Before adding the solution, the settled slurry is moved in the opposite direction. Fresh ore is added in the first flask and the leached residue is rejected at the sixth. Fresh solution is added to the sixth flask and the pregnant liquor is removed from the first. McCreedy et al. (1969) obtained a 90% extraction from the Elliot Lake ores after 6 days using this method and proposed a plant scale system.

4. INDUSTRIAL APPLICATION

Industrial bulk leaching may be divided into heap leaching and in situ leaching, but the basic method remains the same even though there are many variations.

4.1 Heap Leaching

The practical details of industrial heap leaching have been described by Merritt (1971), Cameron (1963) and Cecchetto et al. (1964); a typical construction is shown in Figure 12. The heaps are generally square although space may force them to be oblong. The chosen site should be graded and given a slight slope to one corner to assist drainage. The area should be surrounded by a drainage ditch or alternatively a wooden launder. The prepared ground including the ditch is then sealed with either bitumen sheet, or heavy gauge plastic or bitumen sealed concrete. On top of this sealed layer a drainage bed is constructed. This may be either a pebble bed, rock drainage channels or perforated pipes made from a suitable, corrosion resistant material. The channels or pipes should be aligned with the slope of the site. If plastic sheeting is used as the sealant, then perforated pipes are preferred, and the area can then be covered with .5 m of fine gravel followed by .5 m of coarse rock in order to protect the plastic. The ore is then piled on top of the bed. The drainage ditch or wooden launders empty into either a sealed collecting dam or tank. A barren liquor tank and a pump house complete the site. Economics requires that the arrangement of the heap, channels, dams and pumps should make the most of gravitational flow.

Dimensions of a heap vary with installation, tonnage, the permeability of the ore and available space. Merritt (1971) described a typical heap as 100 x 130 x 10 metre high. However, Cecchetto et al. (1964) reported that the Argentinian piles were only 4 m high while Cameron (1963) reported that

the Portuguese piles were only 2.5 m high. Laboratory experience is that the shorter the pile, the more efficient the extraction.

Exceptional care should be taken in piling the ore. Cameron (1963) reported that the Portuguese heaps were built by hand and that vertical coarse rock drainage channels were incorporated to assist percolation. The principal problem is consolidation of the heap by construction traffic. This occurred at Rum Jungle with the copper sulphide heap. It was planned to build the heap by constructing a ramp to the required height and then back dumping over the prepared areas from this ramp using carefully defined roadways. Unfortunately, the subtleties of heap construction were not understood by the truck drivers and "In practice the trucks ran at random over the entire heap surface reducing the top six feet to fines" (Andersen and Allman 1968).

The heap may be operated by a variety of methods. These are continuous flow, interrupted flow and counter-current flow.

4.1.1 Continuous flow

Fresh leach liquor of either a ferric solution and/or acid solution, or a carbonate solution or simply water, is pumped to the top of the heap. Here it may either be distributed in a number of shallow lakes excavated on the top surface, or by sprays or both. The liquor drains through the heap, solubilising the uranium by whatever method is being applied and ultimately drains into the pregnant liquor dam. The pregnant liquor is pumped to the uranium recovery plant, where the uranium is extracted by ion exchange or solvent extraction and the resulting barren liquor empties into the barren liquor dam. Depending on the chemistry of the heap, fresh leach liquor can then be prepared from the barren liquor, the pregnant liquor, fresh acid, fresh ferric solution and water.

4.1.2 Interrupted flow

In this method, the leach liquor is pumped intermittently to the top of the heap and the heap is allowed to dry out before rewetting. This leads to a reverse capillary effect, which allows extensive leaching of coarse ores. During wetting, capillary forces draw the leach liquor deep into an ore lump. On drying out, pregnant liquor drains from the capillary and, with further drying, will precipitate on the outside surface. Rewetting will wash off the surface uranium and allow fresh leach liquor to be drawn into the capillary.

This may be more effective for coarse ores than continuous flooding because drainage from drying capillaries will be considerably faster than simple ionic diffusion through a static, fluid filled capillary. The remaining operation of the heap will be the same as for continuous flooding.

4.1.3 Counter-current flow

If a series of heaps are built, then a counter-current operation can be practised in which the pregnant liquor from a nearly exhausted heap can be sprayed onto a richer ore heap. The sequence of operations can be repeated with further heaps until the pregnant liquor reaches an acceptable concentration. The exhausted heaps can either be abandoned, which is both unsightly and a pollution hazard, or the Portuguese method may be applied where the top .5 to 1 m exhausted layer can be progressively removed until all the ore is eventually removed from the pad. Apart from the beneficial environmental aspects of this method, it ensures both more efficient recovery and that the concrete pad, which is a significant capital expenditure of the operation, can be reused many times.

4.2 In situ Leaching

The pyritic uranium ores of the Elliot Lake area, Canada, were ideal for bacterial activity once the orebody was exposed and it was soon noticed, after commencement of underground mining in the late 1950's, that the mine waters were becoming acidic and solubilising the uranium. Initially, this water was pumped to the treatment plant for recovery of the uranium. As the area became worked out, several of the companies decided to promote the leaching process in order to recover the remaining uranium from the supporting pillars and low grade areas of the underground workings. The method has been practised at the Stanrock, Milliken, Nordic and Denison mines. The Stanrock mine has probably made the most use of the method, and will be described in detail (McGregor 1966, 1968, 1969).

The orebody was originally a flat laying bed with an average dip of 15° . The method therefore was to spray an area with high pressure hoses (500-700 kPa) with water from a local lake (pH 5.0) every three months. The water was allowed to percolate through the mine and the pregnant liquor collected in a sump. The liquor was neutralised and the resulting slurry pumped to the surface for treatment. Subsequently, low pH barren liquor from the treatment plant was used to promote bacterial activity. Recovery by this method was 5660 kg U_3O_8 in 1961, 12300 kg U_3O_8 in 1962 and 47700 kg U_3O_8 in 1963 when high pressure hoses were introduced. By 1966, a progressive decrease in recovery was noticed and so, to maintain production, sections of the mine were progressively flooded allowing recovery from caved in areas. The addition of the nutrient Silverman 9K showed no appreciable increase in recovery. However, the neighbouring Milliken mine reported an increased yield and decreased cycle time with the use of the nutrient. Denison mines replaced the high

pressure hoses with lawn sprinklers reducing the manpower by a factor of 8.

4.3 Uranium Recovery

Up to the present, heap leaching has been operated in conjunction with conventional uranium treatment plants which require a pregnant liquor in the range 0.2-2 g ℓ^{-1} U₃O₈ (Browning 1972). Natural leaching of stockpiles can readily achieve this concentration and there are a number of mines where the drainage channels around stockpiles have been directed to a sump and the sump liquors pumped directly into the treatment plant.

Leaching of low grade areas under optimum conditions can yield pregnant liquors as high as 5 g ℓ^{-1} U₃O₈ during the early life of the heap (Miller, Napier and Wells 1963), but the average value will be in the range 0.1-0.15 g ℓ^{-1} U₃O₈. By comparison, natural leaching of overburden heaps can only yield liquors of up to 0.05 g ℓ^{-1} U₃O₈.

McGregor (1968) gave a flow diagram of the Stanrock mine. The pregnant liquor at pH 2.4 and between 0.1 to 0.15 g ℓ^{-1} U₃O₈ was pumped into a clarifier before passing through an ion exchange unit. The high grade eluant at 5 g ℓ^{-1} U₃O₈ was pumped to a precipitation plant, while the barren solution at 0.0001 g ℓ^{-1} U₃O₈ and pH 2.0 was returned to the leach sections.

Cordero et al. (1966) reported on Spanish studies of uranium recovery from natural leach solutions. They considered chemical precipitation by either soda, lime, or soda-lime, ion exchange separation and solvent extraction with amines. Even under the best conditions, chemical precipitation with soda from a 1.8 g ℓ^{-1} U₃O₈ solution at pH 2.2 produced a concentrate of only 10.2% U₃O₈ necessitating reprocessing of the concentrate with a high acid consumption. This made the overall process expensive. The ion exchange process using natural leaching solutions at pH 2.3 gave a good concentrate of 80% U₃O₈, the main impurity was iron (7.5%), and the reagent cost 30-35¢ kg⁻¹U₃O₈. The amine extraction for feeds from 0.2 to 2 g ℓ^{-1} U₃O₈, with pH adjusted to 1.2-1.8, also gave good concentrates (78-89% U₃O₈) with a very much lower iron concentration. The reagent costs were 35¢ kg⁻¹U₃O₈ for a 0.5 g ℓ^{-1} U₃O₈ feed and 70¢ kg⁻¹U₃O₈ for a 0.2 g ℓ^{-1} U₃O₈ feed. A mobile ion exchange plant was built to service a number of small mines which produced natural leach liquors. The cost of the unit was \$16,670. Also a transportable amine extraction unit capable of handling liquors down to 0.2 g ℓ^{-1} U₃O₈ was built at a somewhat smaller cost.

4.4 Economics of Heap Leaching

At present heap leaching is unlikely to supersede conventional milling methods because the very large investment needed to set up an exploration and

mining company requires a rapid method for the uranium recovery to give an early economic return on invested capital.

Heap leaching is not a rapid method; however, the continuous counter-current extraction method could become economical. While not applicable to the high grade ore, heap leaching can be applied to the subgrade ore, which, while it may only be 10% of the orebody, could be worth several millions of dollars and, if left untreated, could be a pollution hazard.

Costing a heap leaching method which is being run in conjunction with a conventional treatment plant is difficult because some of the costs are included in the treatment of the high grade ore.

The subgrade ore has to be mined in order to gain access to the high grade ore. Likewise, mill operation and amortisation will be costed for the high grade ore. The capital costs for setting up a heap, over and above those of running the conventional mill, are for pad construction and pumps, while the running costs are those of power and labour. The capital cost of the pad construction can be reduced by repetitive use of the pad.

As a guide, the costing of the Stanrock mine can be used. In 1964, the conventional mining costs at this mine were \$11.2 kg⁻¹U₃O₈ with a profit of 90¢ kg⁻¹U₃O₈, (McGregor 1966, 1968). On converting to solely bacterial leaching, production costs dropped to \$7.28 kg⁻¹U₃O₈ which included \$1.10 kg⁻¹U₃O₈ for heating the mine during winter. On redesigning their pumping system and converting much of their apparatus to corrosion resistant material, they obtained a further saving of \$1.10 kg⁻¹U₃O₈. The Stanrock mine did not crush the ore, which is a major cost in heap leaching, however this can be balanced against the cost of heating.

4.5 Pollution Aspects

The modern development of bacterial leaching in the industrial context followed observations on serious losses occurring in pyrite-laden stockpiles. The autotrophic bacteria are one of the earliest forms of animal life to develop on earth and have been causing transformation of suitable minerals ever since the first reduced minerals were laid down. Their rugged and adaptable nature to extremes of environment has permitted the species to distribute itself around the world. Consequently, whenever a pyrite orebody is exposed by mining, bacterial oxidation can be expected to occur, causing losses of material, and chemical pollution. The problem is particularly serious in the tropics. These areas have a high rainfall and an ambient temperature in the range 25-35°C. Once the orebody becomes wet, bacterial leaching is almost guaranteed. It is now standard practice to store stockpiles under cover

either in a shed or under an impervious blanket of plastic or bitumen. However, to date, very little attention has been paid to pyrite overburden heaps. These heaps are usually many times larger than the orebody and are economically worthless. Consequently, no attention has been paid to them other than dumping in the cheapest possible manner. Once saturated, the pyrites will oxidise to Fe^{3+} and H_2SO_4 , providing an ideal solution for extracting any heavy metal that may be present. The resulting liquors may contain metals at concentrations below those required for economic recovery but well above those which cause serious pollution. For example, copper present as Cu^{2+} (uncomplexed) is toxic to most fish above $0.01 \mu\text{g l}^{-1}$. With the new emphasis on conservation of the environment, it is necessary to give considerable thought to disposal of pyritic waste in order to prevent such pollution. The problem is well known in mine drainage and formed the basis of a definitive review by Lundgren, Vestal and Tabita (1970).

5. CONCLUSIONS

Bacterial oxidation of pyritic ores to produce an acid oxidising solution suitable for leaching heavy metals in situ is a proven process. There are now industrial heaps around the world operating solely in this way. In particular, mines in Canada and Portugal are using this process to recover uranium, a heap has operated in Australia to recover copper and there are several other examples for recovery of copper (Corrans, Harris and Ralph 1972).

Attention has been mainly directed towards bacteria that grow in a strongly acidic environment (pH 2 to 3) such as *Thiobacillus thiooxidans* and *Thiobacillus ferrooxidans*. However, there is every indication that, with suitable development, the method could be extended to more neutral and possibly alkaline conditions. The actual mechanism by which the bacteria achieve mineral oxidation is still not fully understood and elucidation of the reactions may enable the tailoring of bacteria to particular environments for maximum efficiency.

The overall kinetics for leaching uranium is a function of the nature of the ore and the host rock, the rock size, the dimensions and construction of the heap, the concentration of major bacterial nutrients such as pyrites, oxygen and carbon, as well as the presence of minor nutrients such as phosphorus, potassium and ammonia. The pH, $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio, percolation rate and temperature are also controlling parameters. The role of each parameter has not been rigorously defined and there is no universal rate equation. Consequently the present state of the art requires that developmental research be carried out on each ore to quantify the optimum leaching conditions.

Fortunately, laboratory testing does not require extensive apparatus and the optimum condition may be identified with a relatively small research effort.

Current industrial heaps tend to operate for 5 to 7 years. However, with the development of counter-current methods, it may be possible to reduce this time to weeks.

Bacterial oxidation of pyrites can be a major cause of pollution at mine sites and future mining development should take this into account.

6. REFERENCES

- Alexandre, D. and Michel-Briand, Y. (1967) - *Ind. At.*, 11, (11-12), 47.
- Andersen, J.E. and Allman, M.B. (1968) - *Proc. Australas. Inst. Min. Metall.*, (225), 27.
- Anon. (1967) - *Eng. Mining J.*, 168, 75.
- Audsley, A. & Daborn, G.R. (1963a) - *Inst. Min. Metall., Trans.*, 72, 235.
- Audsley, A. & Daborn, G.R. (1963b) - *Inst. Min. Metall., Trans.*, 72, 247.
- Bergey (1957) - 'Bergey's Manual of Determinative Bacteriology', ed. Breed, R.S., Murray, E.G.D. & Smith, N.R., pub. Williams & Wilkins, Baltimore, USA.
- Brierley, C.L. & Murr, L.E. (1973) - *Science*, 179, 488.
- Browning, S.J. (1972) - *Australian Mining*, (5), 48.
- Byrne, S.J. (1957) - *Simposia de la Sociedad Europea de Energia Atomica* (Lisboa-Guarda).
- Cameron, J. (1963) - *Discussion on Natural Leaching of Uranium Ores, Trans. Inst. Min. Metall.*, 72, (7), 507.
- Cecchetto, A.M., Coppa, R.C., Boca, R.D., Licha, A. & Stipanovic, P.N. (1964) - *A/Conf. 28/P/768*.
- Cordero, G., Gasos, P., Merino, J.L. & Suarez, E. (1966) - USAEC A.E.C.-tr-6850.
- Cordero, G., Villarrubia, M. & Hernandez, J. (1973) - Report No. JEN 276.
- Corrans, I.J., Harris, B. & Ralph, B.J. (1972) - *J. S. Afr. Inst. Min. Metall.*, 72, 221.
- Gonzalez, E. & Sedano, A. (1973) - Report No. JEN 272.
- Goren, M.B. (1966) - U.S. Patent 3268, 288.
- Gow, W.A., McCreedy, H.H., Ritcey, G.M., McNamara, V.M., Harrison, V.F. & Lucas, B.A. (1971) - IAEA-SM-135/3.
- Harrison, V.F., Gow, W.A. & Hughson, M.R. (1966) - *J. Met.* 18, 1189.
- Hernandez, J., Cordero, G. & Villarrubia, M. (1973) - Report No. JEN 271.
- IAEA (1972) - *Coordination Meeting on Bacterial Leaching of Uranium Ores, Hacettepe University, Ankara, 11-15 Dec. 1972*.
- Keenan, E.A. (1969) - Ph.D. Thesis 'Bacterial Beneficiation of Uranium Materials', Univ. of NSW, Australia.
- Kelly, D.P. (1971) - *Ann. Rev. Microbiol.*, 25, 177.

- Lacey, D.T. & Lawson, F. (1970) - *Biotechnol. Bioeng.*, 12 (1), 29.
- Lees, H. (1962) - *Bacteriol Rev.*, 26, 165.
- Li, S.H. & Parr, S.W. (1926) - *Industr. Engng. Chem. (Industr.)*, 18, 1299.
- Lloyd, P.J. (1971) - 'The Recovery of Uranium', *Proc. Symp. Sao Paulo*, 17-21 Aug. 1970, pub. IAEA, Vienna, paper IAEA-SM-138/31.
- Lundgren, D.G. Vestal, J.R. & Tabita, F.R. (1970) - *The Microbiology of Mine Drainage Pollution*, Chapter 4 of *Water Pollution Microbiology*, ed. Mitchell, R., Wiley - Interscience.
- McCreehy, H.H., Harrison, V.F. & Gow, W.A. (1969) - *Can. Mining Met. Bull.*, 62, 135.
- McGregor, R.A. (1966) - *Can. Inst. Mining Met., Trans.*, 60, 162.
- McGregor, R.A. (1968) - *Amer. Nucl. Soc., Trans.*, 11, 123.
- McGregor, R.A. (1969) - *Nucl. Appl.*, 6, 68.
- Malouf, E.E. & Prater, J.D. (1961) - *J. Metals*, 13, 353.
- Merino, J.L. & Saez, R.Ma. (1973) - Report No. JEN 273.
- Merritt, R.C. (1971) - 'The Extractive Metallurgy of Uranium', Colorado School of Mines Research Institute, USA.
- Miller, R.P., Napier, E. & Wells, R.A. (1963) - *Inst. Min. Metall., Trans.*, 72, (4), 217.
- Moss, F.J. & Andersen, J.E. (1968) - *Proc. Australas. Min. Metall.*, 225, 15.
- Mouret, P. & Pottier, P. (1961) - *Energie Nucleaire*, 3 (4), 251.
- Mouret, P. (1971) - 'The Recovery of Uranium', *Proc. Symp. Sao Paulo*, 17-21 Aug. 1970, pub. IAEA, Vienna, page 239.
- Mrost, M. & Lloyd, P.J. (1971) - 'The Recovery of Uranium', *Proc. Symp. Sao Paulo*, 17-21 Aug. 1970, Vienna, paper IAEA-SM-135/32.
- Pings, W.B. (1968) - *Colorado School of Mines Mineral Industries Bulletin*, 11, 1.
- Pourbaix, M. (1966) - 'Atlas of Electrochemical Equilibria in Aqueous Solutions', Pergamon, London.
- Ralph, B.J. (1975) - UNSW, Private Communication.
- Schaeffer, W.I. & Umbreit, W.W. (1962) - *J. Bacteriology*, 85, 492.
- Shively, J.M. Decker, G.L. & Greenwalt, J.W. (1970) - *J. Bacteriology*, 101 (2), 618.
- Silverman, M.P. & Ehrlich, H.L. (1964) - *Adv. in Appl. Microbiol.*, 6, 153.
- Silverman, M.P. & Lundgren, D.C. (1959) - *J. Bacteriology*, 77, 642.
- Taylor, H.J. & Whelan, P.F. (1943) - *Inst. Min. Metall., Trans.*, 52, 35.
- Wells, R.A. (1957) - *Simposia de la Sociedad Europea de Energie Atomica* (Lisboa-Guarda, 1957).
- Wenberg, G.M., Erbisch, F.H. & Volin, M.E. (1971) - *Soc. Min. Eng., Trans.*, AIME, 270, 207.

TABLE 1
SOME AUTOTROPHIC BACTERIA

NAME	ACTION	pH RANGE
<i>Thiobacillus thiooxidans</i>	Sulphide Sulphur Thiosulphate Tetrathionate	→ Sulphate 0.5 ↔ 6.0
<i>Thiobacillus ferrooxidans</i>	Thiosulphate Ferrous	→ Sulphate → Ferric 2.5 ↔ 5.8 can adapt to lower pHs
<i>Ferrobacillus ferrooxidans</i>	Ferrous	→ Ferric 2.2 ↔ 4.6
<i>Thiobacillus thioparus</i>	Sulphur Thiosulphate	→ Sulphate 4.5 ↔ 7.8
<i>Thiobacillus concretivorus</i>	Sulphide Sulphur Thiosulphate Tetrathionate	→ Sulphate 2.0 ↔ 6.0
<i>Thiobacillus novellus</i>	Thiosulphate	→ Sulphate 5.0 ↔ 9.0
<i>Thiobacillus coproliticus</i>	Thiosulphate	→ Sulphate slightly alkaline
<i>Thiobacillus neapolitanus</i>	Sulphide Sulphur	→ Sulphate 3.0 ↔ 8.5
	Thiosulphate	→ Tetra- thionate Sulphate
	Tetrathionate	→ Sulphate
<i>Thiobacillus intermedius</i>	?	alkaline

TABLE 2
ELECTRODE POTENTIALS AND
FREE ENERGIES OF CERTAIN CO-ENZYME SYSTEMS

	E°, v	$\Delta E^{\circ}, v$	ΔG°
			kJ/pair
NADH + H ⁺	-0.32		
		0.10	- 19.3
FADH ₂	-0.22		
		0.18	- 34.7
Cytochrome <i>b</i>	-0.04		
		0.29	- 56.1
Cytochrome <i>c</i> (<i>Pseudomonas aeruginosa</i>)	+0.25		
		0.035	- 6.7
Cytochrome <i>a</i> ₃	+0.285		
		0.531	-102.1
Hydrogen	-0.414		
Transfer of 2 e from H ₂ to ½ O ₂		1.230	-237.3
NADH + H ⁺ } NADPH + H ⁺ } Transfer of 2 e to ½ O ₂		1.14	-219.8
Cytochrome <i>c</i> ₁ (<i>Pseudomonas aeruginosa</i>)	+0.225		
Cytochrome <i>c</i> (<i>Pseudomonas denitrificans</i>)	+0.32		
Cytochrome <i>c</i> (<i>Micrococcus denitrificans</i>)	+0.25		
Cytochrome <i>c</i> ₄ (<i>Azotobacter vinelandii</i>)	+0.30		
Cytochrome <i>a</i>	+0.29		

TABLE 3
SILVERMAN 9K NUTRIENT
(Silverman & Lundgren 1959)

Constituent	Concentration, g l ⁻¹
FeSO ₄ · 7H ₂ O	44.2
(NH ₄) ₂ SO ₄	3.0
K ₂ HPO ₄	0.5
KCl	0.1
MgSO ₄ · 7H ₂ O	0.5
Ca(NO ₃) ₂ · 4H ₂ O	0.2
H ₂ SO ₄	To desired pH

TABLE 4
BACTERIAL TOLERANCE
(Pings 1968 & Goren 1966)

Constituent	Maximum Tolerance (g l ⁻¹)
U as U ₃ O ₈	25
Fe as Fe ²⁺	25
Zn	20
Cu	15
Al	10
Ca	10
Mn	4
Mg	3
V as VO ₅	0.5
Mo	0.2
pH	0.5

TABLE 5
INFLUENCE OF BACTERIA ON URANIUM EXTRACTION
FROM BICA ORE + 2% PYRITE
 (Audsley and Daborn 1963a)

Ore	Water	Inoculation	% Extraction
Sterilised	Sterilised	No	42
Sterilised	Sterilised	Yes	65
Not sterilised	Not sterilised	Yes	78
Not sterilised	Not sterilised	No	85

TABLE 6
URANIUM EXTRACTED BY RECIRCULATED
WATER THROUGH BICA ORE + 2% PYRITE
AFTER 20 WEEKS
 (Audsley & Daborn 1963b)

Particle Size	Percentage Uranium Extracted		
	- 13 mm	- 6.5 mm	- 3 mm
Depth cm			
27	53	76	64
54	70	80	60
108	66	65	66
162	51	50	45

TABLE 7
INFLUENCE OF ROCK AND PARTICLE SIZE
ON URANIUM SOLUBILISATION
 (Cordero et al 1966)

Rock	Particle Size mm	% U Extracted
Granite	- 5	93.4
	- 12	95.3
Sandstone	- 5	98.3
	- 12	91.8
Shale	- 12	83.2
	- 25	85.3

TABLE 8a NOTES

- (1) The Urgeirica ore was the Portuguese ore in which excessive uranium leaching, due to bacterial activity, was first noticed. The host rock was principally inert silicates with up to 5% pyrite dispersed through it along with 0.1% U₃O₈ principally as uraninite, UO₂. The pyrite was found to support *Thiobacillus thiooxidans* and *Ferrobacillus ferrooxidans* bacteria.
- (2) The Bica ore was also a Portuguese ore with a similar host rock structure. The uranium (0.15% U₃O₈) occurred mainly as secondary minerals chiefly metatorbernite with some pitchblende. The pyrite was present at less than 1%, together with some finely divided iron oxides, galena, chalcopyrite and marcasite. There was enough pyrite to support the *Thiobacillus thiooxidans* and *Ferrobacillus ferrooxidans* bacteria in the natural state.
- (3) The Valinhas ore was also from Portugal and the host rock was similar to the Urgeirica and Bica ores. The uranium (0.14% U₃O₈) was predominantly present as pitchblende. There was very little pyrite (less than 0.5%), but significant quantities of calcite. This made it a fairly basic ore and in the natural state was found to support the bacteria *Thiobacillus thiooporus*.
- (4) The Dyson's ore came from Rum Jungle. The host rock was principally quartz and hematite in which the uranium (0.27% U₃O₈) was principally dispersed as a secondary mineral. There was no pyrite and the ore was not reported to support bacteria.
- (5) The Mary Kathleen ore had a similar mineralogical composition although the uranium (0.36% U₃O₈) was principally present as uraninite. There was no pyrite and the ore was not reported to support bacteria.
- (6) The Umtali ore came from Southern Rhodesia. The uranium (1.25% U₃O₈) was principally present as pitchblende, and it was intergrown with hematized calcite and contained within calcite veins. The ore contained some chalcopyrite and up to 2% calcite which made it a very basic ore. It was not reported to support bacteria.
- (7) The Elliot Lake ore from Canada is similar to the Urgeirica ore, the host rock being principally quartz. It has a very high percentage of pyrite, 5-10%, in some cases 15%. The uranium was principally present as the refractory mineral brannerite together with some primary minerals, uraninite and coffinite. The ore was found to support bacteria of the *Ferrobacillus Thiobacillus* group.
- (8) The Witwatersrand slimes are the tailings from the Witwatersrand gold fields after treatment for extraction of gold. They tend to be principally inert silica fines with a sulphur content of 3%, principally as pyrite. The slimes support *Thiobacillus ferrooxidans* bacteria.

TABLE 8a
MINERALOGY OF VARIOUS ORES

	Urgeirica ^a (1)	Bica ^a (2)	Valinhas ^a (3)	Dyson's ^a (4)	Mary ^a Kathleen (5)	Umtali ^a (6)	Elliot ^b Lake (7)	Witwatersrand ^c Slimes (8)
Uranium Mineralisation								
uraninite	P	S	P		0.4	0.8	S	
autunite	S							
torbernite	S							
metatorbernite		P	S					
sklodowskite type				0.4				
β-buranophane					0.1	0.2		
brannerite							P	
U ₃ O ₈	0.1	0.15	0.14	0.27	0.3-0.36	1.25	0.07-0.15	0.005-0.02
Sulphur Mineralisation								
pyrite	S	l	0.5				5-10%	P
marcasite		tr	tr			S		tr
chalcopyrite		tr	tr					
galena		tr	tr					
Sulphur								3
Iron Oxides		tr	tr	30-35	4-5	40		
Host Rock								
silicate	P	P	P	60-65	90-95	55-60	P	P
phosphate					2	tr		
carbonate			S			2		

P Principal component; S Secondary component; tr trace component, all other concentrations expressed as percentages.

^a Audsley and Baborn (1963a, b); ^b McGregor (1969); ^c Mroost and Lloyd (1971), Lloyd (1971).

TABLE 8b
Cordero et al. (1966)

	Los Ratones	Penascal	Deposit A	Deposit B	Eureka
Uranium Mineralisation	pitchblende autunite	autunite black oxides	pitchblende coffinite koracite gummities uranotile	coffinite pitchblende uranotile autunite fosfuranilita	pitchblende tucholites gummities carnotite
Gangue	pyrite	pyrite marcasite	calcite iron sulphides limonite	pyrite	calcite siderite pyrite chalcosite malachite azurite
Chemical Composition U ₃ O ₈ %	0.18	0.23	0.062	0.043	0.172
Oxidised S	0.58	0.12	0.21	0.15	0.08
Total S	0.95	1.19	1.64	0.42	0.70
Total Fe	1.43	1.42	4.45	3.90	1.40
P ₂ O ₅	0.31	1.14	0.04	0.08	0.03
CO ₃	0.07	0.60	0.20	0.06	4.85
Ca	0.81	0.76			0.60
Mg	0.25	0.57			0.48
Cu					0.73
Rock Matrix	granite	granite	shale	shale	sandstone

TABLE 8c

Mouret and Pottier (1961)

Ore	%U	% Uranium Extracted			
		3% Pyrite	pH 2	pH 2 and Fe ²⁺	5 g Na ₂ CO ₃
Primary uranium ores, pyrite, some calcite	0.16	79	88	88	
0.13% calcite, primary uranium ores	0.13	33	41	89	68
1.5% calcite, pyrite, primary uranium ores	1.56	3		73	
Primary uranium ores, pyrite	0.63	50		90	
Phosphates, secondary uranium ores	0.095	0.5		32	10
Quartz, pyrite, iron oxides, secondary uranium ores	0.075			96	
Secondary uranium ores	0.079	69	14		
Quartz, feldspar, mica, pyrite secondary uranium ores	0.43	85	73		
Primary uranium ores, calcified	0.23		54		
Quartz, iron oxide, pyrites, asphalt. Uranium distributed through the organics	0.19				62

TABLE 9

TIME LAG BEFORE EFFECTIVE URANIUM EXTRACTION

From the data of Miller, Napier and Wells (1963) and Audsley and Daborn (1963b).

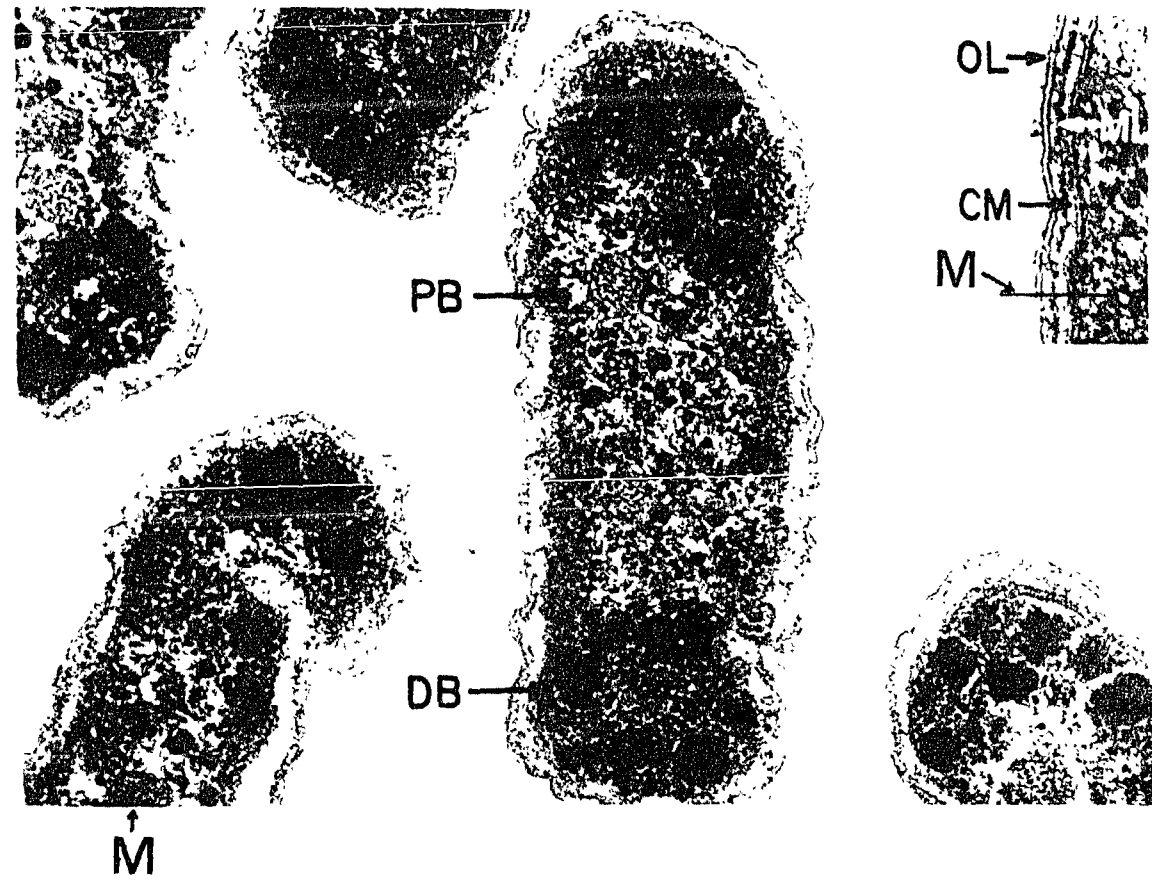
Ore	Basicity	Time Lag (weeks)
Urgeirica	acidic	Nil
Dyson's	neutral	10
Mary Kathleen	neutral	10
Umtali	basic	>60

TABLE 10

EFFECT OF EXCESSIVE FERROUS SULPHATE ADDITION

(Cordero et al. 1966)

Ore	Host Rock	Particle Size (mm)	% Pyrite	% FeSO ₄ ·7H ₂ O	pH Range	Time (weeks)	% U Extracted
Carretona	Granite	<17	4.0	7.1	2.5-1.9	72	41.2
Carretona	Granite	<17	4.5	3.0	2.9-1.9	72	47.3
Rateones	Granite	<12	-	10.0	2.7-1.2	22	90.1
Rateones	Granite	<12	-	5.0	2.7-1.2	22	92.3



PB polyhedral bodies, DB dense bodies; insert of cell wall, OL outer layer of lipopolysaccharide and lipoprotein, ML middle layer and CM the cytoplasmic membrane. M are 100 nm marker bars.

FIGURE 1. ULTRASTRUCTURE OF THIOBACILLUS THIOOXIDANS
 (After Shively, Decker and Greenwalt, 1970)

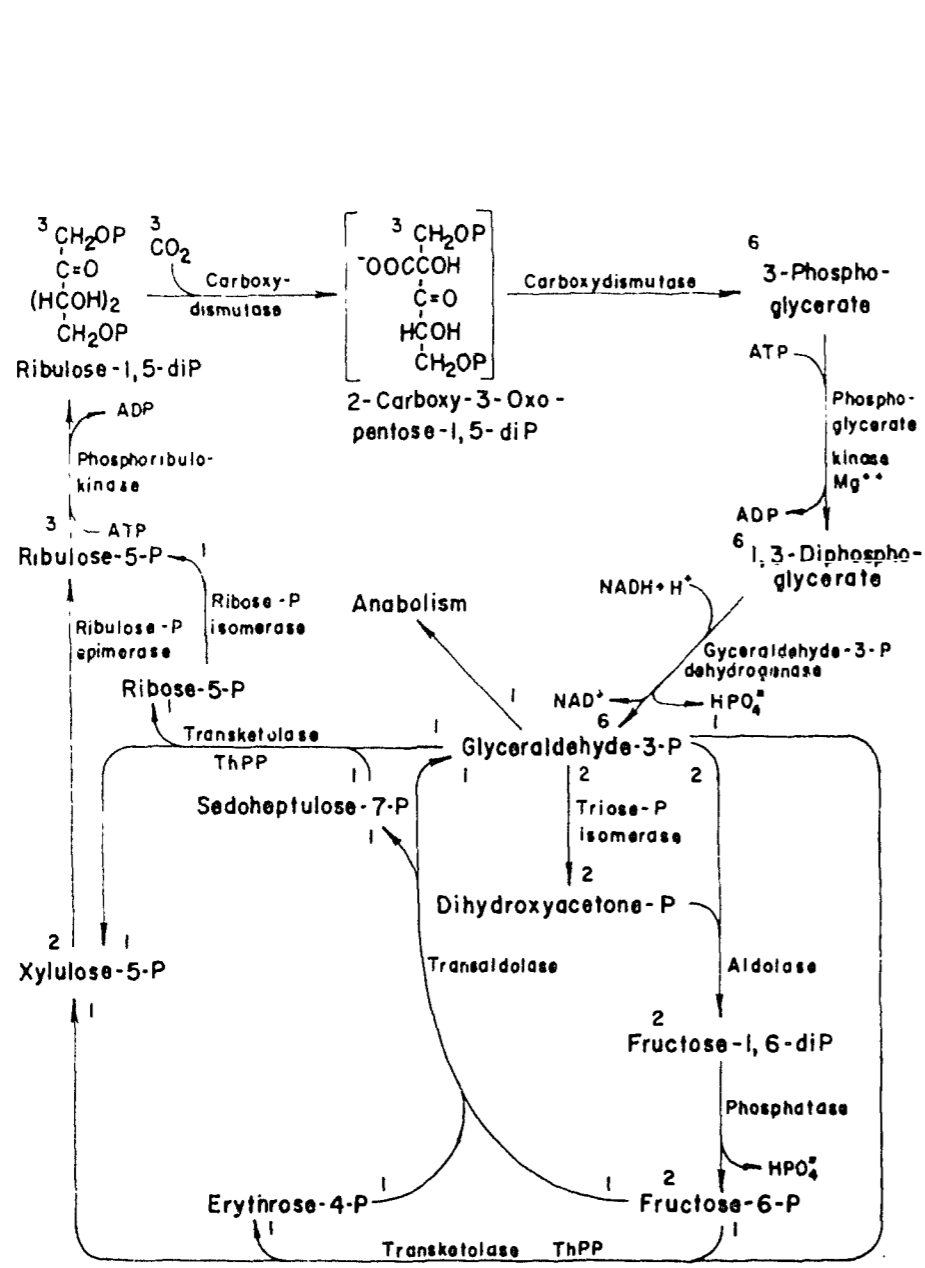


FIGURE 2. THE CALVIN CYCLE

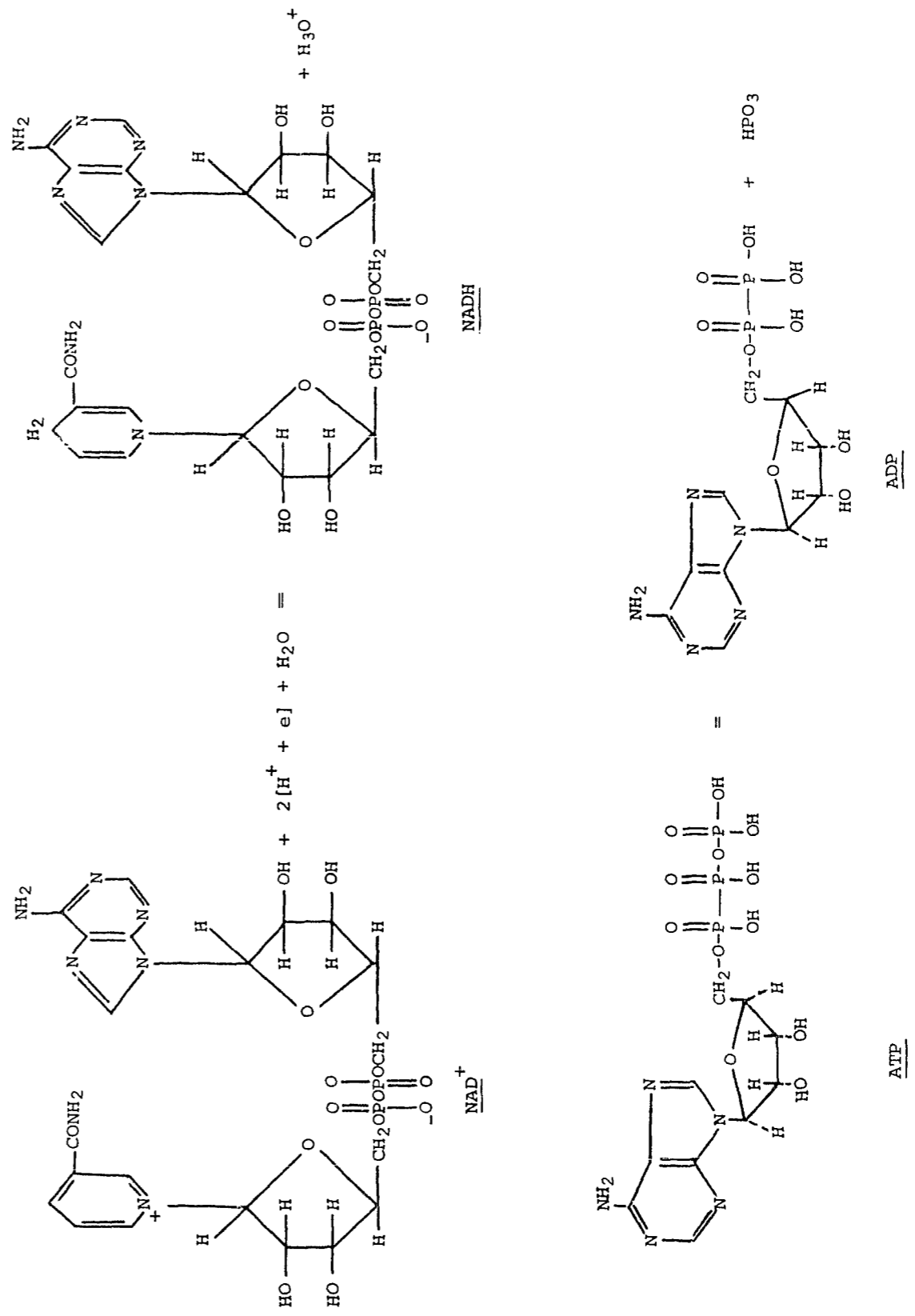


FIGURE 3. THE CO-ENZYMES NAD AND ADP

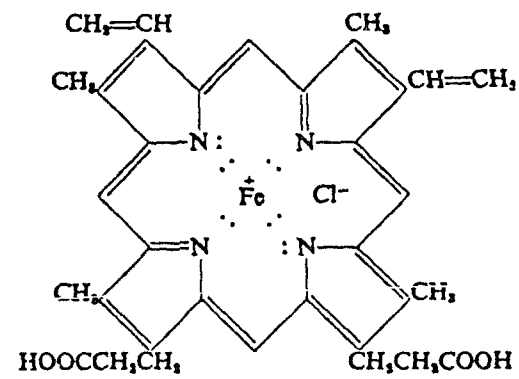


FIGURE 4. THE CYTOCHROME, HEMIN

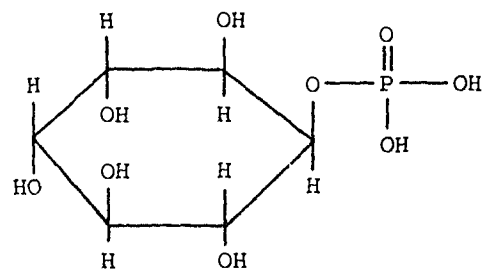


FIGURE 5. PHOSPHATIDYLINOSITOL

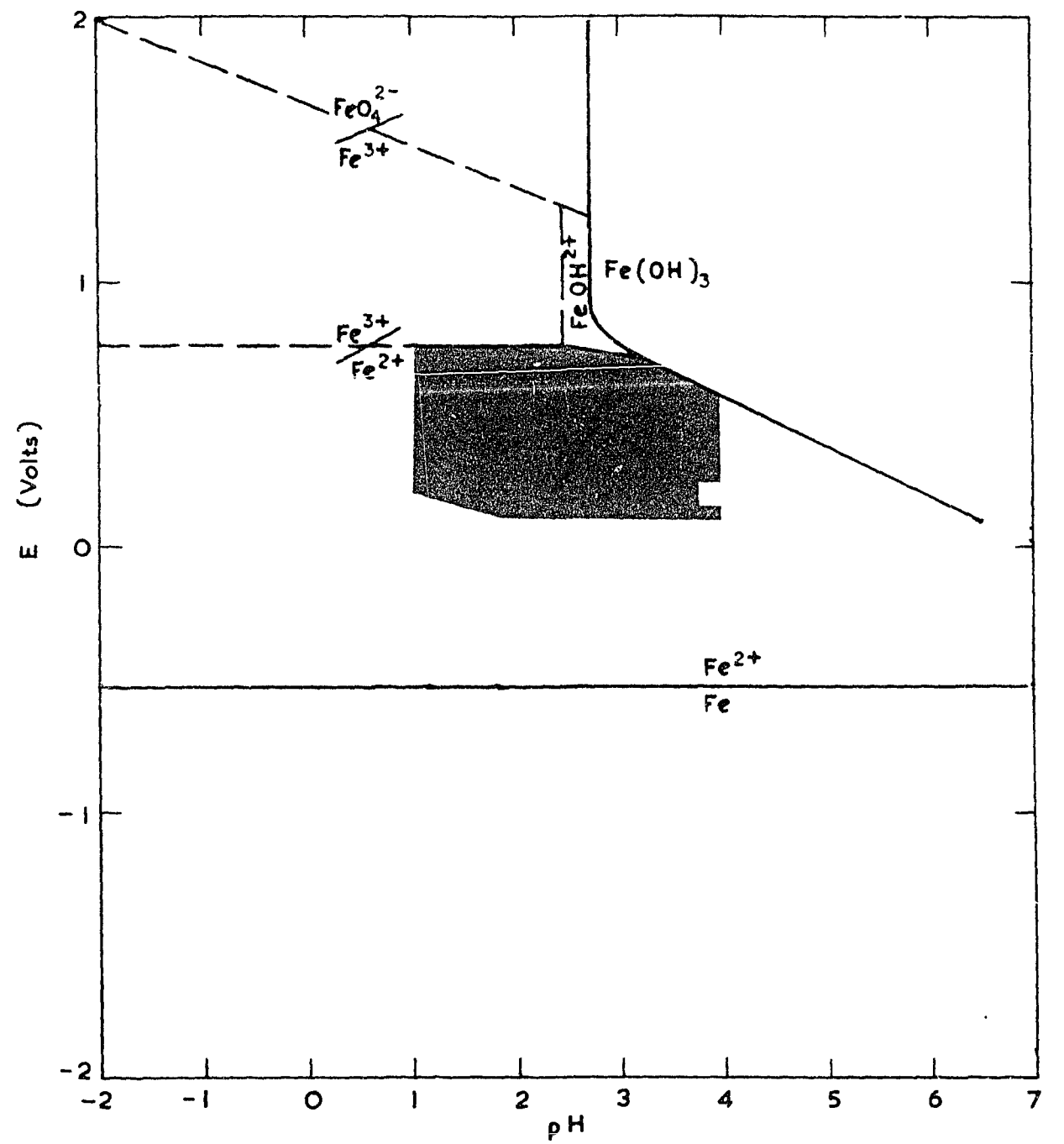


FIGURE 6. POTENTIAL-pH DIAGRAM FOR Fe-U-H₂O SYSTEM AT 25°C IONIC CONCENTRATIONS 10⁻³ M FOR ALL AQUEOUS SPECIES

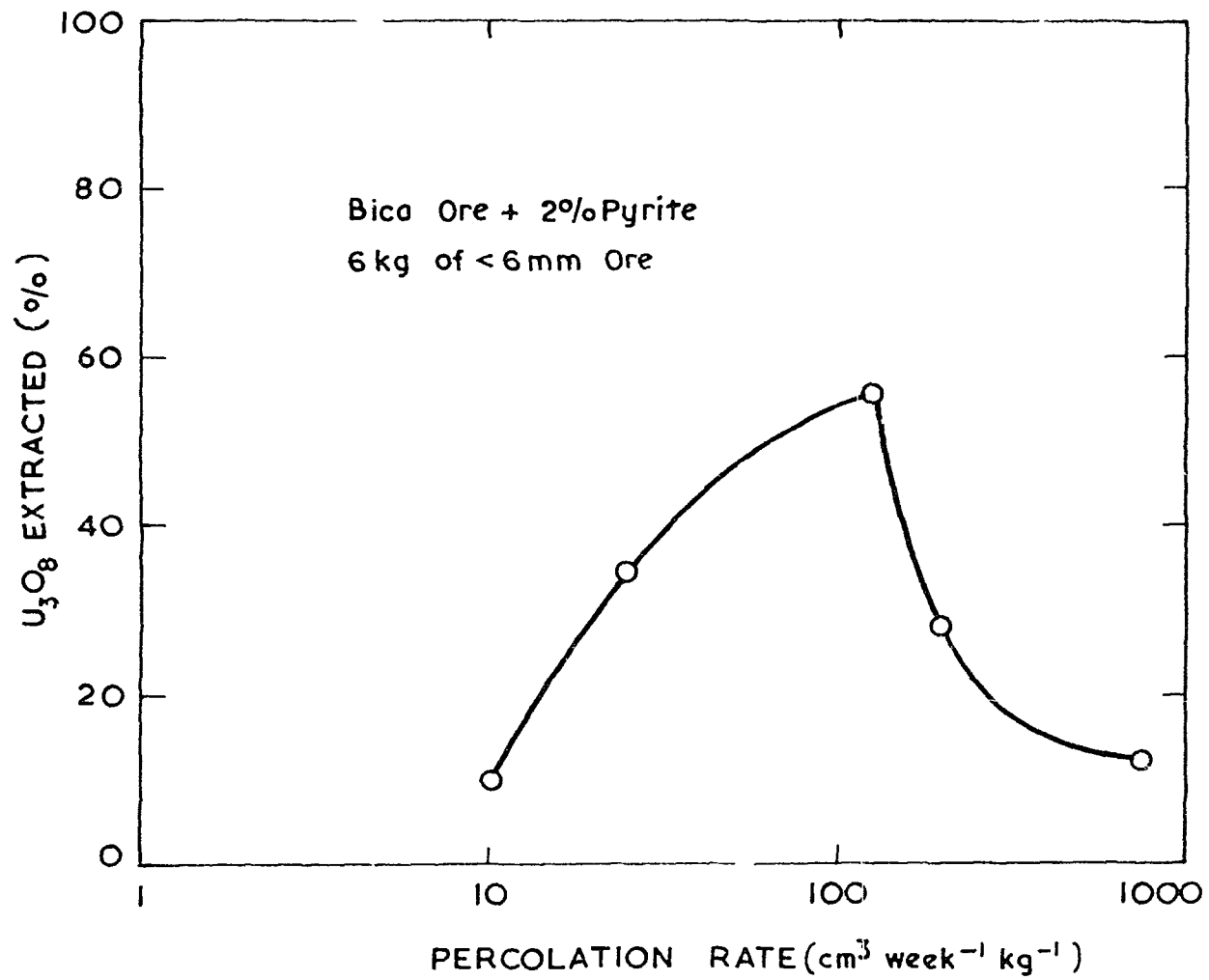


FIGURE 7. URANIUM EXTRACTED AFTER 10 WEEKS AS A FUNCTION OF PERCOLATION RATE (After Audsley and Daborn 1963a)

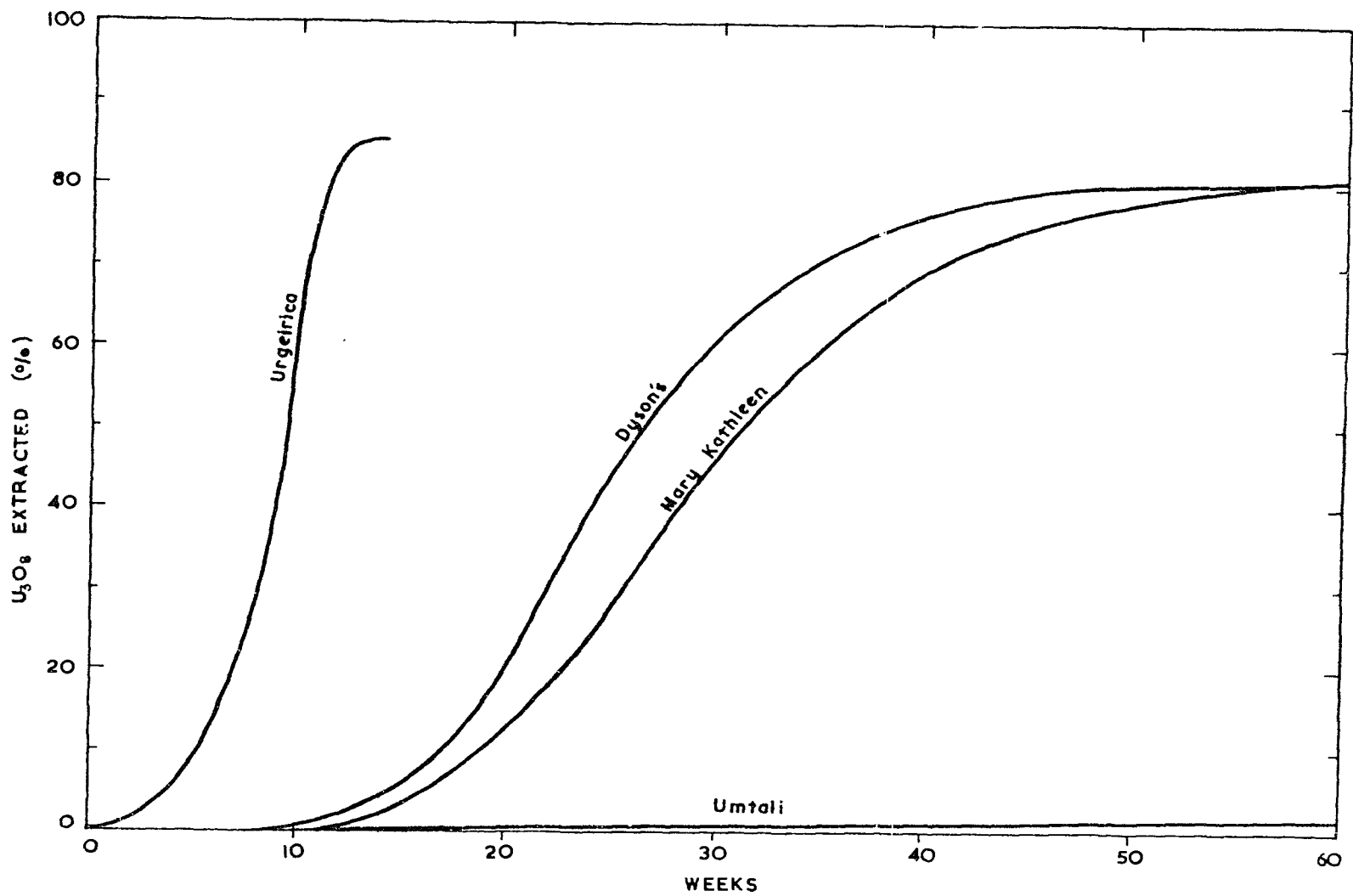


FIGURE 8. URANIUM EXTRACTED FROM VARIOUS ORES AS A FUNCTION OF TIME (After Miller, Napier and Wells 1963, Audsley and Daborn 1963b)

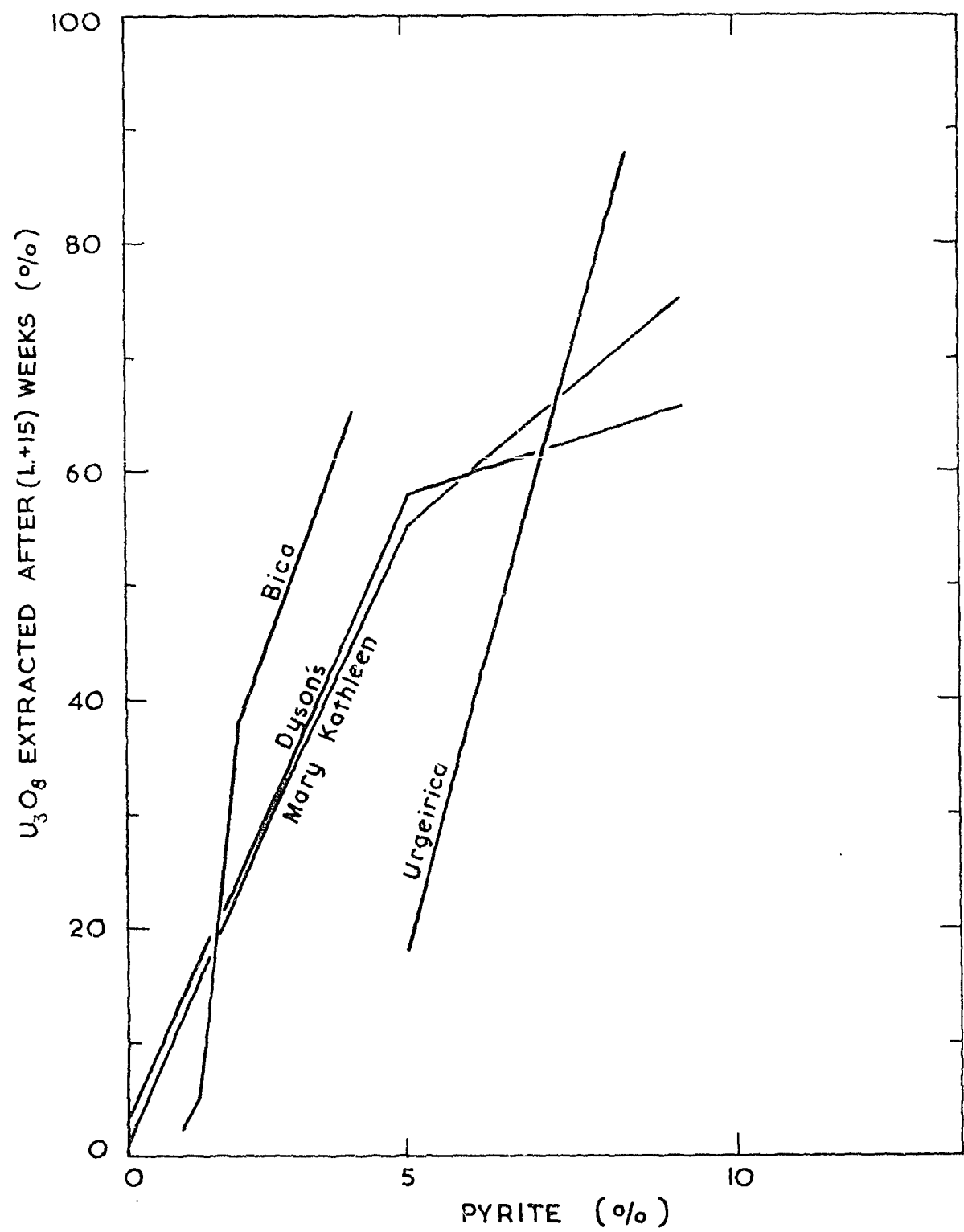


FIGURE 9. URANIUM EXTRACTED AFTER (L+ 15) WEEKS AS A FUNCTION OF PYRITE CONCENTRATION (After Miller, Napier and Wells 1963, Audsley and Daborn 1963b)

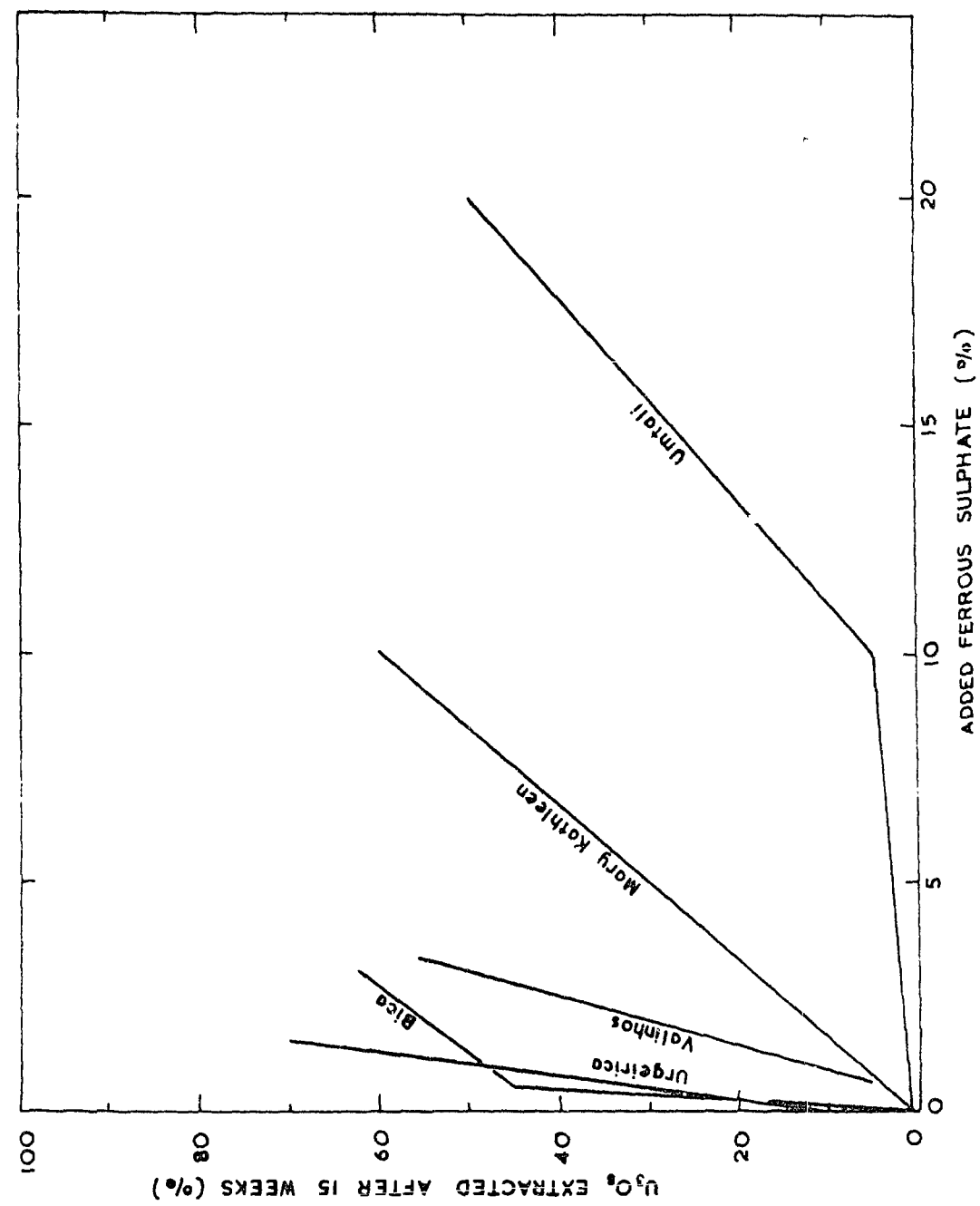


FIGURE 10. URANIUM EXTRACTED AFTER 15 WEEKS AS A FUNCTION OF ADDED $FeSO_4$ (After Miller, Napier and Wells 1963, Audsley and Daborn 1963b)

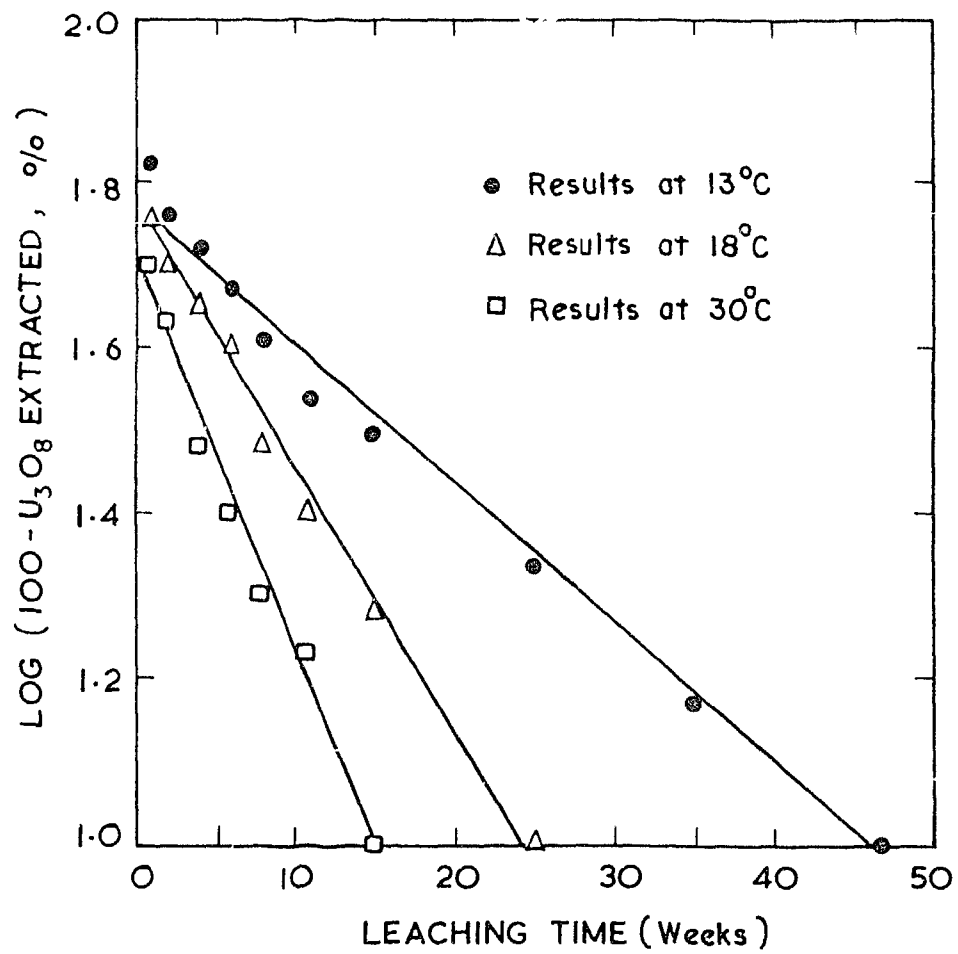


FIGURE 11. URANIUM EXTRACTED AS A FUNCTION OF TIME AND TEMPERATURE (After Gow et al 1971)

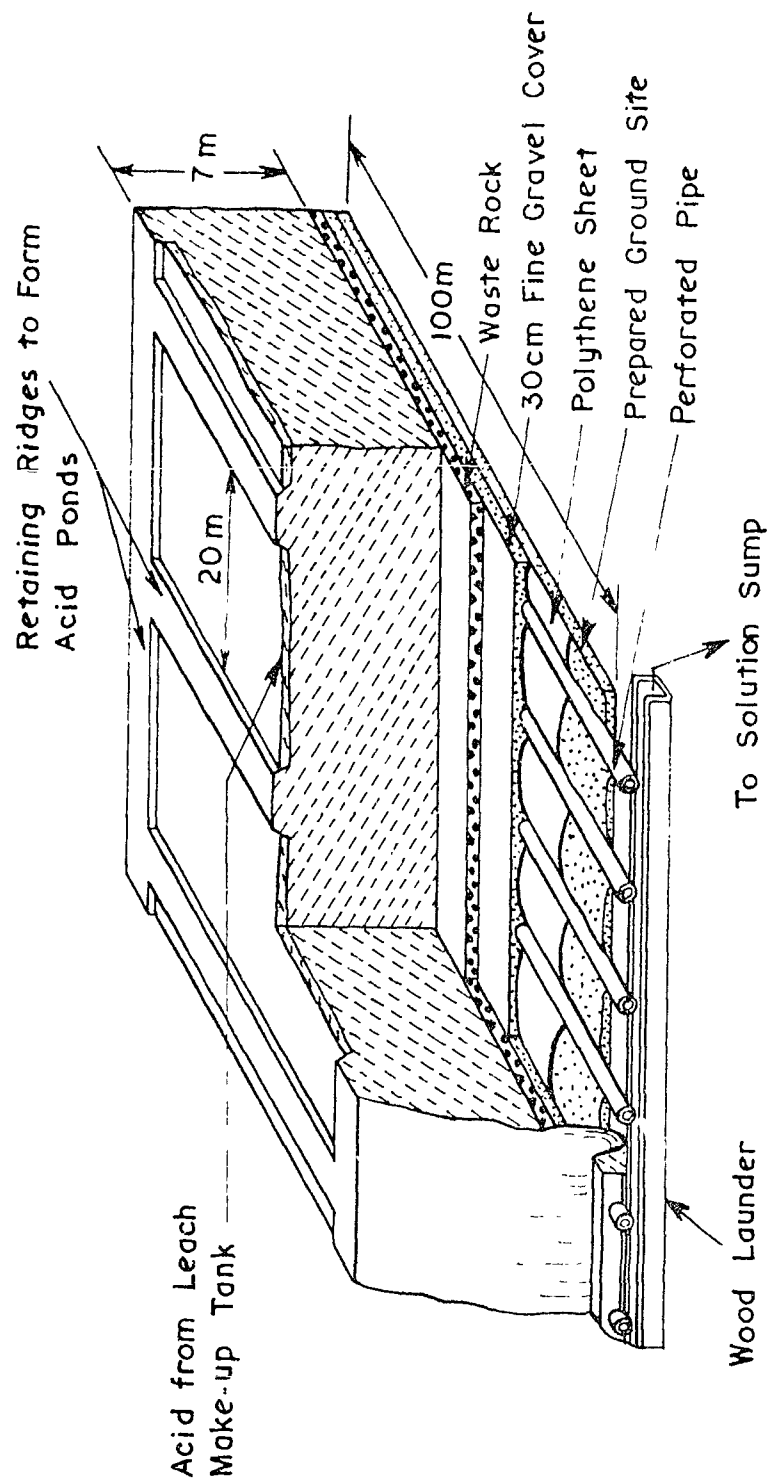


FIGURE 12. SCHEMATIC DIAGRAM OF AN INDUSTRIAL HEAP (After Merritt 1971)