A study of the bioleaching of a Spanish uranium ore. Part I: A review of the bacterial leaching in the treatment of uranium ores

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Abstract

The rapid growth of the nuclear power industry has led to the progressive exhaustion of high grade reserves of uranium ores and new extraction techniques have had to be developed for use with low grade ores. The expense of these techniques is, of course, important and one of the solutions proposed has been percolation leaching with the active participation of micro-organisms. This paper intends to give a general overview of the phenomenon of uranium ore bioleaching, in which a wide variety of bacterial species intervene in symbiotic association. Microbiological activity inside the heap is conditioned by its mineral composition and environmental and operational factors must also be taken into account. The industrial application of these techniques, particularly in Spain, is studied.

1. Introduction

Uranium, which until 1939 had always been considered as a by-product in the extraction of radium, acquired the status of a strategic metal when the properties of U$^{235}$ were discovered. From the beginning of the 1970s uranium extraction metallurgy developed parallel to the development of new nuclear industries.

The principal aim of uranium ore treatment is to obtain concentrates of uranium with a U$_3$O$_8$ content of above 90%. The small quantity of fissionable material (U$^{235}$) found in the ores means that the concentrate must be enriched so that the content of U$^{235}$ increases from 0.71% to approximately 3%. The cost to the nuclear power industry of these steps (the metallurgical production of U$_3$O$_8$ and its enrichment) represents 6–12% of the total production costs [1]. However, before being able to work with the nuclear fuel itself it is, of course, neces-
Deposit

MINING OPERATION
Ores selection by radiometric control

Submarginal ore
- Blasting
- Bulldozing
- Percolation leaching
  - In-situ
  - Dump leaching

Low-grade ore
- Fine grinding
  - Stirred leaching
    - Heap leaching
    - Vat leaching

High-grade ore
- Fine grinding
  - Grinding
  - Stirred leaching
    - Stirred tanks
    - Solid/Liquid Separation
    - Clearing

Leach liquor
- Uranium concentration
- Precipitation
- Thickening and drying

Concentrate of U₃O₈ (Yellow cake)
- Refining

Fig. 1. Flow sheet for the treatment of uranium ores.
sary to obtain the first concentrate and, for this, the ore is usually processed in the manner shown in the flow sheet in Fig. 1.

The solubilization technique used in this process depends on the \( \text{U}_3\text{O}_8 \) content of the ore: a stirred tank is used for high grade ores and percolation leaching for low grade ores. The mineralogical characteristics of the ore also decide the type of operation: either acid or alkaline, depending on the gangue in which the metal is found. Sulphuric acid is the most common leaching agent used in the extraction of uranium [2]. The large quantities of low grade ores from new mines and from the exhaustion of old mines, the increase in the processing costs and a fall in uranium prices has meant that percolation leaching methods have tended to replace stirred methods [3].

As is to be expected, the percolation leaching of ores in which the gangue predominates leads to lower yields and longer dissolution times. Yields fall from 100% to 80%, while attack times increase from several hours to periods in excess of 1 yr [4]. However, the same chemistry is involved in percolation and stirred leaching processes.

2. Chemical reactions

In the leaching of uranium ores with an acidic gangue, ferric acid solutions are used [5]. Because of its reactivity, uranium is found in a great variety of ores, of which only a few are of any economic importance. Among these are uraninite and pitchblende, which represent different crystalline forms of \( \text{UO}_2 \) in vein deposits. In the former, substantial quantities of other elements (Th, Pb and rare earths) are also found while their presence in pitchblende is minimal.

Pitchblende, the principal uranium ore, has the ideal composition, \( \text{UO}_2 \), although no mineral occurs naturally in this form because it is always partially oxidized, with the \( \text{U}^{4+} \) converted to \( \text{U}^{6+} \). This degree of oxidation can reach 60% [6]. When the mineral is over-oxidized (\( \text{U}^{6+} > \text{U}^{4+} \)) the term gummite is used. Hexavalent uranium is rapidly solubilized in an acidic medium such as uranyl ion while the solubilization of tetravalent uranium requires a previous oxidation step to \( \text{U}^{(VI)} \) with ferric ion:

\[
\text{UO}_3 + 2\text{H}^+ \rightarrow \text{UO}_2^{2+} + \text{H}_2\text{O} \quad (1)
\]

\[
\text{UO}_2 + 3\text{Fe}^{3+} \rightarrow \text{UO}_2^{3+} + 3\text{Fe}^{2+} \quad (2)
\]

The presence of sulphate as complexing agent of the uranyl ion is very important:

\[
\text{UO}_2^{2+} + 3\text{SO}_4^{2-} \rightarrow [\text{UO}_2(\text{SO}_4)_3]^{4-} \quad (3)
\]

Its absence favours precipitation of the metal by the following hydrolysis reaction:

\[
\text{UO}_2^{2+} + 3\text{H}_2\text{O} \rightarrow \text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O} + 2\text{H}^+ \quad (4)
\]

According to the literature [8,9] and from a thermodynamic point of view,
hydrolysis of the uranyl ion can be more easy than complexing reactions. However, in the presence of an excess of sulphate ion, complexing reactions can be kinetically favoured with regard to hydrolysis.

A pH of between 1 and 2 is considered suitable for pitchblende leaching [10]. In addition, for rapid uranium extraction kinetics, a high Fe$^{3+}/$Fe$^{2+}$ ratio is necessary, which largely determines the redox potential (Eh) of the solution. For the reaction to be effective it must reach a potential of above 400 mV, in accordance with the Pourbaix diagram (Fig. 2). That is to say, for this technique to be applied the Fe$^{2+}$ produced in reaction (2) must be re-oxidized to Fe$^{3+}$ and recycled. However, concentrations of Fe$^{3+}$ in excess of 3 g/l have no significant effect and it has been established that an Fe$^{3+}$ concentration of 1–2 g/l is normally sufficient for the effective dissolution of tetravalent uranium, with a minimum of 0.5 g/l [12].

At the industrial level, ferric iron regeneration is carried out by adding differ-

![Eh-pH diagram for U-H$_2$O system at 25°C and C = 10$^{-2}$ M.](image)

**Fig. 2.** Eh–pH diagram for U–H$_2$O system at 25°C and C = 10$^{-2}$ M.
cut chemical reagents which are strongly oxidizing and capable of maintaining the redox potential between 400 and 500 mV. The most commonly used oxidants for this have been sodium chlorate, NaClO₃ [13] and pyrolusite, MnO₂ [14]. However, these are expensive and represent a high percentage of the total costs of the process [15]. Another of the problems associated with this process is the environmental one, since the oxidants can release harmful impurities into the leaching circuit (V, Mo, silicic acid). Other, cleaner, oxidants have been suggested as alternatives: hydrogen peroxide [11,16] and permonosulphuric acid (Caro's acid—H₂SO₃). This latter reagent, although having the advantage of being liquid, thus involving no grinding costs, is even more expensive than pyrolusite. Hydrogen peroxide, which at 30°C is a more effective oxidant than the chlorate, can cause precipitation of the uranyl ion:

\[ \text{UO}_2^{2+} + \text{H}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{UO}_4^{2-} + \text{H}_2\text{O} + 2\text{H}^+ \]  

(5)

At the industrial level, hydrogen peroxide is, together with ammonia, one of the most commonly used reagents in the precipitation of uranium as U₃O₈.

3. Bioleaching as an alternative

The bioleaching of uranium ores arose from the need to develop economically viable processes in the treatment of low grade ores. Of the total cost of the process represented in Fig. 1, up to the point of obtaining the yellow cake of U₃O₈ (ADU, ammonium diuranate uranium), 75% is due to the first steps required to obtain the pregnant solution [1]. The importance of having a cheap leaching process can therefore be understood.

The capacity of the micro-organisms which take part in these transformations, principally bacteria of the genus *Thiobacillus* and *Leptospirillum* (Fig. 3), to grow in highly acidic environments with a high heavy metal content (U and Th in our case study) makes this technique a very interesting alternative to conventional processes. The only main drawback from a commercial point of view is the long contact time needed for the uranium solubilization; if environmental conditions are suitable, the process is autosufficient. In addition, savings of up to 50% of the operation costs of a conventional plant can be achieved [18].

The principle of the method lies in leaching the uranium ore with ferric sulphate produced from the pyrite of the ore by bacterial action and which, in turn, can be regenerated by the bacteria (Fig. 4). In other words, during the process the micro-organisms do not attack the uranium ore directly but create the chemical conditions necessary for its dissolution. Zajic [19], however, suggests that the bacteria might attack the uranium oxides directly since oxidation is more rapid in the presence of *thiobacilli* than of ferric iron alone. Recent calorimetric and respirometric research [20] supports this hypothesis, although the rate of such a reaction is 30 times less than that of the microbiological oxidation of the iron. Furthermore, the growth of *Thiobacillus ferrooxidans* or of any other iron-
Fig. 3. Transmission electron micrographs of bacteria involved in the dissolution process of uranium ores. (a) *Thiobacillus ferrooxidans*. (b) *Leptospirillum ferrooxidans*. (c) Sulfur-oxidizing microorganisms (*T3.2*) [67]. (d) Moderate thermophiles.
Fig. 4. Solubilization of pitchblende in a medium containing pyrites and *Thiobacillus ferrooxidans*. The pitchblende can be oxidized microbiologically: directly from U⁴⁺ to U⁶⁺ or indirectly through the Fe²⁺ produced by direct or indirect bacterial attack of the pyrite. The continuous lines indicate the reactions catalyzed by *Thiobacillus ferrooxidans*.

oxidant species using compounds of tetravalent uranium as the sole source of energy has not been described.

In addition, metallic ions may have a specific effect on the enzymes of the metabolic cycle of the micro-organism involved. For example, the uranyl ion (UO₂²⁺) inhibits iron oxidation and the fixing of the carbon dioxide, since it unites with the principal cell components [21]. Nevertheless, toxicity studies [22,23] have demonstrated that the tolerance of *T. ferrooxidans* to uranium can reach concentrations of up to 12 g of U₃O₈/l, similar to those in industrial installations [24]. *Leptospirillum ferrooxidans*, although less sensitive than *T. ferrooxidans* to uranium, can adapt to lower concentrations [25]. Pure cultures of *Thiobacillus thiooxidans* are generally more sensitive to metals in solution than the pure cultures of *T. ferrooxidans* and/or *L. ferrooxidans* [26].

Similarly to *thiobacilli* and *leptospirilli*, the heterotrophic bacteria can adapt to media containing uranium and thorium [27] and can take part, although indirectly, in the bioleaching process of uranium ores. Both fungi (e.g., *Penicillium*) and yeasts (e.g., *Rhodoturula*), like other heterotrophic organisms, act synergistically during leaching to remove the organic matter produced by the autotrophic micro-organisms. This is beneficial to the process since the organic compounds inhibit the growth of the *Thiobacillus* bacteria [28]. On the other hand, certain heterotrophs possess the capacity to accumulate metallic ions, such as uranium itself [29], although they can remove others, which, at certain concentrations, inhibit the growth of some important autotrophic species [27]. Other negative aspects of the presence of fungi and/or yeasts in the bioleaching media include...
their competitive participation in the consumption of oxygen and the secretion of certain organic compounds.

During the past few years, the presence of moderately thermophilic microorganisms capable of growing at temperatures of 45–50°C, which are easily reached in the centre of heaps [30], has been detected. Since 1977, many such organisms have been detected, among which are the genus *Sulfobacillus*. To these must be added extremely thermophilic bacteria capable of oxidizing sulphur, both autotrophically and heterotrophically, and which can grow at 60–80°C (temperatures reached in some industrial operations [25]). *Sulfolobus* is one of these bacteria.

The presence of anaerobic micro-organisms in the lower parts of the heaps is another real possibility, since zones of low or zero concentrations of oxygen can be expected to exist. Under these conditions and in the presence of a reducing agent, such as organic matter, anaerobic bacteria, such as *Desulfovibrio desulfuricans*, are capable of reducing the sulphate ions to sulphide with the consequent precipitation of insoluble metallic compounds.

This capacity to adapt to the environment, together with other influential factors such as pH, energy sources, the presence of organic compounds, etc., shape the bacterial composition of the mine waters of industrial installations until the optimal mix of micro-organisms is reached which is responsible for the bioleaching process. Table 1 shows the characteristics of the principal micro-organisms used in industrial bacterial leaching processes for uranium ores.

The literature [32–35] agrees that it is basically the indirect process which acts in this type of system since, during heap or dump leaching, the direct microbial oxidation of the uranium ores is not significant, as a consequence of the large quantities of ferric iron generated from the pyrite. That is to say, the bacterial leaching of uranium ores is a two-step process: the bacterial leaching of pyrite and the leaching of the uranium ore with the resulting metabolic products of the pyrite biological attack. In this way, the dissolution of the uranium-bearing ores can take place if the pyrite is attacked first.

### 4. Bioleaching and ore mineralogy

Although there has been no definitive study of the influence which the type of uranium ore has on bacterial leaching, the literature [35,36] suggests that the pyrite content of the ore is of fundamental importance. For this reason, this type of attack has not been widely used in the extraction of uranium from its ores since the technology is limited to minerals with a high sulphide content. The ores from eastern Canada are especially susceptible to this kind of process since pyrites is associated with the uranium. On the other hand, the uranium ores from New Mexico, the Rocky Mountains and southern Texas (USA), with their low pyrites content, are less suitable for bacterial leaching. To compensate for this, several studies [31,39,40] have shown the beneficial effect of adding pyrites to uranium-bearing ores. Thus, it is common to add 5 kg/t to Portuguese and Indian ores,
<table>
<thead>
<tr>
<th>Micro-organism</th>
<th>Characteristic</th>
<th>Carbon requirement</th>
<th>Oxygen requirement</th>
<th>pH (optimum)</th>
<th>T* (°C) (optimum)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Thiobacillus ferrooxidans</em></td>
<td>Oxidize: Fe²⁺, S⁰, U⁴⁺, Cu⁺, Se²⁺, Thiosulphate, Tetrathionate, S⁻</td>
<td>O.C.</td>
<td>A.</td>
<td>1.2-6.0</td>
<td>5-40</td>
</tr>
<tr>
<td><em>Thiobacillus thiooxidans</em></td>
<td>Oxidize: S⁰, Thiosulphate, Tetrathionate</td>
<td>O.C.</td>
<td>S.A.</td>
<td>0.5-6.0</td>
<td>10-40</td>
</tr>
<tr>
<td><em>Thiobacillus acidophilus</em></td>
<td>Oxidize: S⁰, organic compounds</td>
<td>F.C.</td>
<td>A.</td>
<td>1.5-6.0</td>
<td>25-30</td>
</tr>
<tr>
<td><em>Leptospirillum ferrooxidans</em></td>
<td>Oxidize: Fe²⁺, Pyrite</td>
<td>O.C.</td>
<td>A.</td>
<td>1.5-4.5</td>
<td>20-40</td>
</tr>
<tr>
<td><em>Sulfobolus thermosulfidooxidans</em></td>
<td>Oxidize: Fe²⁺, S⁰, S⁻</td>
<td>F.A.</td>
<td>A.</td>
<td>1.9-3.0</td>
<td>20-60</td>
</tr>
<tr>
<td><em>Sulfobolus acidocaldarius</em></td>
<td>Oxidize: Fe²⁺, S⁰</td>
<td>F.A.</td>
<td>A.</td>
<td>2.0-7.0</td>
<td>55-85</td>
</tr>
<tr>
<td><em>Acidianus brierlei</em></td>
<td>Oxidize: S⁰, yeast extract</td>
<td>F.C.</td>
<td>S.A.</td>
<td>1.0-6.0</td>
<td>45-75</td>
</tr>
<tr>
<td><em>Pseudomonas</em></td>
<td>Accumulate U, Cu, Pb intracellular</td>
<td>H.</td>
<td>S.A.</td>
<td>7-8.5</td>
<td>4-43</td>
</tr>
<tr>
<td><em>Penicillium</em></td>
<td>Accumulate U, Ra, Pb in the cell wall</td>
<td>H.</td>
<td>S.A.</td>
<td>(5.0)</td>
<td>15-30</td>
</tr>
<tr>
<td><em>Rhizopus</em></td>
<td>Accumulate U, Th, Ra in the cell wall</td>
<td>H.</td>
<td>S.A.</td>
<td>(5.0)</td>
<td>(24-27)</td>
</tr>
<tr>
<td><em>Desulfovibrio desulfuricans</em></td>
<td>Remove U and Cu from the dissolution</td>
<td>H.</td>
<td>An.</td>
<td>(4.0-7.0)</td>
<td>0-44</td>
</tr>
</tbody>
</table>

O.C. = obligate chemolithotroph; F.C. = facultative chemolithotroph; F.A. = facultative autotroph; H. = heterotroph; A. = aerobic; S.A. = strict aerobic; An. = anaerobic.
Table 2
Bioleaching of uranium ores

<table>
<thead>
<tr>
<th>Uranium ore</th>
<th>Chemical composition</th>
<th>Degree of bioleaching</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uraninite</td>
<td>UO₂</td>
<td>+</td>
</tr>
<tr>
<td>Gummite</td>
<td>UO₂₃·nH₂O</td>
<td>+</td>
</tr>
<tr>
<td>Becquerelite</td>
<td>Ca₅U₂O₁₃·11H₂O</td>
<td>+</td>
</tr>
<tr>
<td>Brannerite</td>
<td>(U,Ca,Ce)(Ti,Fe)O₆</td>
<td>+</td>
</tr>
<tr>
<td>Davidite</td>
<td>(Fe,Ce,U)₂(Ti,Fe,V,Cr)₂O₁₂</td>
<td>+</td>
</tr>
<tr>
<td>Coffinite</td>
<td>U(SiO₄)₁₋ₓ(OH)₄ₓ</td>
<td>−</td>
</tr>
<tr>
<td>Uranophane</td>
<td>Ca(UO₂)₂Si₂O₁₂·6H₂O</td>
<td>−</td>
</tr>
<tr>
<td>Sklodowskite</td>
<td>Mg(UO₂)₂Si₂O₁₂·6H₂O</td>
<td>−</td>
</tr>
<tr>
<td>Autunite</td>
<td>Ca(UO₂)₂(PO₄)₂·12H₂O</td>
<td>+</td>
</tr>
<tr>
<td>Torbernite</td>
<td>Cu(UO₂)₂(PO₄)₂·8H₂O</td>
<td>+</td>
</tr>
<tr>
<td>Uranphite</td>
<td>NH₄·UO₂·PO₄·3H₂O</td>
<td>+</td>
</tr>
<tr>
<td>Zeunerite</td>
<td>Cu(UO₂)₂(AsO₄)₂·12H₂O</td>
<td>+</td>
</tr>
<tr>
<td>Carnotite</td>
<td>K₂(UO₂)₂(V₀₄)₂·3H₂O</td>
<td>+−</td>
</tr>
<tr>
<td>Tyuyamunite</td>
<td>Ca(UO₂)₂(V₀₄)₂·3H₂O</td>
<td>+−</td>
</tr>
<tr>
<td>Zippeite</td>
<td>(UO₂)₂(SO₄)(OH)₂·4H₂O</td>
<td>+</td>
</tr>
<tr>
<td>Uranopilite</td>
<td>(UO₂)₂SO₄(OH)₁₈·12H₂O</td>
<td>+</td>
</tr>
<tr>
<td>Johannite</td>
<td>Cu(UO₂)₂(SO₄)₂·(OH)₂·6H₂O</td>
<td>+</td>
</tr>
<tr>
<td>Schroeckingerite</td>
<td>NaCa₃UO₂SO₄(CO₃)₃F·10H₂O</td>
<td>+</td>
</tr>
<tr>
<td>Urano-organic</td>
<td></td>
<td>+</td>
</tr>
<tr>
<td>compounds</td>
<td></td>
<td>+</td>
</tr>
</tbody>
</table>

+ = easy; − = hard; +− = variable.

while 3 kg/t has been demonstrated to be more effective than the previously used 9 kg/t in a Spanish ore. This suggests that the most suitable quantity of pyrite to add to an ore will depend on the mineral content of the ore to be leached and on the characteristics of the pyrite to be added.

Another important facet of bioleaching is the mineralization of the uranium itself. Miller et al. [39] suggested that refractory ores such as brannerite would be difficult to treat. However, in the mines near Elliot Lake (Canada), where this ore abounds, bacterial leaching has been used with good results [41]. Table 2 shows the results of different uranium ores subjected to bioleaching. According to this, oxides, phosphates, sulphates and carbonates are solubilized with relative ease, while the dissolution of silicates is difficult or even impossible.

The effectiveness of the bioleaching process also depends on the nature of the country rock. When this is alkaline it is probable that precipitates will be formed which will hinder the natural percolation of the leaching liquid through the heap. This lowers the uranium yield because some pockets of ore are not attacked. On the other hand, when the country rock is acidic, as in the case of quartz, acid consumption by the rock is low and the process of uranium dissolution is favoured. Another important aspect of the country rock is the quantity of nutrients it supplies. The solid medium should supply at least sufficient minerals for micro-organism growth not to be stopped. Thus, uranium-bearing shales have been shown to be a good material for leaching since they contain all the ingredients
Table 3
Mineralogy of several uranium ores

<table>
<thead>
<tr>
<th>Mine (situation)</th>
<th>Uranium mineralization</th>
<th>Pyrite (%)</th>
<th>Country rock</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oxide</td>
<td>Silicate</td>
<td>Phosphate</td>
</tr>
<tr>
<td>Lilljuthatten (Sweden)</td>
<td>P</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Division Minere of Vendeé (France)</td>
<td>P</td>
<td>S</td>
<td>-</td>
</tr>
<tr>
<td>Urgeirica (Portugal)</td>
<td>P</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Bica (Portugal)</td>
<td>S</td>
<td>-</td>
<td>P</td>
</tr>
<tr>
<td>Valinhas (Portugal)</td>
<td>P</td>
<td>-</td>
<td>S</td>
</tr>
<tr>
<td>Anaconda Company Grants (New Mexico, USA)</td>
<td>P</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Elliot Lake (Canada)</td>
<td>S</td>
<td>P</td>
<td>-</td>
</tr>
<tr>
<td>Midwest Lake (Canada)</td>
<td>P</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ningyo-toge (Japan)</td>
<td>-</td>
<td>-</td>
<td>P</td>
</tr>
<tr>
<td>Bhatin (India)</td>
<td>P</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Dyson's (Australia)</td>
<td>-</td>
<td>P</td>
<td>-</td>
</tr>
<tr>
<td>Mary Kathleen (Australia)</td>
<td>P</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ranger (Australia)</td>
<td>P</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Yeelirrie (Australia)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Umtali (Zimbabwe)</td>
<td>P</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Witwatersrand (South Africa)</td>
<td>P</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

P = principal; S = secondary.
needed by a bacterial medium: sulphides, iron, phosphates, nitrogen, organic substances and micro-elements [42].

Table 3 shows the mineralogy of various uranium ores. The most significant fact is that all, except those which did not contain pyrite, were suitable for the growth of the bacterium *Thiobacillus ferrooxidans*. In addition, those minerals formed principally of silicates showed very low acid consumption, resulting in reduced costs. The most important economic factor, however, remains the minimum concentration of pyrite; that is, the actual quantity needed for bacterial oxidation to take place.

In broad terms, it can be said that if the ore is pyritic, if it has few carbonates, if the uranium is not present in the form of silicates or associated with a phase resistant to the medium and if the iron-oxidizing bacteria can act in a suitable environment (with essential nutrients and no inhibiting agents), the yields of uranium will be high.

Thus, the basic requirements to be borne in mind when considering the suitability of uranium ores for bioleaching are the following:

1. a uranium mineralogy sensitive to bacterial leaching;
2. a permeable country rock which is not too compact;
3. a sufficiently high pyrites content;
4. the absence of basic compounds in the ore;
5. the presence of mineral salts which act as essential nutrients for the microorganisms.

5. Percolation leaching

Once the characteristics of the uranium ore to be bioleached have been established, other aspects related to the good functioning of a percolation leaching system should be considered. The last decade has seen the development of mathematical models [7,25,43] for defining the most important factors controlling a good percolation leaching process and for predicting the metal recovery rate and final yield. These leaching models have shown that aeration of the bed and exothermic reactions, along with the heap geometry (especially height), the proportion of leaching solution and the irrigation method, particle distribution and size, and rock characteristics (on which permeability depends), all play an important role. However, the overall kinetics of the percolation leaching of uranium ore largely depend on parameters whose role has not been clearly defined and, consequently, there is no general equation for the rate. It is also probably true that many of the problems which have arisen are the result of the inadequate design of the ore heaps and of an imperfect knowledge of the conditions and reactions which take place in them.

Thus, aeration of the bed can be favoured by a coarser granulometry and a suitable ratio between width and height (wider and lower) [44]. The construction of the heap must not be forgotten as this will also affect permeability.

In industrial operations, the temperature inside the heap can reach 50°C
and sometimes even more [25]. However, the heat generated in biological and chemical oxidation cannot be regulated and so an excessively high temperature will obviously inhibit bacterial activity while accelerating chemical reactions. Thus, the heap temperature, due to these exothermic reactions, can be a controlling factor in some commercial operations. Changes in temperature within a heap as a result of seasonal changes can cause modifications in the microbial population, favouring the development of mesophilic or thermophilic bacteria [46]. In France, for example, after 10 years of research into bioleaching, it was decided not to apply this technique because the average temperatures were too low [29]. However, this might appear to have been a rather drastic decision since the technique has been successfully adopted in Canada and Hungary [47,48]. Furthermore, since the body of ore is a poor conductor, very little heat is lost. In fact, the temperature inside the heap is independent of external temperatures so that continuous operation is possible even in winter [48].

As regards the form of irrigation, continuous or discontinuous, there are different trends, although it is generally thought that discontinuous irrigation can favour uranium dissolution. In this case, the attack solution is intermittently sprayed onto the surface of the heap and it is allowed to percolate before a new solution is applied, setting up an inverse capillary effect which permits the leaching of coarse ores. During irrigation, the capillary forces draw the liquid into the mass of ore. When irrigation ceases the liquid drains from the capillary and remains on the surface. A new irrigation carries with it the dissolved uranium and the process begins again with the introduction of fresh liquid into the capillary. In this way, discontinuous irrigation can be more effective for coarse ores than the continuous form, since the alternate draining and drying of the capillaries is considerably faster than simple ionic diffusion through a static capillary full of fluid. Thus, alternate irrigation and drying helps to leach coarse particles and eliminate soluble salts from their surface, as well as increasing the diffusion of oxygen and carbon dioxide to the ore's surface, where many of the active bacteria are located. However, the frequency of irrigation is obviously a factor to be considered. Several studies [49] have demonstrated that, in the presence of bacteria, daily irrigation is more effective than weekly. Industrially, the irrigation frequency (cycle) is determined by the rate of evaporation and the concentration of the uranium in the exiting liquid phase [50]. When these factors become critical, irrigation must be restarted.

The correct irrigation rate depends on the ore's permeability. If it is too high, the quantity of water prevents aeration and reducing conditions are established (precipitation of uranium and a halt to the oxidizing activity of bacteria) with the added risk of the solution overflowing from the sides of the heap. Industrial heaps operate at 40–60 cm³ week⁻¹ kg⁻¹ [36]. Cordero et al. [44], working with a pilot plant, found that an increase in irrigation from 35 to 340 cm³ week⁻¹ kg⁻¹ only resulted in an increase in uranium extraction from 55.7% to 59% and from 42.7% to 44.5% under the same experimental conditions. In the laboratory, two methods can be used for irrigation: the leaching solution can be added to a column at the same rate that it is added to a commercial heap, which results in much
poorer solutions when the column is much shorter than the heap [51]; or the solution can be added to a column in quantities based on the weight of the ore contained in the column. This results in solutions much more similar to those of a commercial undertaking.

One of the first studies carried out of uranium ore bioleaching [39] concluded that the technique could be economic on an industrial scale when using ores containing between 0.05% and 0.15% U₃O₈. The uranium metallurgical industry has been using bioleaching to recover uranium from low grade ores for quite some time.

6. Industrial practice

The industrial application of the bacterial leaching of uranium ores is based on three techniques (Fig. 5): (1) percolation leaching; (2) mine waters; and (3) chemical–bacterial leaching.

Of these, static leaching is the method which depends most on microbial attack for uranium recovery. It has been estimated that with this method, bioleaching is responsible for a large part of the solubilized uranium [52]. The success of percolation leaching depends, then, largely on the performance of the microorganisms taking part in the process.

The annual production of U₃O₈ from mine waters is estimated at 3,000 t [53], an important additional source to that produced by stirred tank and percolation leaching. Processes which combine chemical and bacterial leaching have also been applied to uranium recovery [54,55]. These processes require less oxidant and give better extraction results.

Although the first commercial production of uranium by bacterial leaching was in 1957 (Urgeirica mine, Portugal), the catalytic involvement of T. ferrooxidi-
dans in the solubilization of uranium from its minerals was not understood until the 1960s [56,57]. Since this time, bioleaching has been practised on an industrial scale in many places in the world and in some countries it is the main extraction method used [38,47,57,58].

Recent calculations have put the production of Canadian uranium involving some form of bioleaching at between 10% and 20% [59]. During the last 20 years other countries, such as USA, Brazil, South Africa and Australia [48,50,53,60,61], have also developed operations involving the participation of bioleaching microorganisms, although not in a controlled manner. It is, however, the control of the processes involved which is the key to the success of this technique.

Spanish companies have been using the first two techniques since the 1970s. Spain, after France, has the second largest proven reserves of uranium in Europe and is also the second largest producer [62], with reserves of 40,000 t of U₃O₈ (80% of which are commercially exploitable) and a production of 270 t/yr [63].

All of the Spanish production comes from the FE mine at Saelices el Chico, Salamanca. The morphology of this deposit has been described in other studies [64,65]. The deposit at Salamanca is very heterogeneous, with veins (where the
<table>
<thead>
<tr>
<th>OPERATION</th>
<th>CHARACTERISTICS</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-situ leaching</td>
<td>Submarginal ores obtained by blasting; ore treated for 5-25 years with an operational capacity of $4 \times 10^6$ t of ore.</td>
</tr>
<tr>
<td>Dump leaching</td>
<td>Submarginal ores obtained by bulldozing; ore treated for 3-20 years with an operational capacity of $5 \times 10^6$ t of ore.</td>
</tr>
<tr>
<td>Static</td>
<td>Low grade ores obtained by fine grinding; ore treated for 1-2 years with an operational capacity of $3 \times 10^5$ t of ore.</td>
</tr>
<tr>
<td>Heap leaching</td>
<td>Similar to leaching in heaps but for 10-30 days and with an operational capacity of $5 \times 10^5$ t of ore.</td>
</tr>
<tr>
<td>Vat leaching</td>
<td>Waters collected after rain in open pit mines.</td>
</tr>
<tr>
<td>Mine waters</td>
<td>Biooxidation of exhausted solutions previously used in agitation leaching. For the treatment of high grade ores obtained by fine grinding and grinding.</td>
</tr>
</tbody>
</table>

Fig. 5. Percolation bacterial leaching methods for the treatment of uranium ores.
uranium ores are found) flanked by large masses of country rock (mainly silicates). However, the processes used for dissolving the uranium have not been studied so thoroughly.

The method used for recovering uranium at this mine has changed from the acid percolation technique, with a consumption of 30 kg H$_2$SO$_4$/t ore to percolation leaching with a mild acid (2 kg H$_2$SO$_4$/t ore). Thus, all the uranium produced in Spain is through bioleaching: 11% is from mine waters and the rest from leaching in heaps.

However, Spain is not self-sufficient in uranium and research is centring on the internal phenomena of the heaps. In the processes used at present, where bacteria are very active in the heaps, the defective knowledge of how the environmental conditions affect uranium biodissolution has been one of the major limitations to increasing production. This is borne out by the fact that production by static leaching has been increasing by 10–15 t U$_3$O$_8$/yr [33].

The principal aim of any study into the leaching step of the process must concentrate on improving present techniques by examining the phenomenon of bioleaching and the use of this biotechnology. This idea is supported by the fact that similar studies [66] into copper have provided valuable information which has been used in commercial leaching operations.

Any predictions into how the system works must be based on laboratory experiments and semi-pilot and pilot schemes. All microbiological, chemical, mineralogical and engineering aspects of the process must be examined.

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References


[37] Silver, M., Bacterial leaching of uranium from a rock sample from the Cobalt Plate area, Roberts Township, Ontario. CANMET, Sept. (1980), 14 pp.


