

# Solution Mining and In Situ Leaching

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Solution mining and in situ leaching of copper, water-soluble salts, and uranium are discussed in this chapter. Among the water-soluble salts are boron compounds, lithium compounds, magnesium chloride, potassium chloride, and various sodium compounds including table salt.

## DEFINITIONS

The terminology used in this section follows industry conventions but is intended to be generalized and may differ from the definitions used by specialists such as those in the field of hydrology.

- *Solution mining* includes all methods for dissolving or liquefying minerals or materials and capturing the resulting fluid for commercial recovery of contained values. “Solution mining is an interdisciplinary field involving geology, chemistry, hydrology, extractive metallurgy, mining engineering, process engineering, and economics” (Bartlett 1992).
- *In situ leaching* (ISL) is a form of solution mining that relates to extraction of metals, elements, or compounds from an undisturbed location or mineral deposit.
- An *aquifer* is a formation beneath the ground surface that not only contains water but also is capable of producing water, for example, by way of extraction through a well.
- An *aquitard* is a formation either above or below an aquifer that resists the flow of water.
- The *permeability* of a geologic structure, usually a sedimentary unit for the purposes of this chapter, is a measure of the capability for transmitting a fluid. The rate at which a fluid can be transmitted over a specific distance in a specific time interval is defined experimentally in darcies. One darcy equals a flow rate of  $1 \text{ cm}^3/\text{s}/\text{cm}^2$  of flow cross section for a fluid having a viscosity of 1 cP under a pressure gradient of 1 atm/cm.
- *Porosity* in a rock or sedimentary unit is quantified by the ratio of pore volume to the volume of the rock. This can be approximated by one minus the ratio of bulk density of a core section to the expected specific gravity of a

massive fragment of the same material, both expressed as weight per unit of volume.

## COPPER MINERALS

In the broadest sense of the term, *copper solution mining* refers to the extracting and recovery of copper by dump and stockpile leaching, heap leaching, and ISL methods. This section will focus on the ISL of copper. Regardless of the method, solution mining is an extremely site-specific endeavor and very dependent on the geologic setting and copper mineralogy. Bateman (1951) summarized important copper minerals associated with the three major zones of a typical copper deposit. This information is listed in Table 1.

Common copper minerals in the uppermost portion (oxidized zone) are classified for the most part as oxyanion

Table 1 Zones of mineralization for copper

Mineralized Zone	Mineral	Simplified Formula
Oxidized zone (secondary)	Native copper	Cu
	Malachite*	$\text{Cu}_2(\text{OH})_2\text{CO}_3$
	Brochantite*	$\text{Cu}_4(\text{OH})_6\text{SO}_4$
	Antlerite*	$\text{Cu}_3(\text{OH})_4\text{SO}_4$
	Atacamite*	$\text{Cu}_2(\text{OH})_3\text{Cl}$
	Azurite*	$\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$
	Chrysocolla*	$\text{CuSiO}_3 \cdot 2\text{H}_2\text{O}$
	Cuprite*	$\text{Cu}_2\text{O}$
	Tenorite*	$\text{CuO}$
	Chalcantite*	$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
Supergene enrichment zone (secondary)	Chalcocite*	$\text{Cu}_2\text{S}$
	Covellite	$\text{CuS}$
	Native copper	Cu
Hypogene zone (primary)	Chalcopyrite	$\text{CuFeS}_2$
	Bornite	$\text{Cu}_5\text{FeS}_4$
	Enargite*	$\text{Cu}_3\text{AsS}_4$
	Tetrahedrite*	$\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$
	Tennantite*	$\text{Cu}_{12}\text{As}_4\text{S}_{13}$
	Covellite	$\text{CuS}$

Source: Forrester 1946

\*Always in relative descending position indicated.

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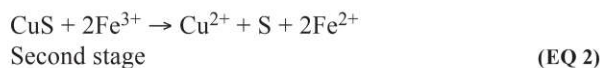
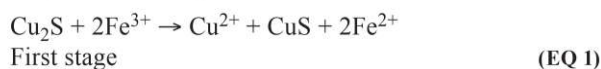
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Table 2 Dissolution reactions for selected copper minerals

Mineralized Zone	Mineral	Leaching Reaction
Oxidized zone (secondary)	Native copper	$\text{Cu} + 2\text{H}^+ + \frac{1}{2}\text{O}_2 \rightarrow \text{Cu}^{2+} + \text{H}_2\text{O}$
	Malachite	$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 + 4\text{H}^+ \rightarrow 2\text{Cu}^{2+} + \text{CO}_2 + 3\text{H}_2\text{O}$
	Brochantite	$\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2 + 6\text{H}^+ \rightarrow 4\text{Cu}^{2+} + \text{SO}_4^{2-} + 6\text{H}_2\text{O}$
	Antlerite	$\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2 + 4\text{H}^+ \rightarrow 3\text{Cu}^{2+} + \text{SO}_4^{2-} + 4\text{H}_2\text{O}$
	Atacamite	$3\text{CuO} \cdot \text{CuCl}_2 \cdot 3\text{H}_2\text{O} + 3\text{H}^+ \rightarrow 4\text{Cu}^{2+} + 2\text{Cl}^- + 6\text{H}_2\text{O}$
	Azurite	$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 + 6\text{H}^+ \rightarrow 3\text{Cu}^{2+} + 2\text{CO}_2 + 4\text{H}_2\text{O}$
	Chrysocolla	$\text{CuO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O} + 2\text{H}^+ \rightarrow \text{Cu}^{2+} + \text{SiO}_2 \cdot x\text{H}_2\text{O} + (3-x)\text{H}_2\text{O}$
	Cuprite	$\text{Cu}_2\text{O} + 2\text{H}^+ \rightarrow \text{Cu}^{2+} + \text{Cu} + \text{H}_2\text{O}$
	Tenorite	$\text{CuO} + 2\text{H}^+ \rightarrow \text{Cu}^{2+} + \text{H}_2\text{O}$
Supergene enrichment zone (secondary)	Chalcocite	$\text{Cu}_2\text{S} + 2\text{H}^+ + \frac{1}{2}\text{O}_2 \rightarrow \text{Cu}^{2+} + \text{CuS} + \text{H}_2\text{O}$ First stage
	Covellite	$\text{CuS} + 2\text{H}^+ + \frac{1}{2}\text{O}_2 \rightarrow \text{Cu}^{2+} + \text{H}_2\text{SO}_4$ Second stage
	Native copper	$\text{Cu} + 2\text{H}^+ + \frac{1}{2}\text{O}_2 \rightarrow \text{Cu}^{2+} + \text{H}_2\text{O}$
Hypogene zone (primary)	Chalcopyrite	$\text{CuFeS}_2 + 16\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow \text{Cu}^{2+} + 17\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+$
	Bornite	$\text{Cu}_5\text{FeS}_4 + 36\text{Fe}^{3+} + 16\text{H}_2\text{O} \rightarrow 5\text{Cu}^{2+} + 37\text{Fe}^{2+} + 4\text{SO}_4^{2-} + 32\text{H}^+$
	Enargite	$\text{Cu}_3\text{AsS}_4 + 35\text{Fe}^{3+} + 20\text{H}_2\text{O} \rightarrow 3\text{Cu}^{2+} + 35\text{Fe}^{2+} + \text{H}_3\text{AsO}_4 + 4\text{SO}_4^{2-} + 37\text{H}^+$
	Covellite	$\text{CuS} + 8\text{Fe}^{3+} + 4\text{H}_2\text{O} \rightarrow \text{Cu}^{2+} + 8\text{Fe}^{2+} + \text{SO}_4^{2-} + 8\text{H}^+$

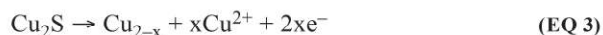
minerals (i.e., hydroxides, carbonates, sulfates, chlorides). Naturally, these minerals, along with tenorite, are of special importance because they dissolve rapidly in acid solution. Chrysocolla dissolves in acid solution with the formation of a remnant layer of  $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ . The dissolution kinetics follows a shrinking core model involving ion diffusion through the hydrated silica product layer, whereas acidic dissolution of cuprite involves a disproportionation reaction that yields only half of the copper to solution. Native copper is the only mineral that requires an oxidant for leaching. In general, the dissolution kinetics of the oxide copper minerals is relatively fast as compared with the sulfides. Table 2 shows the leaching reactions for the copper minerals listed in the various mineral zones.

Under normal conditions, secondary and primary copper sulfide minerals require the presence of an oxidant for dissolution. In aqueous solution, dissolved oxygen serves the role. Pyrite commonly found in the supergene enrichment and hypogene zones can undergo aqueous oxidation to yield an acid ferric sulfate solution that can effectively dissolve copper sulfide minerals. The acid ferric sulfate dissolution of copper sulfide appears to have a reasonably straightforward leaching reaction. For example, the leaching of chalcocite can be represented by the following reactions:



However, the fundamental leaching of chalcocite is much more complex than characterized by the general reactions shown in Equations 1 and 2. Compositionally intermediate phases between chalcocite and covellite include several non-stoichiometric copper sulfides that comprise a progressive dissolution series. In order of decreasing Cu:S ratio, these minerals include djurite ( $\text{Cu}_{1.94}\text{S}$ ), digenite ( $\text{Cu}_{1.8}\text{S}$ ), anilite ( $\text{Cu}_{1.75}\text{S}$ ), geerite ( $\text{Cu}_{1.6}\text{S}$ ), spionkopite ( $\text{Cu}_{1.4}\text{S}$ ), and yarrowite ( $\text{Cu}_{1.12}\text{S}$ ). Sulfide minerals have excellent semiconducting properties, and chalcocite and covellite are no exception. In fact, covellite is characterized by metallic-like conduction. Therefore, copper sulfide dissolves in aqueous solution according to an electrochemical mechanism. The anodic

dissolution step for the first stage of chalcocite dissolution is illustrated by the following general reaction:



Acid ferric sulfate dissolution of chalcocite up to about  $x = 0.9$ , corresponding to 45% copper recovery, exhibits relatively fast kinetics. The dissolution of covellite is considerably slower.

Primary copper minerals are sparingly soluble in acid ferric sulfate solutions. Chalcopyrite, economically the most important copper sulfide mineral, has been recognized for many years (Sullivan 1933) as having extremely slow leach kinetics. Even under relatively aggressive conditions, leaching is slow. Numerous kinetic investigations have focused on chalcopyrite to better understand the leaching fundamentals. Surface passivation is believed to play a major role in retarding the leaching rate of chalcopyrite.

### Historical Examples

The historical fabric of copper solution mining is very rich. Passive hydrometallurgical systems for the extraction and recovery of copper have been used for millennia. These systems refer to the recovery of copper-bearing solutions from natural seeps and springs, and from drainages associated with copper mining activities. Early attempts in China to recover copper by passive methods have been described by Pu (1982) and Lung (1986) in considerable detail. Pharmacologists in the East Han Dynasty (25–220 AD) clearly understood the formation of gall (copper sulfate) springs and described in exquisite terms the precipitation of copper on iron from its solution. Engineering leaching systems for in situ copper extraction are more recent. These modern examples clearly demonstrate the application and integration of various scientific and technological disciplines, including hydrometallurgy, hydrology, geology, geochemistry, rock mechanics, environmental chemistry, and process engineering.

### Passive Systems

An interesting early example of passive solution mining is the recovery of copper-rich solution from the ancient mines on Cyprus by the Romans. Galen (see Angelatou 2004), a naturalist and physician, reported in 166 AD the operation of ISL of copper on Cyprus.



Surface water was allowed to percolate through the permeable rock, and was collected in amphorae. In the process of percolation through the rock, copper minerals dissolved so that the concentration of copper sulfate in solution was high. The solution was allowed to evaporate until copper sulfate crystallized.

Pliny (23–79 AD), in *Historia Naturalis XXXIII–XXXV* (Rackham 1952), reported that a similar practice for the extraction of copper in the form of copper sulfate was widely practiced in Spain. The recovery of copper from mine drainages at Rio Tinto, Spain predates the large-scale commercial heap leaching operations (1876) described by Taylor and Whelan (1942). In 1556, Diego Delgado observed and reported copper cementation at Rio Tinto, and Don Alvaro Alonso de Garfias was granted a patent to recover copper by iron cementation from mine water in 1661.

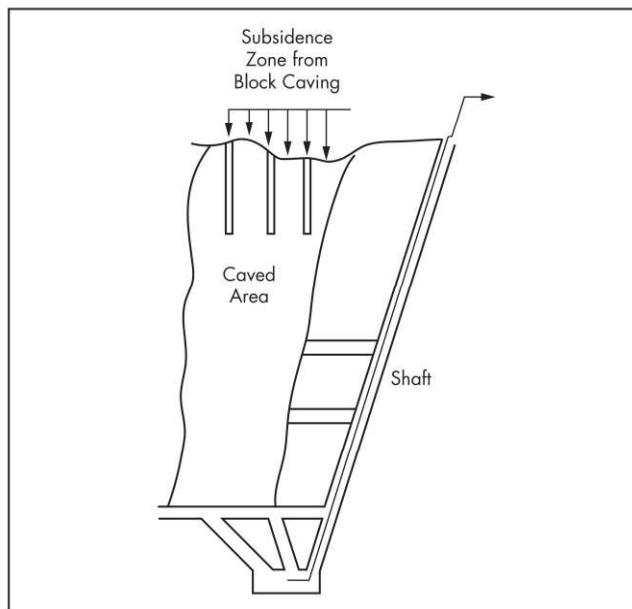
Bushnell (1911) described crude attempts by Morgan as early as 1888 to recover copper from mine drainage in Butte, Montana, United States. Improved attempts by Miller to recover copper by cementation from water originating from the St. Lawrence mine were marginally better. In 1901, Ledford secured a three-year lease on the water from the St. Lawrence and Anaconda mines at a 25% royalty. This was a very successful enterprise and, when the lease expired, the companies decided to build their own precipitation plants. By 1906, similar passive solution mining was extremely well developed at Bisbee, Arizona, United States.

### Engineered Systems

Copper ISL can be conveniently divided into two primary activities. One method involves the ISL of copper values associated with old mining remnants (i.e., pit slopes, block caving subsidence zones, underground stopes). The other comprises the extraction of copper from the confines of a deposit in its original geologic setting (i.e., undisturbed ore). This is commonly referred to as “true” ISL. This ISL method can be performed with or without matrix modification (permeability enhancement). Blasting, hydraulic fracturing (“hydrofracturing”), and chemical stimulation have been suggested as ways to improve deposit permeability.

Greenwood (1926) reviewed the ISL of copper at Cananea Consolidated Copper Co. in Sonora, Mexico, in the 1920s. Underground leaching of remnant copper ore in old shrinkage stopes was accomplished in a controlled fashion. Solutions were allowed to infiltrate naturally through old workings, or in some cases, solution was delivered to the surface of broken ore via sprays in perforated pipe and allowed to percolate through the stope. Bulkheads were constructed in certain drifts to collect and store leach solution. In-mine cementation launders were installed in select locations to recover copper. This avoided pumping solutions to a surface recovery plant.

**Miami mine.** The Miami mine located near Miami, Arizona, is the oldest continuously operated ISL facility in the world (Kyle et al. 2011). Block caving of the ore body created a huge surface subsidence area containing broken and highly fractured low-grade mixed copper oxide–sulfide material. The first attempts to leach this material in place were in 1942 with only the application of water. This proved unsuccessful since there was not enough pyrite in the rock to maintain the autogenous generation of acid. Application of a solution containing about 5 g/L  $\text{H}_2\text{SO}_4$  was effective in leaching the copper. Solution has been applied with sprays, via ponds,



**Figure 1** Representation of the in situ leaching of a block caved subsidence zone

and by injection holes. Ponding proved to be ineffective and was discontinued. Cased injection holes, with a perforated bottom section, reach an average depth of 59.5 m (195 ft). Leach solution percolates by gravity from the surface and the injection points through the caved ore and then through raises and drawpoints until it reaches the final haulage level, about 305 m (~1,000 ft). Solution flow is controlled by weir boxes in the underground workings. Solutions are pumped to the surface and a solvent extraction electrowinning (SX-EW) plant. A general pictorial representation of the Miami system is shown in Figure 1.

**Old Reliable.** The Old Reliable project carried out by Ranchers Exploration and Development Corporation is a special example of an in situ operation incorporating matrix modification. Longwell (1974) reported that the ore body was a nearly vertical breccia pipe containing 3.6 Mt ( $4 \times 10^6$  st) of 0.80% Cu. The most abundant copper minerals were chalcocite, chalcopryrite, malachite, chalcantite, and chrysocolla. Historic mining operations had removed approximately 2.72 kt (30,000 st) of ore from two main adits at the 30.5-m and 61-m (100-ft and 200-ft) levels and associated workings. Development mining was done to prepare the ore body for blasting (i.e., rubblization). This consisted of an additional adit located 51 m (167 ft) above the 30.5-m (100-ft) level and extra crosscuts, which resulted in a total of 2,591 m (8,500 ft) of tunnels and crosscuts. Ranchers in partnership with E.I. du Pont de Nemours and Company designed a 3.63-Mt (4-million-lb) ANFO (ammonium nitrate and fuel oil) blast using 1,829 m (6,000 ft) of coyote tunnels for emplacement of the explosives and stemming. The blast was detonated on March 9, 1972, and it was estimated that fragmentation resulted in a mean particle diameter of 22.9–25.4 cm (9–10 in.) in the ore zone. The hillside was terraced with 6.1-m (20-ft) benches varying from 4.6 to 54.9 m (15–180 ft) wide. Leach solutions were applied by a sprinkler system at a total solution flow rate of 4.17 m<sup>3</sup>/min (100 gpm), equivalent to an application rate of 0.183 L min<sup>-1</sup> m<sup>-2</sup> (0.0045 gpm/ft<sup>2</sup>). Leach solution percolated



through the rubblized ore, and pregnant leach solution (PLS) flowed from the hillside at about the position of the existing water table to a catchment basin. Copper was recovered by cementation on scrap iron in a simple launder plant.

ISL was conducted at the Old Reliable mine during two periods: initially from August 1972 to September 1974, and resumption of operation from August 1979 to January 1981. A total of 5.898 kt (13 million lb) of copper was recovered during these two phases of leaching. This represented a total copper recovery of approximately 20%. Even at this low level of copper extraction, the project was an economic success; however, it was in many ways a technical disappointment. Operational problems included solution channeling and the formation of a perched water table.

**White Pine.** Conventional mining and milling operations at the White Pine mine located in the Keweenaw Peninsula region of northern Michigan, United States, were terminated in 1995. Prior to this, Copper Range Company, the operating entity, had initiated a test program to evaluate the potential of ISL at the White Pine mine. The Michigan Department of Environmental Quality issued a permit in 1993 to perform the necessary test work. The plan was to conduct in-stope leaching of rubblized ore with acid ferric sulfate solutions and collect the PLS for copper recovery by SX-EW. The resource available for ISL was estimated at ~189 Mt, or million metric tons (208,207,000 st), averaging 1.04% Cu. Copper minerals in the White Pine deposit occur principally in two forms: as a very fine-grained chalcocite ( $\text{Cu}_2\text{S}$ ) and as native copper (Cu). The chalcocite accounted for an estimated 85%–90% of the contained copper value.

Room-and-pillar mining was the principal ore extraction method used at White Pine. Remnant pillars were to be rubblized by a controlled blast with a resulting collapse of the mine. Certain portions of the mine had already collapsed by natural processes. Leaching was to be accomplished by circulation of acid ferric sulfate solution through rubble piles created from the blasted pillars. Pregnant leach solution would be collected and pumped to a surface SX-EW plant. In May 1996, Copper Range Company announced approval of permits to in situ leach the remnant ore in the White Pine mine; however, opposition from environmental groups and regional Native American tribes was extremely strong and the project was postponed. One contentious issue was the delivery of sulfuric acid across tribal lands in Wisconsin. On May 30, 1997, Copper Range Company declared an end to the project.

### Laboratory Simulation Techniques

Metallurgical testing is a critical step in the evaluation and development of a copper ore body for ISL. An ore testing program relies on the receipt of representative samples either as individual samples or as composites. Ore samples are usually obtained from an exploration drilling program. They are received as small- or large-diameter diamond core or possibly as cuttings and chips from percussion drilling. These samples should be accompanied by a comprehensive geologic description (core log). In terms of ore characterization, the first task is to obtain a total copper assay by standard analytical techniques. This usually is followed by a determination of the acid soluble (oxide) copper content. Early in an ore characterization program, a carefully planned and executed process mineralogy study should be carried out. This will identify and quantify the key mineralogical attributes of the ore, including ore mineralogy, gangue mineralogy, the presence of

deleterious minerals and elements, grain size and shape, mineral assemblages, surface coatings, and texture. Process mineralogy studies can be carried out by a combination of optical and electron microscopic techniques. Automated systems such as mineral liberation analysis (MLA) instruments are an extremely valuable tool for quantitative process mineralogy information. Sequential diagnostic leach tests are another useful procedure in evaluating the ore mineralogy.

Leaching tests usually follow a sequence from bottle roll experiments to small and large column tests, and whole core leaching tests. These tests are preliminary and help provide important data for the design of a pilot field experiment.

### Bottle Rolls

Cyanide bottle-roll tests are an industry-standard initial step in evaluating the leaching characteristics of gold ores. These tests have been successfully adapted to assessing the leaching performance of copper ores and to determining lixiviant requirements. Bottle-roll tests are performed at ambient temperature and pressure and are usually conducted for relatively short times (~24–72 hours) using a fairly coarse feed size, equivalent to a top size of approximately 4 mesh (4.7 mm [~0.2 in.]). Ore slurries are prepared by pulping the coarse ore with leaching solution to reach 40–50 wt % solids. Solution samples are withdrawn from the bottle at prescribed time intervals and analyzed by standard techniques for dissolved copper, pH, free acid, and certain elements and species as required. When the test is terminated, the slurry is filtered to separate the PLS from the solid residue. The PLS volume is measured and the solution analyzed. The leached residue is carefully washed, dried, and analyzed; alternatively, it is screened and each size fraction analyzed to determine metal extraction as a function of particle size. Bottle-roll tests represent a rapid metallurgical test that provides vital information regarding ultimate copper recovery as a function of screen size, copper recovery rate, and maximum sulfuric acid consumption.

### Column Leach Tests

The next phase of a metallurgical test program typically consists of conducting leaching experiments in columns. These tests provide more detailed information about the copper recovery, kinetic data, and reagent consumption. In general, column leaching tests provide a systematic study of mineralized ore types using larger quantities of sample and a larger particle size. Columns are normally operated for extended periods of time. There are several benefits to column leaching: (1) it can serve to optimize the lixiviant chemistry; (2) it can provide a more accurate picture of acid consumption; (3) it can define cation loading; and (4) it can be operated under locked-cycle conditions. All of these benefits help establish the criteria for larger tests.

Columns can be operated under both percolation and inundation (flooded) conditions. Furthermore, they can be leached in sequential order to simulate solution “stacking,” where reagents are added to low-grade PLS, which is then returned to the circuit in an effort to increase PLS grade. Frequently, columns are run in a locked-cycle mode to more accurately simulate actual processing conditions. In a locked-cycle test, after the PLS reaches a certain copper concentration, it is directed to a copper solvent extraction (SX) circuit. Dissolved copper is extracted and the raffinate is recycled to the leaching circuit after addition of makeup water and reagents. If the PLS is below the set copper concentration, the weak PLS is



returned directly to leaching after makeup water and reagent adjustments. It is critical that steady state be achieved during locked-cycle experiments. Under locked-cycle leaching, the system reaction chemistry dictates that all PLS will eventually be treated by solvent extraction.

After a thorough analysis of all leach solutions, the leach residues are carefully rinsed and dried, and the residue metal content determined. Physical examination of the residues can yield valuable information regarding factors such as physical degradation. In addition, MLA examination of residues can quantitatively determine factors such as preferential copper mineral dissolution, the generation of fines and degradation, the precipitation of second phases, the degree of ion exchange by clays, and copper mineral alteration, such as replacement of copper by aluminum in chrysocolla, expressed as  $(\text{Cu,Al})_2\text{H}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ .

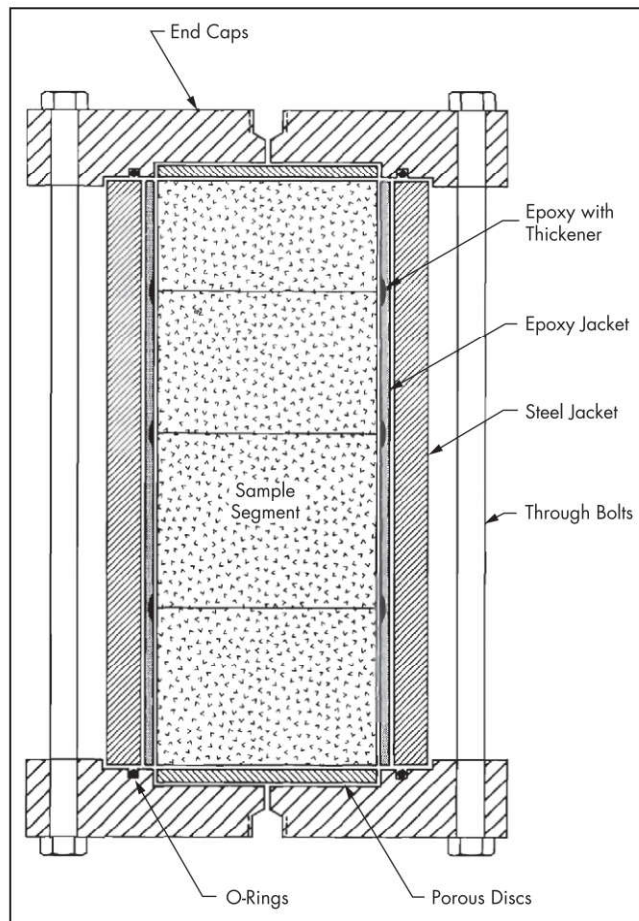
### Whole Core Experiments

Whole core leaching experiments more accurately simulate the chemical and hydrological interactions at the solution/rock interface. This is especially true for copper mineralization that is distributed along fractures and within pore spaces of the rock. Therefore, leach fluids will more likely approximate the solution chemistry produced during in situ mining. Leach parameters such as copper concentration in the PLS, copper recovery, acid consumption, and gangue mineral reactions

can be determined more precisely. Special apparatuses can be designed and utilized to leach the core under pressure. These experimental systems allow the study of pressure as a variable and the real-time monitoring of permeability changes during leaching. An increased permeability may result when substantial amounts of copper dissolve from fracture surfaces and pores. If significant enough leaching occurs, channels may form and solution short-circuiting may result. Permeability may actually decrease if second-phase solids such as gypsum precipitate along fluid channels or within pores. Core-leaching experiments also furnish important information regarding the physical nature of the leached sample when postmortem examinations are performed.

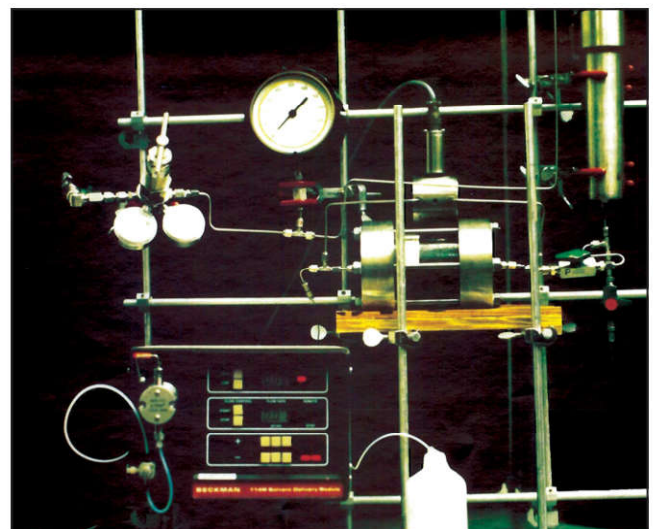
Paulson and Kuhlman (1989) have documented in detail various laboratory core-leaching apparatus and experiments. Three systems were designed: (1) a low-pressure system with an acrylic reaction cell; (2) a medium-pressure system with a polyvinyl chloride (PVC) reaction cell; and (3) an elevated-pressure system with stainless-steel components. The low, medium, and elevated pressure systems could handle pressures up to 345 kPa, 1,034 kPa, and 6,895 kPa (50 psi, 150 psi, and 1,000 psi), respectively. All three systems were designed to operate under axial flow conditions. A cross-sectional schematic of the elevated-pressure core-leaching cell is depicted in Figure 2. The main components are constructed of Type 316 stainless steel. The entire experimental setup for the elevated-pressure cell is shown in Figure 3.

Hiskey and Oner (1992) discussed the use of a laboratory system for leaching of large whole-core samples that was designed to operate at moderate pressures (<3,450 kPa [ $<500$  psi]). This system was designed and fabricated to operate under radial flow conditions. Leach fluids flowed from the outside perimeter of the core to a center collection well. Copper-bearing PLS moved from the center well by displacement to a collection vessel that was sampled on a regular basis. Experiments were conducted with a 103-mm (4-in.)-diameter core sample and a core section length of 103 mm (4 in.). A 25.4-mm (1-in.) center well was drilled in the core to serve as a production well. The system was designed for convenient removal of the core during the course of the test. The partially



Source: Paulson and Kuhlman 1989

**Figure 2** Elevated-pressure core-leaching cell



Source: Paulson and Kuhlman 1989

**Figure 3** Experimental setup for whole core leaching



leached core could be examined by macro computed tomography (CT) imaging to determine the development of leach channels and solution pathways.

### Box Experiments

The large whole core-leaching systems described earlier work well with competent intact core samples. Core samples that are highly fractured and fragmented would require another system. HDI Curis, at its Florence Copper Project (M3 Engineering and Technology Corporation 2013), developed a unique box method for laboratory leaching of natural highly fractured and unconsolidated core. In these tests, rectangular boxes made of transparent welded plastic sheet were loaded with multiple sections of fractured core, undisturbed as much as possible, and contacted with leaching solution flowing normal to the long axis of the core. Each core section was wrapped in plastic screen mesh to preserve the size, shape, position, and orientation of the core fragments. The stabilized core was then loaded horizontally into the boxes on a layer of paraffin wax to support the weight of the core interval and to prevent solution channeling around the sample. The spaces between the ends of the core and the box were also filled with paraffin wax to restrict fluid flow to the central portions of the core. In addition, interstitial spaces and large gaps between core fragments were filled with acid-washed silica sand to encourage fluid flow through the core intervals. Dilute aqueous sulfuric acid, typically 10 g/L free  $\text{H}_2\text{SO}_4$ , was introduced to one end of a sealed box at a hydraulic head of about 0.305 m (12 in.), as prescribed by the aquifer injection permit, and drained by gravity from the other end. Subsequent tests were conducted in vertical stainless-steel cylinders that enabled leaching at a pressure of 689.5–827.4 kPa (100–120 psi) to match the approximate hydraulic head over the mineralized formation. Another description of the Florence Copper Project is included in a comprehensive analysis of copper ISL by Sinclair and Thompson (2015).

The laboratory simulation technique used by Excelsior Mining Corp. for its Gunnison ISL copper project is also worthy of note (M3 Engineering and Technology Corporation 2017). Its “core tray” method involved exposing the core only at major fractures, using epoxy resin to coat the unfractured rock, minimizing consumption of acid by barren gangue. Leaching solution flowed along the top surfaces of the horizontal core samples, and solution drained downward through exposed mineralized fractures. This method was expected to provide more reliable indications of copper extraction from exposed mineralization and acid consumption per unit of copper dissolved than could be determined from a field trial. Leaching solution was initially applied at a concentration of 1 g/L free  $\text{H}_2\text{SO}_4$  that was gradually increased to 15 g/L.

With box experiments, it is difficult to assess permeability effects; however, other leach data can be fully evaluated, including data from lock-cycle tests. As with the large whole-core leaching experiments, the box tests can be run for extended times, often more than 200 days. They can also include rinse cycles and postleach studies of the core.

### Lixiviant Chemistry and Gangue Mineral Interactions

The main criteria determining the choice of leaching agent (lixiviant selection) depend primarily on the physical and chemical properties of the material to be leached. Other factors that are important in the selection process are reagent cost, selectivity toward the particular material to be leached, ability

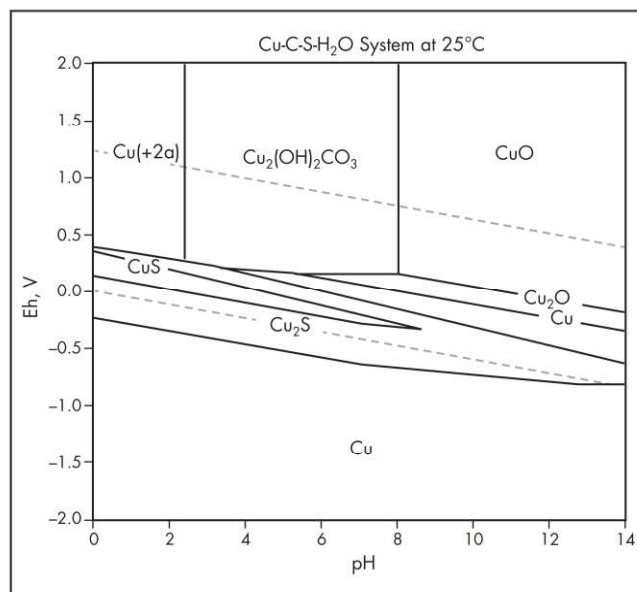


Figure 4 Eh–pH diagram for the Cu–S–O–H<sub>2</sub>O system at 298 K

to regenerate the leaching agent, and the chemical stability of the leaching agent. Three important conditions are taken into account when determining the appropriate lixiviant for a given mineral phase: (1) solution pH, (2) type of oxidant, and (3) the role of complexing ligands. All three factors can be suitably evaluated using oxidation potential–pH relationships and the graphically effective Eh–pH diagram.

### Eh–pH Diagrams

The Eh–pH (Pourbaix) diagrams are thermodynamic stability diagrams showing equilibrium relationships between solid (mineral) phases, as well as dissolved species. These drawings are an excellent means of treating geochemical, mineral, and hydrometallurgical equilibria. They represent a convenient and efficient means of graphically displaying a large amount of thermodynamic data. Constructing the Eh–pH diagram is quite simple for a single element system; however, it becomes extremely complex for multicomponent systems. An excellent source of information on the application of Eh–pH relationships to hydrometallurgy is by Pourbaix (1966). Garrels and Christ (1965) have developed the details of constructing Eh–pH diagrams and have discussed various diagrams of interest to copper geochemistry and extractive metallurgy. Several software packages model reaction chemistry and equilibria. The Outotec HSC Chemistry software has a comprehensive and fairly robust Eh–pH feature. The equilibria for the Cu–S–C–H<sub>2</sub>O system at 298 K, dissolved species activity  $10^{-3}$  M, and pressure of 101.3 kPa (1 atm) are depicted in Figure 4. This diagram shows that for economic copper leaching to occur, the Eh must be relatively high and the pH relatively low (i.e., the upper left-hand corner of the diagram).

### Gangue Mineral Interactions

Dreier (1999) has provided an excellent discussion of the interactions between gangue minerals and the lixiviant and the controlling role of Eh–pH microenvironments. He states that “the principal obstacle to successful leaching is the persistence within the leaching system of low Eh–high pH microenvironments.” Low-grade copper porphyry ores consist mostly



**Table 3** Different categories of gangue mineral reactivity

Gangue Reactivity	Minerals	Example Mineral Formulas
Highly reactive	Calcite	$\text{CaCO}_3$
	Dolomite	$\text{CaMg}(\text{CO}_3)_2$
	Siderite	$\text{FeCO}_3$
Reactive	Hornblende	$\text{Ca}_2(\text{Mg,Fe,Al})_5(\text{Si,Al})_8\text{O}_{12}(\text{OH})_2$
	Pyroxene	$[\text{Ca,Na}](\text{Mg,Fe,Al})[\text{Si,Al}]_2\text{O}_6$
	Ca plagioclase	$\text{Ca}(\text{Mg,Fe})_3\text{Si}_4\text{O}_{12}$
Moderately reactive	Orthoclase	$\text{KAlSi}_3\text{O}_8$
	Biotite	$\text{KFe}_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$
	Albite	$\text{NaAlSi}_3\text{O}_8$
Slightly reactive	Quartz	$\text{SiO}_2$
	Sericite	$\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$
	Kaolinite	$\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_8$
Nonreactive	Quartz	$\text{SiO}_2$

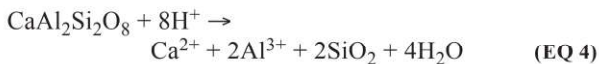
Adapted from Dreier 1999

of rock-forming minerals and alteration products. These silicate components are the main source of acid consumption and to a large degree control the leaching behavior of copper ores. If the ore contains significant amounts of carbonate minerals, they also consume large amounts of acid. Dreier has divided silicate and carbonate minerals into five categories according to the rate at which they react with acid. Table 3 shows some representative silicate minerals for these five categories.

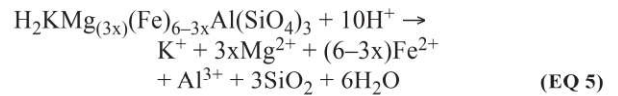
Dissolution rates and degree of acid consumption for rock-forming minerals are shown in Figure 5. This figure was adapted from Dreier. The dissolution rates of K-feldspar and Ca-plagioclase at pH 2 are  $2 \times 10^{-15}$  and  $2 \times 10^{-13}$  moles  $\text{cm}^{-2} \text{ s}^{-1}$ , respectively. By comparison, the leaching rate for chrysocolla at pH 2 is approximately  $1 \times 10^{-4}$  moles  $\text{cm}^{-2} \text{ s}^{-1}$ .

The overall dissolution reactions for several of the silicates shown in Figure 5 are given as follows. Reactions 4 and 5 illustrate the general stoichiometry for the acid-consuming nature of Ca-plagioclase and biotite, respectively.

Ca-plagioclase:

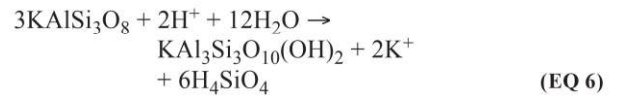


Biotite:

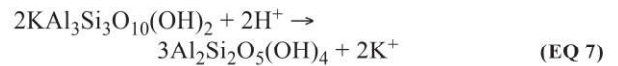


Acid consumption, on a molar basis, is very high for these silicate minerals. Even though the actual rate of dissolution is extremely slow, the huge amount of silicate surface available for reaction in the microenvironment results in an enormous macro effect on solution pH. The following sequence of reactions illustrates the consumption of acid associated with the dissolution and alteration of K-feldspar.

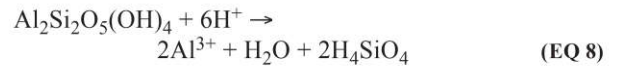
K-feldspar alteration to K-mica:



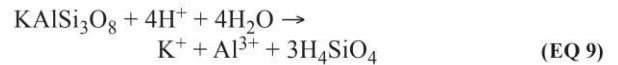
K-mica alteration to kaolinite:



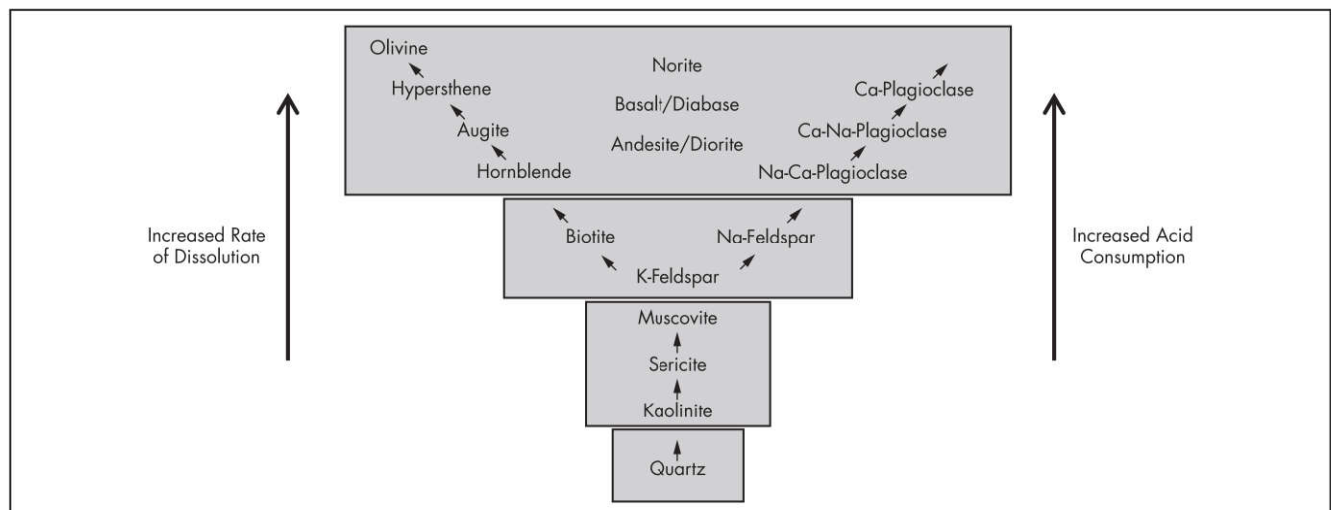
Kaolinite dissolution:



Overall reaction:



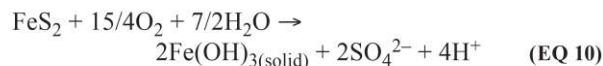
The main acid-generating reaction in copper-leaching systems is the aqueous oxidation of pyrite. Pyrite ( $\text{FeS}_2$ ) is an extremely common sulfide mineral and is found in a wide variety of geologic settings. It is present in porphyry copper deposits ranging from 2% to 6% by volume. Pyrite oxidizes very slowly in the presence of oxygen and ferric ion; however, its aqueous oxidation is aided by the presence of autotrophic bacteria. Acid generation by pyrite from direct oxidation with dissolved oxygen occurs according to the following reaction:



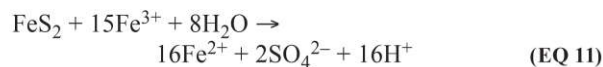
Adapted from Dreier 1999

**Figure 5** Relative acid dissolution rates for some silicate minerals and the resulting acid consumption





The corresponding reaction with ferric ion as the oxidant is



Acidithiobacillus microbes, which are indigenous with sulfide minerals, serve to catalyze the oxidation of ferrous ion to ferric and the oxidation of elemental sulfur to sulfate, both of which facilitate the acid-generating capacity of pyrite. Ferric ion hydrolysis to form hydrated hematite, hydronium jarosite, or jarosite salts results in the generation of acid. The molar ratio of pyrite to copper is important in maintaining the autogenous generation of acid in copper deposits. If it is too low, acid needs to be added to the system to maintain stable leaching conditions.

### Pilot-Scale In Situ Leaching Tests

Pilot-scale tests were extensions of batch agitated (beaker) leaches and static small-diameter column tests and were intended to provide scale-up information needed for design of a commercial operation.

### Lawrence Livermore Laboratory

Project Plowshare was a U.S. Atomic Energy Commission (AEC) program to develop the use of nuclear explosives for peaceful construction purposes. One application was the use of a contained nuclear explosive to break ore in a deep-seated disseminated primary copper deposit prior to in situ chemical mining. In essence, a rubblized chimney of broken ore would be constructed well below the water table. The plan was to introduce oxygen or air into the bottom of the chimney through drill holes and recover copper PLS through a solution recovery well. Lewis et al. (1972) described the results of a pilot-scale experiment conducted at the Lawrence Livermore Laboratory to simulate and model the chemistry of copper extraction from a chalcopyrite ore.

A pilot-scale leaching experiment was conducted in a large, specially constructed autoclave with an internal capacity of 4.4 m<sup>3</sup> (43 ft<sup>3</sup>). The autoclave was hand loaded with 5.8 t (6.4 st) of primary porphyry copper ore from the San Manuel mine, Arizona. The ore was mainly quartz and sericite with minor amounts of feldspar, chlorite, biotite, and calcite. The predominant copper mineral was chalcopyrite, and the copper content was 0.7% Cu with a pyrite/chalcopyrite mole ratio of 2.0. The particle size distribution was 0.1–160 mm (0.004–6.3 in.), and approximately 50% of the ore had a particle size greater than 80 mm (3.15 in.). A total of 1.4 m<sup>3</sup> (370 gal) of distilled water was added to the vessel. After it was sealed, the autoclave was operated at 90°C and 2.76 MPa (400 psi) oxygen pressure. Oxygen flow rate was 2.4 × 10<sup>4</sup> cm<sup>3</sup> (standard temperature and pressure, STP) min<sup>-1</sup> (6.34 gpm) (first 90 days) and 1.2 × 10<sup>4</sup> cm<sup>3</sup> (STP) min<sup>-1</sup> (3.17 gpm) (remainder of the test) to account for the consumption of oxygen by the leaching reactions. Autoclave leaching was allowed to proceed for more than 717 days. Fractional copper dissolution at this point was 0.43. Acid-generating reactions produced a rapid decrease in solution pH to about 1.7 in the first 60 days. This was followed by a slight increase in pH to 1.9, which stayed relatively constant for the remainder of the test.

A mixed kinetic model for leaching the chalcopyrite ore was proposed by Braun and co-workers (1974). The rate

of reaction was controlled by the rate of oxygen diffusion through the reacted shell of the ore fragment to unreacted sulfide particles. The reaction zone is only a few sulfide particle diameters in thickness. Overall kinetics are directly associated with physical aspects such as particle porosity, ore and mineral density, surface roughness, and tortuosity. This was acceptable for the particulate system employed, but the chemical reaction model would require integration with a hydrologic model to create a predictive reactive fluid flow model for actual ISL and scale-up to a field pilot test.

### Magma Copper Company

The Florence Copper Project is a copper in situ leach target located in Pinal County, Arizona approximately 5.6 km (3.5 mi) from the town of Florence. The HDI Curis laboratory core-box program described earlier was a sequel to the Magma investigation. The ore body is a porphyry copper deposit containing approximately 390 Mt (430 million st) of copper oxide ore that lie 137–366 m (450–1,200 ft) below the surface. Mineralization in the oxide zone comprises principally chrysocolla with lesser amounts of “copper wad,” tenorite, cuprite, native copper, and only traces of azurite and brochantite. The copper grade averages 0.33% Cu. The oxide zone is located below the water table at a depth of roughly 137 m (450 ft) below ground level. Ambient groundwater elevation is between 61 and 70 m (200 and 230 ft) above the top of the oxide zone. There is a 6.1–12.2 m (20–40 ft) clay layer approximately 18–33 m (60–100 ft) above bedrock, which acts as an upper aquitard, and there is a low-hydraulic conductivity layer beneath the bedrock oxide unit. These confining aquitards serve to control the vertical movement of solutions.

Magma Copper Company acquired the Florence property from Continental Oil Company (Conoco) in July 1992. In January 1993, Magma commenced a prefeasibility study and concluded that ISL and SX-EW was the preferred technique for developing the Florence deposit. Magma was purchased in January 1996 by Broken Hill Proprietary Company Limited, creating BHP Copper Inc. Work at Florence continued with planning for a field optimization test facility to demonstrate hydrologic control and to validate predicted copper recovery. The BHP test facility consisted of a pilot five-spot well pattern (see the description later in this chapter) with adjacent observation wells and a solution storage tank and evaporation pond. A total of 20 wells were drilled for the test facility. Four injection wells were drilled on a spacing of 21.6 m (71 ft) with a center recovery well. During the test, an injection rate of 0.15 m<sup>3</sup> min<sup>-1</sup> (40 gpm) was applied to each well with an aggregate solution recovery rate of 0.70 m<sup>3</sup> min<sup>-1</sup> (190 gpm). The test operated for approximately 90 days and successfully demonstrated that the ore zone had sufficient hydraulic conductivity to support fluid flow in the pattern and that hydraulic control of injected fluids could be maintained. Robertson and Hall (2011) have discussed in detail the hydrologic parameters associated with the Florence Copper Project. Current copper recovery estimates project approximately 70% Cu recovery in four years of commercial well-field production.

### Kennecott Copper Corporation

In 1967, Kennecott Copper Corporation announced plans to conduct a nuclear mining experiment at its Safford deposit located approximately 14.5 km (9 mi) northeast of Safford, Arizona. The project, called “Sloop,” was part of the AEC’s



Plowshare Program. The proposed nuclear blast would produce a rubbleized chimney of fragmented ore approximately 134 m (440 ft) high and 61 m (200 ft) in diameter, containing about 1.18 Mt (1.3 million st) of copper ore. Fortunately, a nuclear device was never detonated at Safford; however, Kennecott during the late 1960s and most of the 1970s conducted an extensive investigation of “true” ISL of the Safford deposit.

The Safford test program involved many scientists and technologists and, for the time, a huge expenditure of research and development funds. It was estimated that Kennecott expended more than \$20 million for this project over a three-year period. The Safford ore body was a deep-seated target with primary sulfide mineralization and extremely low permeability. Deep wells were placed in two-spot and five-spot patterns. The ore horizon was between 975 and 1,000 m (3,200 and 3,280 ft) at depth, and the formation had 3% porosity. Laboratory core data in five wells indicated permeabilities ranging from 0.001 to 0.4 mD. Conventional acid ferric sulfate leaching was unsuccessful. A field test at 981–1016 m (3,218–3,332 ft) deep using 0.1 molar  $\text{NH}_3$  and 2 molar  $\text{NH}_4\text{NO}_3$  solution injected at  $18.9 \text{ L min}^{-1}$  (5 gpm) showed significant permeability enhancement under these conditions. Little has been published regarding the Kennecott in situ project at Safford.

#### USBM/Asarco/Freeport

In 1988, the U.S. Bureau of Mines initiated a cooperative agreement with Asarco to investigate in situ recovery of copper at the Santa Cruz joint venture (Asarco and Phelps Dodge, later Freeport-McMoRan). The Santa Cruz deposit is located approximately 11.3 km (7 mi) west of Casa Grande, Arizona. A field experiment was planned and executed during the early 1990s. The deposit is moderately deep oxide mineralization, lying between 366 and 549 m (1,200 and 1,800 ft) deep. The mineralized zone contains approximately 88 Mt (97 million st) of ore averaging 0.7% acid soluble copper. At Santa Cruz, atacamite ( $\text{Cu}_2(\text{OH})_3\text{Cl}$ ) and chrysocolla ( $\text{CuO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ) are the predominant copper oxide minerals occurring as fracture-fillings in quartz monzonite and granodiorite porphyry. The deposit was considered too deep to mine by conventional surface methods and too low-grade for underground mining.

Considerable laboratory research was performed by the USBM as part of this project. Physical, mineralogical, and chemical features of the ore body were characterized by this research. Field research involved a five-spot well pattern with additional monitoring wells drilled to a targeted depth. Initial measurements collected hydrologic data that included salt-water tracer tests in the five-spot pattern. The tracer experiments started on March 14, 1991, and continued through July. Tracer solution was injected at a rate of  $0.087 \text{ m}^3 \text{ min}^{-1}$  (23 gpm) at a surface pump pressure of 1,585–1,998 kPa (230–290 psi). All but one of the recovery wells delivered solution with slowly increasing salt concentrations. Near the end of the salt tracer phase, a bromide slug experiment was tried. Environmental permitting was required for acid leaching at the pilot test facility. During the permitting process, a small SX-EW plant with a capacity of  $0.19 \text{ m}^3 \text{ min}^{-1}$  (50 gpm) was constructed. Acid leaching of the ore body from the pilot five-spot commenced in January 1996 at an injection rate of  $0.095 \text{ m}^3 \text{ min}^{-1}$  (25 gpm). Regrettably, the USBM was closed at about the same time and documentation of the results from this test is sketchy at best. One valuable outcome from the

Santa Cruz project was the publication of the *Generic In Situ Copper Mine Design Manual* (Davidson 1988), which is available to the public.

#### WATER-SOLUBLE MINERALS

Because of the nature of their solubility, water-soluble minerals present somewhat unique opportunities for their extraction and recovery. Water-soluble minerals are extracted from seas, lakes, salars, brine reservoirs, abandoned underground mines, and bedded deposits for the concentration of salts and mineral products. Brines containing soluble minerals are withdrawn directly from natural bodies of brine using pumps or brine elevators and from shallow aquifers using surface trenches or wells. Naturally occurring brines are also pumped from deeper brine aquifers for the recovery of soluble minerals. Solution mining or ISL of soluble mineral beds using ambient or high-temperature water or engineered brines is utilized to selectively extract targeted minerals.

Solution mining of bedded deposits may be preferred to conventional methods when deposits are too deep or too geologically complex for conventional underground mining. Avoiding hazardous mine gases, such as methane or hydrogen sulfide; eliminating the need to place personnel at increased depths; leaving insoluble impurities in the solution caverns; and minimizing the surface tailings storage requirement all favor a solution mining option. Solution mining is more energy-sensitive than conventional mining and consumes more water per short ton of product; therefore, the availability of water and access to inexpensive energy or solar evaporation are important differentiators.

Halite ( $\text{NaCl}$ ), referred to herein as salt; potash ( $\text{KCl}$ ); and trona ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot \text{H}_2\text{O}$ ) represent the largest product volumes produced by solution mining. Approximately 50% of the United States' 2014 salt production, 44.1 Mt (49 million st) was extracted by solution mining (Bolen 2015). Magnesium chloride, sodium sulfate, borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ), lithium, bromine, and iodine are also produced from soluble sources. In addition to the mineral value, the storage capacity of the resulting void may have commercial value in the storage of hydrocarbons and compressed gases. These solution cavities are also used for the disposal of wastes.

The recovery of soluble minerals from surface expressions such as seas, lakes, and shallow aquifers is presented elsewhere in this handbook, specific to the individual commodity. Therefore, this section focuses on the solution mining of nonbrine, subsurface deposits.

The extraction of subsurface soluble minerals by dissolution of the mineral represents some of the earlier methods of mining. Chinese miners used bamboo drills and bamboo pipes to extract salt brines from deep brine reservoirs or from salt beds as early as 300 BC (Warren 2006). In the 1920s, German attempts at solution mining of carnallite ( $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) were unsuccessful and were abandoned. Success was finally achieved for carnallite in the 1980s by DEUSA at Bleicherode/Kehmstedt in Germany. Following multiple unsuccessful attempts, solution mining has only had a broader commercial application in the last 50 years. In the 1960s, solution mining was expanded to include the extraction of potash from sylvite ore ( $\text{KCl}$ ) at Kalium's (now Mosaic's) Belle Plaine operation in Saskatchewan, Canada. In the 1980s, Royal Dutch Shell (now Nedmag) started solution mining bischofite ( $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ) and carnallite at the Veendam mine in the Netherlands, and in the 1990s, FMC (now Tronox) started solution mining of



trona ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ) in Wyoming, United States. In addition, borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) is solution mined in California, United States, and nahcolite ( $\text{NaHCO}_3$ ) was solution mined from bedded deposits in western Colorado, United States.

The brines extracted from solution mines may be delivered to evaporative pans, solar ponds, evaporators, and crystallizers to recover the soluble mineral. Some salt operations are captive to chlor-alkali plants (Kyle et al. 2011). With rock salt, total evaporation is often required. For other salts, such as potash, cooling the brines recovers the mineral and mother liquor is produced, heated, and returned to the mine for restoration of the brine.

### Principles and Key Parameters

A multitude of variables must be considered in the design and decision to use solution mining. Key considerations include the following:

- Thickness of the deposit and depth of the deposit
- Grade of the deposit and nature and quantity of associated impurities
- Depth and temperature of the deposit
- Uniformity of the deposit bedding and the absence of anomalies
- Geomechanics of the deposit and overlying rock members
- Homogeneity and extent of the deposit
- Dip of the deposit
- Proximity of overlying aquifers

Soluble minerals do not have the strength of hard rock minerals; they plastically deform when stressed, and creep is exacerbated by elevated temperatures. Impurities will influence the phase chemistry of the extraction brines and, along with temperature, will influence the rate of dissolution. Stability relationships in complex brines are defined with the aid of classical phase chemistry.

### Dissolution

The main dissolution mechanism is free convection or density-driven movement and mixing at the cavern walls. The boundary layer at the cavern side walls is influenced by cavern flow patterns, wall roughness, and impurities. Denser saturated brine flows downward along the cavern walls creating convection currents, flow along the walls, and brine density stratification in the cavern. Unsaturated brines are convected upward. This results in a brine concentration gradient that determines the rate of dissolution. Dissolution rates are a direct function of temperature and the concentration gradient or an inverse function with brine saturation. As a result of the concentration gradient, increased dissolution rates occur higher on the cavern wall and at the roof of the cavern and, if unmanaged, result in caverns with the shape of an inverted cone. The dissolution rate at the roof of the cavern is 1.5–2 times the dissolution rate of the side walls. Therefore, immiscible liquids or compressed gases, such as oil, diesel fuel, nitrogen, and air, are used to create an inert blanket at the top of the cavern. In addition to the inert blanket, the injection flow rate, the progressive relocation of injection and extraction strings, and the routine reversal of injection and extraction flows can be managed to determine the shape of the cavern. The Solution Mining Research Institute supported a significant volume of research work on salt dissolution and the development and measurement of solution-mined cavern shapes; Nigbor (1982)

provides a good summary of the work by Snow, Durie, Jessen, Saberian, and others.

There is a contrast in dissolution methods for different soluble minerals that is best described by comparing solution mining of salt and potash. In the case of salt, solution caverns are mined in relatively high-purity deposits resulting in brine-filled voids with the relatively small accumulation of insoluble materials at the base of the cavern. Dissolution by convection is relatively unobstructed. For potash that is less pure, 30%–40% KCl, there are two methods of dissolution: one dissolves both the salt and the potash, and another selectively dissolves the potash, taking advantage of sylvite's relatively higher solubility at elevated temperatures, and leaving the salt in the cavern. The latter approach results in caverns containing a honeycomb of mineralization as the target mineral is removed and the insoluble minerals remain behind (Husband 1971). This honeycomb obstructs the natural convection patterns and decreases the relative dissolution rates. In the case of potash, after the initial cavern development is completed to create a void and a functioning level of surface area, approximately 60% of the deposit is not potash and, depending on the mining method, may not be solubilized and thus remains underground.

Cavern production is the product of the dissolution rate and surface area. During cavern development, additional surface area is created as the cavern size increases, thereby increasing the overall mass production from the cavern.

### Solution Mining Methods

Solution mining methods can be divided into pressurized and unpressurized systems, with the majority of minerals extracted from pressurized systems. In a pressurized system, high-pressure pumps inject water or brine into the mining cavern, displacing brines as extraction brines. Depending on the pressure drop of the system, extraction brine is directly displaced or assisted by lift pumps. In a nonpressurized system, brine is pumped into an open cavity, such as mine workings and flows, to a lower point in the mine where the saturated extraction brine is pumped to the surface via vertical wells.

Production wells in a pressurized system are similar to oil and gas wells. After casings are established for the protection of local aquifers, typically there are three concentric production strings. The inert blanket is managed through the outer annulus, while the injection and extraction brines are introduced or removed through the remaining annulus or the final string, depending on preference for direct or reverse cavern flow.

The pressurized systems can be configured as single-, dual-, or multi-well caverns. Single-well configurations are common for mining in salt domes or for the development of storage caverns where long, cylindrical Thermos-shaped caverns are preferred. A dual-well system is common in bedded salts where two wells are paired to provide lateral cavern growth and overlap of the caverns. When dual-well systems establish hydraulic connectivity, they have the advantage of being much more productive than a single-well cavern and produce brine with increased saturation. Salt mining since about 1955 has used hydraulic fracturing to initially connect the two wells. Paired well spacing can vary depending on bed thickness and designed cavern roof span. This configuration is used in potash solution mines in Saskatchewan and Europe. Multi-well systems are usually the product of mature single- or dual-cavern systems where caverns are allowed to overlap



or wells are required in later development to remove stranded brine from subsurface topographically low points or sumps.

An alternative to vertical wells is the use of horizontal well technology adopted from the oil and gas industry. Directional drilling is used to develop horizontal wells in the seam or just below thin mineralized seams. A second horizontal well and sometimes a series of lateral wells are developed to intercept the first well, establishing a dual-well system. White River Nahcolite Minerals in Rifle, Colorado, and Intrepid Potash in Moab, Utah (United States), use this method.

### Applications

Salt is solution mined at depths from 400 to 2,900 m (1,312–9,512 ft), with the deepest cavern at Frisia Salt in the Netherlands. Single-well caverns are generally constructed in salt domes, and caverns range from 500 to 800 m (1,640–2,624 ft) high. An inert blanket is used to manage the diameter of the cavern, typically 50–100 m (164–328 ft) in diameter, and is used in the case of direct circulation. After the development of a sump for the accumulation of insoluble materials is complete, the extraction tubing is progressively raised to form a near-cylindrical cavern. The injection string may need to be raised as the cavern matures and insolubles accumulate at the bottom. Flow rates are initially very low to provide high brine concentrations and increase as the cavern develops and increased surface area is created. High flows can be maintained after about a year of development, and the life of successful solution caverns may be as long as 30–40 years (Warren 2006).

Since the 1930s, the Trump method, identified by an inert blanket, has been used to control vertical development. Since the 1950s, dual- and multi-well caverns are generally used for salt in bedded deposits, using the Trump method (Nigbor 1982). Wells located between 60 and 183 m (197 and 600 ft) apart are operated as single wells until the caverns connect. At that time, one well is converted to the injection well and the other well is converted to the extraction well.

In Saskatchewan, Canada, the rule of thumb is to use conventional mining to a depth of 1,100 m (3,608 ft) and to use solution mining at depths greater than 1,450 m (4,756 ft) (Halabura and Hardy 2007). Mosaic's Belle Plaine operation is the largest potash solution mine and extracts potash from three ore members at a depth of 1,600 m (5,248 ft); bed thicknesses vary from 9 to 15 m (30 to 49 ft). The new K+S Bethune Project is in the final stages of construction and will extract potash from the same members at similar depths. A dual-well configuration is used with 9–14 caverns directionally drilled from one pad or cluster. Thirty or more clusters may be in various stages of development to support the level of potash production. The spacing between the paired wells determines the areal extent and the roof span of the cavern. The developed cavern will have a near-oval shape with cylindrical-type walls. Cavern spacing within the cluster is predetermined to retain boundary pillars between the caverns in each cluster. Cavern spacing is designed to provide a 30%–40% extraction ratio. At deposit depth, the spacing between the paired wells ranges from 80 to 100 m (262 to 328 ft) and salt temperatures are approximately 57°C (135°F). Mosaic's Hershey operations solution mined potash in a similar manner from 1990 to 2013 in Michigan at bed depths of 2,300 m (7,544 ft) (Plosz 2005).

The solution mining method employs five stages of development and operation, summarized as follows.

1. **Sump development:** A sump is solution mined with fresh water at the base of each well in the salt bed just below the potash bed. The inert blanket is managed to prevent dissolution of potash.
2. **Undercut:** Solution mining with fresh water continues in the salt bed until connection is established between the two wells. The inert blanket is used to limit vertical growth in the caverns.
3. **Roof development:** Solution mining with fresh water continues with injection into one well and extraction from the paired well. The flow may be alternated from well to well, and the roof is developed to about 50%–60% of the designed cavern roof area.
4. **Primary mining:** Hot fresh water is used to solution mine both the salt and the potash, creating the mining cavern. Progressive horizontal cuts from 1.5 to 3.0 m (5–10 ft) and cyclic injection are used to increase the height of the cavern until the cavern reaches the top of the potash beds.
5. **Secondary mining:** Solution mining switches from hot fresh water to hot recycle brine from the plant to selectively dissolve sylvite from the walls and the roof.

In some cases, a forced roof collapse is used in preparation for mining with hot recycle brine. Cavity development lasts four to five years, and the cavities can produce for more than 20 years. About 70% of production originates as primary mining and 30% as secondary mining. For potash mining, injection brine temperatures of 10°–20°C (50°–68°F) greater than the salt temperature balance dissolution rates and energy losses to wall rock (Asch et al. 2013).

DEUSA solution-mines potash from carnallite at Bleicherode in Germany. The company uses a dual-well system with hot dissolution. This is a complex system, and magnesium and potassium levels must be closely controlled to avoid blinding beds or increasing potash losses by precipitating KCl in the caverns. Mining occurs in a 50°C (122°F), 33-m (108-ft) bed at 400 m (1,312 ft) deep with a well spacing of 60 m (197 ft) and uses a compressed air blanket. Hot magnesium chloride mother liquor from the process, which is saturated in NaCl but undersaturated in KCl, is heated to 80°C (176°F) and injected into the cavern. Carnallite is leached and NaCl precipitates out in the cavern, whereas KCl and MgCl<sub>2</sub> report to the brine. Because of the high solubility of magnesium chloride, halite and kieserite (MgSO<sub>4</sub>·H<sub>2</sub>O) have limited solubility and remain behind in the cavern. Eight percent of the cavern volume is filled with insoluble residues. The extraction brine reports to the process plant where carnallite and halite are crystallized and the resulting mother liquor is used to produce bischofite or returned as injection brine. The carnallite is decomposed to produce magnesium chloride brine, leaving sylvite and halite crystals. A hot leach and crystallization step recovers the sylvite from the halite.

Even more complex phase chemistry and geomechanics are encountered at the Veendam mine, which solution mines magnesium from carnallite and bischofite beds at depths of 1,400–1,800 m (459–5,904 ft) and in situ temperatures of 80°C (176°F). A double-well system is used and, with experience, well spacing increased progressively from 100 to 140 to 200 m (328 to 460 to 656 ft). Bischofite is very plastic and paste-like at these depths and squeezes into the cavern. Cavern pressures must be managed to control the convergence of the cavern, and the cavern diameter remains almost constant



as dissolution and convergence are balanced. An estimated 30%–40% of the production is generated from salts squeezed into the cavern. Salt is “squeeze mined” in a similar fashion at Frisia, where 100°C (212°F) salt squeezes into the cavern; managed convergence and dissolution result in constant cavern sizes.

Solution mining of potash also occurs from unintentionally or intentionally flooded underground workings, such as the Potash Corporation of Saskatchewan’s Patience Lake (Canada), and Intrepid’s Moab and HB (Carlsbad, New Mexico, United States) operations. Salt-saturated brine is injected at a higher elevation in the workings, and sylvite is dissolved from pillars through convection as the brine migrates to the low spots in the mine. As the brine stratifies, the concentrated brine reports to the lower areas of the mine and is pumped to the surface using vertical wells. Sylvite is recovered either in ponds that are cooler relative to underground temperatures, or in solar ponds or crystallizers.

The development of horizontal caverns is also used at Moab and at White River Nahcolite. Directional drilling is used to intercept another well bore, either horizontal or vertical, maintaining bed contact just below the base of the target mineral bed. Hot water is used to undercut the target mineral bed and to increase the surface area of the developing cavern. Moab uses lateral wells and a pitchfork design to connect to the target well, whereas White River develops parallel pairs of horizontal and vertical wells to create a chamber and pillar arrangement (Day 1994). Hot-salt saturated brine or water are used, respectively, to mine the two deposits.

In 1996, FMC began introducing trona tailings into abandoned underground workings. The transport brine migrates to lower areas in the mine panels, leaching pillars and increasing the alkalinity of the brine. The brine is returned to the surface using vertical wells. The ability to process the brine was critical to the project’s success, and an evaporation, lime neutralization, decahydrate crystallization, and monohydrate crystallization (ELDM) process plant was developed where evaporation and liming produce a concentrated brine. Sodium carbonate decahydrate crystals are recovered and converted to sodium carbonate monohydrate. The deposition of tailings and recovery of leach brines is practiced by other Wyoming operators as well.

Also similar to potash practice, the Granger trona mine in Wyoming was flooded in 2007 to solution mine the pillars and remaining ore. Mine water is pumped from low spots in the mine for processing.

Fort Cady Minerals solution mines borax at Hector, California. Weak hydrochloric acid is injected into colemanite beds 300 m (984 ft) deep to extract boron-rich brines to the surface.

### Environmental Considerations

Salts deposits and beds form impervious zones and provide a barrier to solution releases from caverns. Leaching with saturated brines further minimizes the potential for solution migration beyond planned cavities. In North America, deep-well injection is used to dispose of bitterns or purged brines, whereas in Europe, ocean, sea, or riverine disposal is also used. Precise brine accounting and monitoring wells are used to ensure that all mine and disposal solutions are appropriately contained and managed.

Subsidence associated with solution mining can also be regulated, depending on local governmental agencies. It is a

key permit limitation, especially for deeper solution mines, and regulatory subsidence limits are integral to development and operating strategies. Surface monitoring programs, including the use of light detection and ranging, are common.

### URANIUM DEPOSITS

Refer to Chapter 12.41, “Uranium,” for a discussion of uranium chemistry, conventional milling, solution treatment, precipitation, product specifications, and other considerations relevant to conventional uranium ore processing.

### Historical Examples 1960–1990

Solution mining in its simplest form is typified by treatment of mine water that has been enriched through dissolution of uranium by oxygenated groundwater. This has probably been done in many mining districts, but it has been reported that in 1965, Kerr-McGee and United Nuclear-Homestake Partners jointly produced about 91 kg (200 lb) of  $U_3O_8$  daily from approximately  $11.4 \text{ m}^3 \text{ min}^{-1}$  (3,000 gpm) of mine water in the United States at Ambrosia Lake District, New Mexico (Merritt 1971). In this case, uranium probably was present as anionic uranyl tricarbonate complexes and water treatment was effected with transportable resin ion exchange columns that were eluted at the owners’ mills.

Engineered solution mining, or in-place leaching, involves the intentional introduction of leaching solutions into an ore body after the ore has been rendered permeable and provisions have been made for solution collection and treatment. There have been many examples for various metals and minerals, but the following apply specifically to uranium.

During the 1960s, Canmet had a bacterial leaching program that led to a cooperative agreement with the Kerr-Addison and Agnew Lake mines. A 0.61-m (2-ft) diameter by 4.6-m (15-ft) column was loaded with 1.8 t (2 st) of Agnew Lake uranothorite ore and leached with solutions that were acidified by bacterial oxidation of pyrite and pyrrhotite in the ore. The test predicted 70% uranium extraction in one year, leading to a test in which a stope containing 45 t (50 st) of broken ore was leached for 30 weeks, dissolving 57% of the uranium (Ehrlich and Brierley 1990).

This encouraging information led Kerr-Addison in 1976 to invest \$37 million in an underground bacterial leaching project at Agnew Lake. The anticipated production rate was 453,700 kg (1,000,000 lb)/yr of  $U_3O_8$ , but actual production in 1977 was only 31,760 kg (70,000 lb). Because of the steep dip of the ore zone, solution distribution in the inclined rubblized stopes was poor. This factor and other complications led to closure of the project in 1980.

In 1984, Denison Mines and Canmet began development of another underground bioleaching project for uranium recovery from the Denison ore body. An extensive study was made to optimize rock fragmentation, bacterial nutrients, spraying versus flooding, solution temperature, and other variables. Commercial production began in 1987 and 381,125 kg (840,000 lb) of  $U_3O_8$  were recovered during that year. A major contributor to the success of the project was a very favorable ore body configuration that allowed blasting of the upper ore zone down into the cavities in the lower ore zone that had been mined by the room-and-pillar method (Ehrlich and Brierley 1990).

True ISL of uranium was begun in 1963 by Utah Construction and Mining in Wyoming’s Shirley Basin. Leaching was done with a sulfuric acid solution, and annual



production was about 90,744 kg (200,000 lb) of  $U_3O_8$  through 1970. However, Utah determined that ISL costs were higher than those obtained by conventional milling at other company operations, so the Shirley Basin ISL project was replaced with a conventional mine and mill (Pool 2000). Several ISL operations began in Texas, United States, during the mid-1970s. In the United States, it is common to refer to ISL as ISR for “in situ recovery.”

### Physical and Chemical Constraints for In Situ Leaching

Although there are many geologic classifications of uranium deposits, the type that is most conducive to ISL of uranium is the so-called roll-front deposit characterized by deposition of uranium minerals under a reducing environment immediately down gradient of an oxidizing environment. The physical setting is usually an ancient stream channel or “paleochannel,” and mobile hexavalent uranium has been reduced to relatively insoluble tetravalent uranium by agents ranging from sulfide ion to carbonaceous material such as decaying wood. Bhattacharyya et al. (2017) discussed the discovery of evidence revealing biogenic reduction of hexavalent uranium.

For ISL to be carried out with effective hydraulic control, the uranium-mineralized zone must be situated beneath or enveloped within an aquifer. Ideally, this zone will be essentially horizontal and will be bounded above and below by aquitards such as clay layers. During the development phase of the project, a thorough understanding of groundwater hydrology must be established. With the aid of core drilling, the combined grade and thickness of uranium mineralization is defined for each core intercept and a mine plan devised that will ensure access to an economically viable reserve expressed in pounds of recoverable  $U_3O_8$ .

Hydraulic control of an ISL well field requires that slightly (0.5%–2%) more water must be withdrawn from the aquifer than is injected into the mineralized formation. This excess water is balanced by bleeding an equivalent flow rate from the processing plant as a barren solution (either SX raffinate or ion exchange [IX] strip solution) that must be discarded. Ordinarily, this bleed stream is evaporated in a lined pond, but an injection well may be needed under unusual circumstances such as a site with high rainfall and negative net annual precipitation.

### Technical and Economic Advantages Versus Conventional Milling

Compared with conventional milling using either an acidic or alkaline lixiviant, ISL occupies and disturbs less surface area, allowing less expensive closure and minimal audible and visible impact on residences and commercial entities. An in situ operation likely will create an evaporation pond that must eventually be closed and reclaimed, but it will leave neither waste rock nor tailings. Although each project is unique, it is fair to generalize that an in situ uranium operation will also require less capital investment and have lower operating and maintenance costs than conventional milling. It may also be less expensive than heap leaching; an instructive comparison for a specific collection of deposits has been published by Beahm (2007).

In contrast to conventional open pit mining, ISL requires fewer pieces of major equipment such as blasthole drills, excavators, haul trucks, crushers, grinding mills, leach tanks, and residue washing thickeners. Consequently, capital costs may be lower, depending on the cost of well field development and

well drilling. Because of its relative simplicity, uranium ISL potentially offers quicker project development and engineering, faster ramp-up to design capacity, and possibly a higher return on invested capital. Furthermore, the lack of dependence on drilling, blasting, crushing, and grinding equates to less energy needed per unit of production. Likely, radiation exposure also will be minimized.

### Economic Disadvantages

The ISL method typically dissolves less uranium than a conventional milling circuit and more slowly, for the following reasons:

- Because of channeling and short circuiting of the leaching solution, contact with mineralized grains is relatively poor.
- Oxidation of  $U^{4+}$  is the rate controlling step, and oxidant contact may be ineffective.
- Sulfide minerals will react with the oxidant, producing sulfuric acid and reducing lixiviant pH.

Domestic uranium production by ISL expanded during the 1970s, and by 1981 there were 11 operations, mostly in southern Texas. Initially, sulfuric acid solutions were injected, but in nearly all cases, alkaline leaching solutions were adopted later. Ammonium carbonate was tried, but aquifer restoration was difficult, so sodium carbonate/bicarbonate solutions and oxygenated groundwater with added carbon dioxide became the preferred lixiviants. Declining uranium prices led to closure of some of these operations, along with nearly all of the conventional mines and mills, but some ISL mines continue to produce uranium and new ones have been added in the United States in Wyoming, Texas, and Nebraska.

### Well-Field Design and Operation

ISL wells for uranium extraction are generally adaptations of conventional water well designs. They are drilled with rotary rigs, and the drill hole is reamed to a diameter of 17.8–25.4 cm (7–10 in.) Usually, three casing centralizers are used, and the casings are typically 10–15 cm (4–6 in.) PVC or fiberglass-reinforced plastic, the latter being preferred for higher pressures and corrosive solutions. The casings are cemented up to the surface from the bottom (“point”) of the casing, and the drill hole through the mineralized sandstone is uncased and may be under-reamed to increase formation contact area. If there are multiple economic zones, the casing is perforated to match depths of mineralized intervals, and the perforated sections are lined with stainless-steel screens.

The most common well pattern is a five-spot, which is a square configuration with a central injection well and a production well at each corner. Corner-to-corner spacing is typically 15–61 m (50–200 ft) with an average of about 23 m (75 ft). Well depths are typically 61–274 m (200–900 ft) but may reach 610 m (2,000 ft) in some overseas operations. Submersible stainless-steel pumps are used in the United States and Australia, but air lifts are preferred in the former Soviet Union because of operational simplicity and low cost. Figure 6 illustrates a typical well completion technique as practiced in the western United States. It is based on a drawing provided by Uranium Energy Corporation and typifies that company’s well completion technique at the Palangana mine near Duval City, Texas.

A fence of monitor wells is installed around the well field to detect migration of leaching solutions outside the active



patterns and to intercept and extract those fluids before they contaminate the aquifer. Typically, some monitor wells are completed in the aquifer overlying the production zone, as well as in the aquifer underlying the production zone. A ring of monitor wells encircles the wellfield. At the Palangana mine, the ring wells are spaced 122 m (400 ft) outside the outer production wells in the field. The monitor wells are cased to ensure that solutions are controlled.

The solution flow rate from a single well cased to a 10-cm (4-in.) nominal diameter and reamed to 20 cm (8 in.) diameter in the screened intervals will typically be 19–76 L min<sup>-1</sup> (5–20 gpm). Flow rate can be estimated using the following equation (Huff 2002):

$$Q = (1.035 \times 10^{-4} kh(\Delta p)) / \mu [\ln(d/r_w) - 0.619] \quad (\text{EQ 12})$$

where

- Q = flow rate, gpm
- k = permeability, millidarcies, mD
- h = vertical ore interval open to flow, ft
- $\Delta p$  = applied differential pressure, psig
- $\mu$  = fluid viscosity, cP
- ln = natural logarithm
- d = spacing between injection and production wells, ft
- $r_w$  = well bore radius, not casing radius, ft

Conversion of this equation to metric units is potentially misleading, especially since formation permeability is universally

expressed in millidarcies, and the darcy is a mixture of metric and conventional units. Commercially viable uranium roll front formations typically have permeabilities in the range of 300–1,000 mD. Pregnant and barren leach solutions ordinarily have viscosities of 0.8–1.0 cP.

Typical ore grades are in the range of 0.04%–0.15% U<sub>3</sub>O<sub>8</sub>, and well bores are logged electrically or radiometrically to define mineralized bed thicknesses and grades. The grade-thickness product (G×T) is used in reserve calculations, and a typical cutoff is in the range of 6–30.5 cm% (0.2–1.0 ft%) U<sub>3</sub>O<sub>8</sub>, depending on uranium price and expected production costs. In the United States, the most common ore minerals are uraninite and coffinite and both are readily oxidized. Accessory minerals include quartz, clays, feldspars, calcite, pyrite, and carbonaceous materials.

Injected leach solutions contain an oxidant, usually oxygen or hydrogen peroxide, at concentrations of 50–500 mg/L. In the United States, the lixiviant is typically oxygenated groundwater to which carbon dioxide is added to complex uranium and to adjust alkalinity to pH 7–9. The carbon dioxide concentration is about 500–1,000 mg/L. In this case, the dissolved uranium is complexed as uranyl tricarbonates. In Australia and Kazakhstan, the lixiviant is dilute sulfuric acid and the dissolved uranium is complexed as uranyl sulfate. Alkaline leaching is necessary when the calcium carbonate content of the ore renders sulfuric acid uneconomic. However, alkaline leach extractions are lower than those obtained with sulfuric acid, and alkaline leaching is roughly twice as

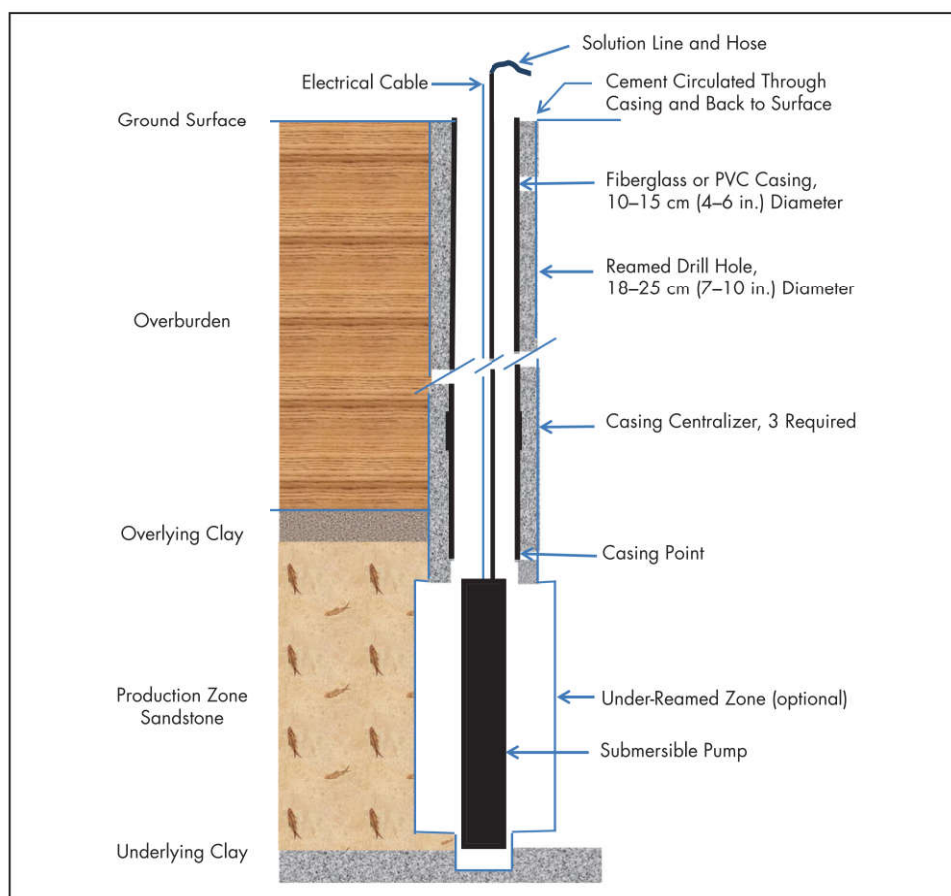


Figure 6 In situ well completion technique (not to scale)



expensive. The uranium concentration in the PLS is normally in the range of 35 to 200 mg/L  $U_3O_8$  (Stano 2002; Pool 2000; WNA 2017a).

In practice, the PLS is pumped to a holding tank, clarified, and pumped through IX columns loaded with strong-base anionic resin beads. The resin is eluted (stripped) with alkaline or acidic chloride solution, concentrating the uranium by a factor of 5–20. The resulting eluate is neutralized and uranium is precipitated. Precipitation with ammonia produces ammonium diuranate crystals, whereas precipitation with hydrogen peroxide yields uranyl peroxide. The precipitated slurry is thickened, filtered or centrifuged, and dried. Most U.S. operations now use rotary vacuum dryers that have virtually no particulate emissions. The barren solution after IX is reconstituted and injected into the well field. It is common for PLS from small remote well fields to be treated with portable IX columns that can be eluted at a central processing plant.

Aquifer restoration requirements vary among countries and may be subject to local regulatory considerations. In Australia and in former Soviet Union countries, the groundwater may be so poor and the site so remote from habitation that restoration requirements are minimal. In the United States, restoration may be required on an individual element basis, which can be very expensive. Furthermore, groundwater quality in the United States ranges from good in Wyoming and New Mexico to relatively poor in Nebraska and Texas. Restoration of an aquifer is done by injecting clean water or by drawing aquifer water through the mined patterns and treating, for example, by reverse osmosis (RO). The clean RO permeate is injected into well patterns while the brine is either evaporated or injected into a disposal well. Radium is removed from waste solutions by resin ion exchange or precipitation with barium chloride.

### Lixivants and Gangue Interactions

As noted previously, sulfuric acid solutions react with calcium carbonate, and more than 2%  $CaCO_3$  in a mineralized formation will usually consume an uneconomical amount of acid unless local acid costs are unusually low. Furthermore, the gypsum reaction product may gradually reduce permeability and impair solution flow rates. In alkaline leaching, the most likely gangue reaction is with naturally occurring gypsum, where dissolved sodium carbonate ions will react to form soluble sodium sulfate while precipitating calcium carbonate.

### Laboratory Simulation Techniques

Representative core intervals from throughout the deposit can be subjected to standardized simulation procedures to establish the responsiveness of the uranium minerals to oxidation and complex formation and to subsequent recovery of a commercially acceptable product.

Pressurized bottle rolls are a common method for alkaline ISL, where a pulverized sample is added to five pore volumes of lixiviant containing low concentrations of hydrogen peroxide and sodium bicarbonate. The bottle is pressurized to expected formation hydrostatic pressure with gaseous carbon dioxide and is rolled for 24 hours. The depressurized slurry is filtered, the solids are repulped with fresh solution, and the bottle is again pressurized. This sequence is repeated for a total of 30 pore volumes and a metallurgical balance is calculated on the basis of solution volumes and assays and residue solids weight and assay. For sulfuric acid leaching, it is acceptable to

simulate ISL using vertical plastic columns, as is done during simulation of heap leaching of oxide copper ores or nonrefractory gold ores. The laboratories at several ISL operations in the United States conduct leaching tests at ambient pressure. At least one commercial laboratory adds sodium carbonate to the lixiviant, rather than relying on the carbonate/bicarbonate equilibrium.

These laboratory techniques will predict maximum reagent consumption and maximum uranium dissolution, so a conservative factor should be applied to the results, based on the experience of the client and the laboratory manager. Also, laboratory tests on small pulverized samples should not be relied on to predict with any reliability the performance of a well pattern unless sampling and compositing have been done diligently. In uranium formations for which there is little or no ISL experience, it is essential to drill and leach a commercial-scale well pattern. As a general rule, overall recovery of uranium to yellowcake is in the range of 60% to 75% with alkaline leaching and 70% to 85% with acidic leaching.

### Commercial In Situ Operations

In 2016, 48% of the world's uranium was produced by ISL operations in Kazakhstan, Uzbekistan, the United States, Australia, China, and Russia. Global ISL production in 2016 was 30.06 million kg (66.25 million lb) (WNA 2017a). Most ISL operations produce 454–2,269 million kg/yr (1–5 million lb/yr) of  $U_3O_8$ , but the largest consolidated ISL operation in Kazakhstan, a Katco/Areva joint venture, produced more than 4 million kg (8.8 million lb) in 2016, down slightly from 2014 and 2015. In contrast, total 2014 ISL production in the United States was 1.13 million kg (2.48 million lb), down from a peak of 1.92 million kg (4.23 million lb) in 2014 (WNA 2017b).

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