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MODELS TO OPTIMIZE THE EVALUATION AND EXTRACTION OF URANIUM FROM SEDIMENTARY ORE DEPOSITS WITH APPLICATIONS TO IN-SITU LEACHING

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MODELS TO OPTIMIZE THE EVALUATION AND EXTRACTION OF URANIUM FROM SEDIMENTARY ORE DEPOSITS WITH APPLICATIONS TO IN-SITU LEACHING

by

JOHN EDWARD ODDO

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

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HOUSTON, TEXAS

MAY, 1980
ABSTRACT

With increasing demands for nuclear power supplies, more efficient means of evaluation and extraction of sedimentary uranium ore deposits, which form 96% of the U.S. reserves, are required. The fluvial, deltaic, and near-shore marine sands and associated lignites of the Texas coastal plain uranium deposits can assist in the need for increased nuclear power supplies.

Tetravalent uranium is essentially immobile, while hexavalent uranium is easily complexed and very mobile in sedimentary aqueous systems. Fixation of uranium in the sediments seemed to be controlled by sorption and/or reduction by organic matter, \( \text{H}_2\text{S} \), clays, zeolites, and carbonates. Texas uranium ore typically occurs in roll-front type deposits and these are discussed in conjunction with fixation and mobilization mechanisms.

The basic strategies of the carbonate and acid leach systems are discussed. By monitoring effluent uranium and Rn-222 and cumulative uranium and Rn-222 extracted, it is shown that predictions can be made concerning mining efficiency, degree of secular equilibrium, future profitability, and mining duration.

Dissolution Eh-pH diagrams constructed by assuming an infinite source of uraninite in water with various complexing agents are shown to agree more accurately with kinetic data of uraninite dissolution than conventional stability Eh-pH diagrams. At pH values between 6.0 and 9.0, the reduced reaction rate in this pH range, the first order dependence of the oxygen partial pressure and the hydrogen ion concentration, and the first order dependence of the carbonate at low concentration and zero dependence at higher concentration can be explained by the formation of \((\text{UO}_2\text{)}_3\text{(OH)}_5^+\) predicted by the dissolution diagram. It is proposed that carbonate leach systems be operated at pH values between 9.0 and 10.0 and sulfate acid leach systems may be operated at a pH as high as 3.0.

Utilizing evidence that uraninite dissolution is not diffusion limited and
that in-situ leach solutions are quite undersaturated with respect to uranium, it is shown that uraninite dissolution is independent of hydrological parameters with the exception of the flow rate which regulates oxidant introduction to the ore body. The La Place source and sink equation is utilized to gain insight into parameters which can be adjusted to maximize mining efficiency while constraining the leach system. The optimum well spacing in an in-situ leach system is found to be a complex function of flow rate, the mobilization inhibiting factor (MIF), the rate of total oxidation of the aquifer, and the ability of the well system and the aquifer to confine the system.

The results of the research are used to generate models to optimize parameters in the in-situ leach. The models are found to predict values in good agreement with literature values for uranium in-situ leach operations.
ACKNOWLEDGMENTS

This thesis research and subsequent documentation has been accomplished at the Department of Geology of The Rice University which provided me with excellent educational and material support.

The following specific acknowledgments are made:

To Dr. John A.S. Adams who suggested the research and supported its development conclusion and to the entire thesis committee whose many recommendations were of great assistance.

To The Rice University Departmental Committee on Fellowships and Scholarships for their support in awarding me The Eleanor and Mills Bennett Fellowship in Hydrology.

To the Welch Foundation for continued support through Grant #C-009 to Dr. J.A.S. Adams.

To the Bendix Corporation for partial support under Bendix Contract #50-51-5156 to Dr. J.A.S. Adams.

To my fellow graduate students within the Geology Department, in particular to Enio B. Pereira, for their help, assistance, and discussions.

To Maria E. Barragan for secretarial assistance and to Maria E. Cundiff for providing partial support with the drafting.
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VII-1 THE ESTIMATES OF QUANTITIES FOR AN ORE BODY 20 METERS IN HEIGHT USED TO CONSTRUCT FIGURE VII-8. 89
I. INTRODUCTION

Although the future of nuclear power has been somewhat uncertain and despite slightly lower forecasts than a few years ago, nuclear power is rapidly becoming an energy alternative to fossil fuels not only in this country, but the world. For the present, uranium reserves are being developed at an adequate rate to fulfill present needs, however, a manyfold increase in reserves is needed to keep pace with projected increased demands in the latter part of the twentieth century. The development of uranium deposits in southeast Texas can play a major role in meeting the requirements of the United States in the future (Nininger, in press). The Department of Energy (D.O.E.), has estimated that uranium found in sandstone and conglomerate deposits comprise 96% of the total U.S. reserves (Report No. GJO-100(77), 1977). Texas coastal plain deposits rank third in the U.S. with estimated total reserves of 0.25 million tons of uranium, which is more than 10% of the U.S. total. The uranium occurs in two principle types of deposits: 1) in association with sandstone type deposits of the Goliad, Oakville, Catahoula, Frio, and upper-Jackson and 2) in Tertiary Wilcox, Yegua-Jackson, and upper-Jackson lignites (Huang, 1978). For the most part, these are fluvial sands and coastal plain deposits dipping toward the Gulf of Mexico at less than 3° with inherent bar and channel sands, mudstones, deltaic sequences, lignites, and other sediments of high variability (Galloway et al., 1979). (A more detailed description of the general geology of southeast Texas is the subject of the next chapter.) These fluvial, deltaic, and barrier sands tend to be discontinuous and anisotropic in nature and segregation of the uranium into more permeable aquifer channels has taken place with later fixation and concentration of the uranium to ore grade.

Oxidized uranium (hexavalent) is generally soluble in groundwater, whereas reduced uranium (tetravalent) is for the most part insoluble (Hostetler and
Garrels, 1962). This generality, however, is complicated by many other factors such as pH, temperature, complexing and chelating agents available, sorption phenomena, and total ionic strength (Langmuir, 1978).

It will be the purpose of this work to consolidate many geochemical and hydrogeological parameters in order to formulate models which reflect the fixation and subsequent mobilization of uranium in sedimentary systems. Although simplifications will be made in these models, it will be the intention of this work to determine variables of primary importance.
II. GENERAL GEOLOGY

The sedimentary beds which comprise the Texas Gulf Coast uranium province are late Eocene to Pliocene fluvial and nearshore deposits gently dipping into the Gulf of Mexico at less than 3°. The beds characteristically strike parallel to the gulf coast (Figure II-1). Interbedded with these are volcanic rhyolites, trachytes, and trachyandesites (Eargle et al., 1975). A stratigraphic section in the south Texas uranium belt is shown in Figure II-2.

THE JACKSON GROUP

The Jackson Group (principally the Whitsett Formation) is the major host rock for the first uranium deposits discovered. The Jackson and the underlying Yegua Formation consist of sand, mud, and lignite deposited in the upper part of a major progradational cycle. Depositional systems include an east Texas delta system and a south Texas strandplain and barrier bar system bounded by shelf and lagoonal deposits. The Jackson includes strike oriented coastal barriers and several wave-dominated cuspate deltas that prograde across the mud dominated coastal plain into the open Gulf of Mexico. Lagoonal deposits in the Jackson consist of restricted marine faunas and lignite beds. Downdip from the barrier sand belt are the shelf deposits which consist of light colored fossiliferous and glauconitic muds. The uranium occurs in the upper Jackson coastal barrier bars and associated facies and in the lignites (Fisher et al., 1970).

THE FRIO CLAY

During Oligocene (?) time continental deposition formed the Frio Clay. The Frio is characterized by light-green lacustrine clays and tuffaceous clays crossed by several fluvial-channel units 30-45 meters thick (Galloway et al., 1979).

THE CATAHOULA TUFF

The transition between the Oligocene and the Miocene is uncertain but
FIGURE II-1

Map of south Texas showing major geologic features. (Modified from Eargle et al., 1971.)
Stratigraphic section in the south Texas uranium province. Crosses indicate units from which uranium has been extracted. (Modified from Galloway et al., 1979.)
<table>
<thead>
<tr>
<th>GEOLOGIC UNIT</th>
<th>DESCRIPTION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quaternary</td>
<td></td>
</tr>
<tr>
<td>Pleistocene</td>
<td></td>
</tr>
<tr>
<td>Floodplain alluvium</td>
<td>Sand, gravel, silt, and clay</td>
</tr>
<tr>
<td>Fluvial terrace deposits</td>
<td>Sand, gravel, silt, and clay</td>
</tr>
<tr>
<td>Pleistocene Deweyville Formation, Beaumont Clay, Montgomery Formation, Bentley Formation, and Pleistocene(?) Willis Sand</td>
<td>Sand, gravel, silt, and clay</td>
</tr>
<tr>
<td>Goliad Sand</td>
<td>Fine to coarse sand &amp; conglomerate; calcareous clay; local medium to coarse sandstone. Strongly calcified.</td>
</tr>
<tr>
<td>Fleming (Logarto) Formation</td>
<td>Calcareous clay and sand.</td>
</tr>
<tr>
<td>Miocene</td>
<td></td>
</tr>
<tr>
<td>Oakville Sandstone</td>
<td>Calcareous, crossbedded, coarse sand. Some clay and silt and reworked sand and clay pellets near base.</td>
</tr>
<tr>
<td>Tertiary</td>
<td></td>
</tr>
<tr>
<td>Oligocene</td>
<td></td>
</tr>
<tr>
<td>Chusa Tuff</td>
<td>Calcareous tuff; bentonite clay; some gravel and varicolored sand near base. Soledad in Duval County, grades into sand lenses in northern Frio and adjacent counties.</td>
</tr>
<tr>
<td>Soledad Conglomerate</td>
<td></td>
</tr>
<tr>
<td>Fant Tuff</td>
<td></td>
</tr>
<tr>
<td>Frio Clay (Southwest of Karnes County)</td>
<td>Light-gray to green clay; local sand-filled channels.</td>
</tr>
<tr>
<td>Recent</td>
<td></td>
</tr>
<tr>
<td>Fossing Clay</td>
<td>Chiefly clay, some lignite sand</td>
</tr>
<tr>
<td>Torrilla Sandstone, Cullinam Sandstone</td>
<td>Very fine sand</td>
</tr>
<tr>
<td>Dupose</td>
<td>Silty, sand, clay, and lignite</td>
</tr>
<tr>
<td>Deweesville Sandstone</td>
<td>Mostly fine sand; some carbonaceous material</td>
</tr>
<tr>
<td>Conquiste Clay</td>
<td>Carbonaceous clay</td>
</tr>
<tr>
<td>Dilworth Sandstone</td>
<td>Fine sand, abundant Ophiomorpha</td>
</tr>
</tbody>
</table>
 occurred during deposition of the Catahoula Tuff. The Catahoula Formation is considered the potential source rock for the uranium deposits in south Texas primarily because the present uranium content is lower than tuffs of similar composition (Dux, 1971 and Mackallor, 1973), although the direct relationships of the ore-bearing rocks to the source is unclear (Huang, 1978).

Beginning in late Oligocene time and extending well into the Miocene, extensive volcanic activity resulted in the deposition of the Catahoula which lies unconformably on the Jackson and conformably downdip on the Frio Clay. While the Catahoula is composed principally of brown to gray tuff, it contains fluvial sandstones and conglomerates, especially in Duval county. The Soledad member contains rounded boulders and pebbles (up to 0.3 m. in diameter) of vesicular and amygdaloidal lava that probably originated in west Texas and northern Mexico (Eargle et al., 1975).

The Catahoula was deposited by the Gueydan fluvial system of the Rio Grande Embayment and by the Chita-Corrigan fluvial system of the Houston Embayment. These two systems then interfinger along the western margin of the San Marcos Arch. Evidence that the facies in each system stack vertically is obtained from regional interpretive-log cross section. The two systems grade downdip into the Frio deltaic and barrier-strandplain systems. The uranium deposits presently known are found in the Gueydan fluvial system (Galloway et al., 1979).

THE OAKVILLE FORMATION

The coarse fluvial sandstones, tuffs, and claytones of the Oakville Formation were deposited by rejuvenated streams bringing elastic material from the Edward Plateau and the Llano uplift. Finer grain deposits resulted from the seaward fanning out of the large channels (Eargle et al., 1975).

The Oakville is sedimentologically and compositionally distinct and can
be traced in outcrop on the southwest to south-central Duval County where it is onlapped by a veneer of Pliocene Goliad gravel and caliche to the Brazos River on the northeast. Oakville in the subsurface is difficult to distinguish from underlying Catahoula and overlying Fleming deposits without well samples. As the Oakville and Fleming Formations constitute a major Miocene depositional episode on the Texas coastal plain, discriminating between the two is difficult and divisions between the two are somewhat arbitrary. The Oakville is the generally coarse sand-rich basal unit and is consequently a better aquifer and perhaps the most significant uranium host due to its permeability and sinuous continuity (Eargle et al., 1975).

THE FLEMING FORMATION

The Oakville grades upward into the finer, ferruginous, mixed load fluvial sediments of the Fleming Formation. The increasing red color upward in the Fleming probably indicates a drier climate in Fleming time (Eargle et al., 1975). Although the Catahoula Formation was deposited at the height of volcanic activity and ash-fall across the Gulf Coastal Plain, continued volcanic activity and the reworking of older sediments incorporates much volcanic ash and detrital mud into the Fleming and the underlying Oakville Formations.

THE GOLIAD FORMATION

Overlying the Fleming Formation are the light gray calichified, sediment of the Goliad Sand (Pliocene). The sands are medium to coarse at the base and grade upward to fine to medium sands both containing pink calcareous clay. The arid climate continued and stream channels were formed that originated in West Texas, New Mexico and perhaps as far west as the ancestral Rockies. The Goliad sediments are overlain by similar Pleistocene deposits. A summary of the geologic history of the south Texas Coastal Plain can be found in Table II-1.
<table>
<thead>
<tr>
<th>Structural Event</th>
<th>Depositional Event</th>
<th>Hydrologic Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eocene</td>
<td>Deposition of Jackson Group</td>
<td>Regional ground-water discharge in lower Coastal Plain Systems</td>
</tr>
<tr>
<td></td>
<td>Frio Clay locally deposited; deposition of Catahoula Formation (Gueydan fluvial system)</td>
<td>Jackson aquifer confined; regional recharge of Jackson subcrop beneath tuffaceous Gueydan; uranium actively released from ash; recharge of buried Gueydan aquifers</td>
</tr>
<tr>
<td>Oligocene</td>
<td>Deposition of Oakville Formation</td>
<td>Decreasing recharge of Jackson and Gueydan aquifers</td>
</tr>
<tr>
<td>Miocene</td>
<td>Deposition of upper Fleming (Lagarto) Formations</td>
<td>Confinement of Oakville aquifer</td>
</tr>
<tr>
<td>Pliocene</td>
<td>Deposition of Goliad Formation</td>
<td>Decreased recharge of Oakville aquifer</td>
</tr>
<tr>
<td>Pleistocene-Recent</td>
<td>Sea level fluctuation causes valley incision by major Coastal Plain streams; and evolution of existing topographic relief and Coastal Plain topography</td>
<td>Activation of shallow to intermediate ground-water flow systems in areas of</td>
</tr>
</tbody>
</table>

Table II-1 Summary of the Geologic History of the South Texas Uranium Province (modified after Galloway et al., 1979).
III. SOUTHEAST TEXAS URANIUM DEPOSITS

The controls for uranium fixation in Texas sandstone deposits are of two general types: 1) a sorption phenomenon and/or 2) the reduction of the more mobile $\text{U}^{+6}$ ion. Huang (in press) states the uranium is usually found in association with one or more of following: lignite or disseminated organic matter, clays (particularly smectite), zeolites (particularly clinoptilolite), and carbonate rocks and calcite. Other workers have cited hydrogen sulfide or methane to assist in the reduction process (i.e. Eargle et al., 1975)

Methods of uranium extraction are typically the in-situ leach process and conventional surface mining. The in-situ leach process will be described in a later chapter.

Although not all SE Texas ore deposits are of the roll-front type, many are, and a brief discussion of these deposits and how they form is warranted. Roll-front type deposits (Figure III-1) typically are formed when solutions carrying small amounts of dissolved uranium (greater than about $10^{-6}$ M $\text{U}$) encounter environments conducive to fixation. The actual fixation process in the host medium may be varied and be a function of multiple processes.

Uranium mineralization occurs principally in roll-type deposits along oxidation-reduction interfaces which vary widely in configuration. These sandstones are usually bounded above and below by aquitards or aquicludes which inhibit vertical migration of solutions and subsequent vertical oxidation. The roll-front, then, is confined to a zone parallel to the strike and perpendicular to the bedding plane. The physical characteristics of the host bed vary widely, sometimes within the same stratigraphic unit. Grain sizes can vary from very fine to conglomeritic and sorting from fair to poor. Permeabilities are highly variable and range from 0 to 5000 md. and the direction of permeability is generally highly anisotropic with horizontal to vertical ratios as high as 10:1 (Larson, 1978). The ore grade
FIGURE III-1

Example of a roll-front type uranium deposit typical of south Texas ores. Shown also are some common mineralogic and element associations. (Modified from Larson, 1978.)
deposits are formed at oxidation–reduction interfaces where oxidizing solutions from surface recharge areas encounter reduced conditions (less than about 0.2 v.) in the aquifer. A single event of mineralization could not account for such large uranium occurrences, however, and the roll-front probably migrates in the aquifer, concentrating and reconcentrating the ore as the oxidation interface migrates in the aquifer.

Although Eargle et al. (1975) contend the primary fixation mechanism of the uranium is reduction by H₂S gas along faults from oil deposits at depth, numerous uranium occurrences are associated with organic matter, clays, zeolites, and abundant pyrite. This indicates the actual fixation process may be much more complicated in some cases than indicated by Eargle and his co-workers.

The fixation of uranium by organic matter is presently not well understood and is probably a complex process depending on prevailing Eh-pH conditions, chemical make-up of ore bearing solutions, and the mineralogy of the host rocks. Szalay (1964) reports significant absorption of uranium by humic acids from peat bogs (the geochemical enrichment factor is about 10000/l for UO₂²⁺) and suggests this as the primary fixation process. This phenomenon is reported experimentally to be most effective at a pH of 5. However, since the uranium bearing solutions were assumed to be alkaline from the alteration of the tuffaceous rocks and from the weathering of carbonate material, this mechanism is of unknown importance.

Absorption by organic matter is known to occur in the Whitsett formation lignites (and others) as well as in roll fronts. Blaster (1974) has suggested that kerogenous material may act as sorbent for uranium and that complex uraniferous hydrocarbons can be formed. Doi et al. (1975) report that poorly coalified organic matter has the highest affinity for uranium over a wide range of pH. Although each of these associations is poorly understood, the evidence is unmistakable
that organic matter plays an important role in the fixation mechanisms for uranium in SE Texas.

Although the sorption of uranium is well established, it is unclear whether uranium is sorbed and then reduced with later conversion to a mineral form or whether uranium can be reduced with the direct conversion to a mineral species simply by the proximity of the organics; both mechanisms are probably in operation on the micro scale. Doi et al. (1975) also report the absorption and co-precipitation of uranium with limonite which is consistent with the abundance of limonite in transition ore zones.

Clays are important sorption media for uranium (Doi et al., 1975 and Huang, 1978), although it is not clear whether direct sorption on the clay particle or reduction of the uranium by organics associated with the clay is the primary fixation mechanism. The ability of clay particles to adsorb uranium is not only important in relation to original fixation, but also as a secondary fixation mechanism after the uranium has been mobilized in an in-situ leach situation.

In the oxidized zone the precipitated uranium occurs principally in the hexavalent state. The common ore minerals in SE Texas are tyuyamunite, äutunite, trace amounts of carnotite, and minor uraninite (Huang, 1978 and Eargle et al., 1975). Eargle and Weeks paper (1978) points out that at the Mabel New mine in the Live Oak area the mineralogy more resembles the Colorado Plateau with the high silicate minerals boltwoodite and weeksite.

The oxidized ore zone is probably indicative of the beginnings of remobilization of the uranium into solution as the roll front migrates. The organic matter is oxidized and the reduced iron is converted from pyrite to the hydroxy forms which may sorb uranium in solution as stated above.

Uranium mineralogy in the reduced zone is primarily uraninite, however, coffinite and uraninite coexist and this combination is fairly abundant (Eargle
et al., 1975). Jonas and Omer (1979) have studied the Oakville formation and report, however, that the uranium occurs in the silt-size fraction. After concentrating the uranium by heavy liquid fractionation to an excess of 43,000 ppm $U_3O_8$, no discernable X-ray pattern was identifiable. This led them to believe the uranium occurs as an amorphous oxide.
IV. URANIUM IN-SITU LEACH MINING

The definition of in-situ leach mining or solution mining in this work will be that taken from Larson (1978):

"...that selective mining technique whereby the ore mineral(s) that has not been transported from its geologic setting is preferentially leached (dissolved) from the surrounding host rock by the use of specific leach solutions and the mineral value(s) recovered."

As in that report the definition is intended to include the use of explosives or hydraulic fracturing techniques to increase permeabilities and surface areas inside the ore bodies, but does not include dump or heap leaching where the ore is removed from its geologic setting. This is not meant to imply that various in-situ leach mining techniques are not applicable to some heap leaching operations.

A general description of an in-situ leach operation would consist of injection wells where the leachate or lixiviant solution is pumped into the ore and production wells, situated some distance away, where the pregnant leach solution is recovered. The uranium is then removed from solution, usually on resin exchange columns. (For a description of recovery systems see Traut et al., 1976 and Merrit, 1977).

Well spacings and configurations are varied and will be the subject of a later chapter of this work. For the present, common well patterns are the five spot and the seven spot pattern (Figure IV-1). The most common and perhaps the most efficient well pattern as indicated by computer models (Bommer and Schechter, 1978) is the five spot pattern, although it will be shown in a later chapter that the assumptions associated with these models may be difficult to substantiate.

Leach solutions vary widely, but generally two basic strategies have developed. One technique is the acid leach or the lowering of the pH of the
FIGURE IV-1

Representations of the seven and five spot well patterns common in the in-situ leaching of uranium.
ore to about 1 or 2 with $\text{H}_2\text{SO}_4$ and proceeding to oxidize the uranium and complex it with the $\text{SO}_4^{2-}$ anion (Larson, 1978). The resulting complex is soluble and can be recovered at the production wells. The oxidation is performed either by hydrogen peroxide or oxygen under pressure. Because of the instabilities of $\text{H}_2\text{O}_2$ and the cost, many concerns in SE Texas are converting to $\text{O}_2$.

Problems with the acid leach are corrosion of well equipment, loss of acid to calcium carbonate, environmental objections to the low pH which may result in a desorption and mobilization of heavy metals in the environment, and the instabilities of some rock forming minerals, principally feldspars, in an acid media. The feldspar problem may be the most serious in that they begin to break down to clay minerals and clog the aquifer resulting in decreased permeability. This is one cause of aquifer plugging.

By controlling the systems $\text{K}_2\text{O} - \text{Al}_2\text{O}_3 - \text{Si}_2\text{O}_2 - \text{H}_2\text{O}$ and $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$, a steady state equilibrium can be obtained with the rock forming minerals and stability can be maintained (Riese and Popp, 1979). The leach solution is then in disequilibrium with the ore minerals, but in static equilibrium with the rock forming minerals. Recently, Tweeton et al. (1979) has pointed out that uranium recovery is enhanced with the $\text{H}_2\text{SO}_4$ acid leach over the carbonate leach and that environmental considerations appear favorable. He points out that radium is less soluble in the acid medium and that arsenic and selenium were within the EPA guidelines for drinking water.

The most common leach mechanism is the carbonate leach and is the preferred method in SE Texas in-situ leach operations. This should not be interpreted to mean that this method is more applicable to the problem especially in light of recent evidence (Tweeton et al., 1979). In this procedure the oxidized uranium is complexed with a carbonate anion at pH values of about 7 to 10. The most common carbonate compounds are ammonium carbonate/bicarbonate
and sodium carbonate/bicarbonate. Recently, environmental objections to the ammonia released by ammonium carbonate leachates has indicated a growing popularity in sodium carbonates. The chemical interaction between the rock forming minerals and the lixiviant solution must again be closely monitored or calcium carbonate may precipitate and plug the aquifer.
V. GEOLOGIC TRADEOFFS IN URANIUM SOLUTION MINING

The function of each of the parameters involved in the in-situ leaching of uranium (i.e. pH, ionic strength, lixiviant composition, etc.) must be analysed individually as well as in group fashion in order to obtain a critical understanding of the problems involved in solution mining. In maximizing one variable, the other variables are certainly affected, and the results of those affects, positive or negative, must be realized. The maximizing of optimum variables while minimizing detrimental effects gives rise to certain geologic trade-offs. It is the object of this chapter to point out one aspect of these trade-offs.

SECULAR EQUILIBRIUM

Since the early 1950's with the recognition of uranium as a valuable resource, gamma ray spectrometry has been recognized as a valuable tool in uranium prospecting. The emission of a 1.76 MeV gamma ray from bismuth-214 in the uranium-238 decay series is the measurement of particular interest in uranium prospecting. The ratio of bismuth-214 to uranium-238, however, is a function of the secular equilibrium of each particular occurrence. Secular equilibrium exists in a system when the rate of decay of a daughter is equal to the rate of the parent such that:

$$\lambda_1 N_1 = \lambda_2 N_2 = \lambda_3 N_3 = \ldots = \lambda_n N_n$$

where $\lambda$ is the decay constant and $N$ is the number of atoms of parent and daughter (Bateman, 1910). The number of each respective daughter atoms in a secular equilibrium situation is then:

$$N_n = \frac{\lambda_1 N_1}{\lambda_n}$$

If a uranium occurrence is in exact secular equilibrium, gamma spectrometry (from bismuth-214) will give an accurate indication of the uranium concentration. The case of exact equilibrium, however, is an ideal situation and
it is more proper to speak of the degree of secular equilibrium in sedimentary systems. For an excellent discussion of secular equilibrium the author suggests Faure (1977).

MINING EFFECTIVENESS: A MEASURE

The most fundamental trade-offs in solution mining are the effectiveness of mining techniques as a function of low grade ore profitability. Assuming a log normal distribution of uranium (Duval et al., 1971, Deffeyes and MacGregor, 1978), as mining effectiveness improves, the profitable reserves will increase logarithmically.

To maintain that the mining industry is capital intensive is an understatement. Large amounts of capital are required for licensing procedures, equipment, and operating funds until such time that an operation "turns the corner" and becomes profitable. Figure V-1 illustrates graphically the large investment and considerable initial delayed profit which tails off as the ore body becomes depleted.

Knowing one's position on this profitability curve is essential in predicting the future viability of an ore deposit. In the remainder of this chapter, it will be the authors' intent to develop a measure of the mining efficiency which may be referred to in conjunction with others using radiometric and isotope data to determine relative concentrations of uranium and the post-uranium daughters.

Upon the initiation of solution injection and recovery from an in-situ leach operation, uranium yield will rise to a peak level (Figure V-2). As the ore becomes depleted, however, no amount of injected solution will generate a profitable situation. Again knowing the position on this graph would be valuable information.

Excursions from secular equilibrium especially in sedimentary ore deposits vary widely (Pereira, 1978) and severely limit the simple conversion of gamma
FIGURE V-1

Graphical representation of the investment vs. profitability curve in which delayed profit "tails off" as the ore becomes depleted.
FIGURE V-2

Graphical representation of the rise in extracted uranium which decreases as the ore becomes depleted.
radiation counts to uranium concentration. Uranium is quite mobile in comparison to some of its daughters in sedimentary systems in an oxidizing environment, but in a reducing environment, the daughter elements (i.e. radium) may be more easily transported in solution. These variations in mobility give rise to secular disequilibrium within an ore occurrence. Bismuth-214 which emits the gamma ray usually counted and extrapolated to uranium concentration is a post-radon daughter. Rn-222 is a inert gas with little reactive chemistry and is now believed to be more mobile in the sediments than the 3.8 day half-life would indicate. Although the overall disequilibrium factor within the same ore occurrence may be constant (Sherborne et al., 1979), variations in secular equilibrium within the same ore body (not to mention the same region) makes a standard simple conversion of gamma ray counts to uranium concentration very hazardous without sufficient knowledge of the degree of disequilibrium in each specific instance.

The ratio of the uranium indicated by gamma radiation to the chemical uranium present is a measure of the degree of secular equilibrium:

\[ \frac{\lambda_{\text{B}}(\text{Bi-214})}{\lambda_{\text{U}}\text{U}_{\text{chem}}} < 1.0 \].

This ratio should invariably be less than 1.0 when considering an entire ore body, but by no means is always less than 1.0. For example in the trailing edge of a roll-front occurrence, the radiometric uranium will outweigh the chemical uranium and in the leading edge of a roll-front the inverse is true. This is a function of the mobility of uranium in relation to the daughters. This ratio is usually known in the coarse evaluation stage of a uranium occurrence.

Another ratio which can easily be obtained in the coarse evaluation stage is that of the Rn-222 to the chemical uranium. This ratio can also be used to determine the degree of secular equilibrium:

\[ \frac{\lambda_{\text{R}}(\text{Rn-222})}{\lambda_{\text{U}}\text{U}_{\text{chem}}} < 1.0 \].
Rn-222 gas in recovered solutions can also be economically monitored to yield an accumulated sum of total effluent Rn-222 from the ore.

In the initial stages of mining, the effluent solutions will have a relatively high concentration of Rn-222 which will decrease with continued mining (Figure V-3). After a certain lag time the uranium will begin to peak. This lag time is a function of the lack of chemistry of Rn-222 and its solubility in water, and the kinetics of the dissolution, diffusion, surface phenomena, etc. in mobilizing the uranium (Figure V-4).

In a hypothetical case, assume twice as much uranium exists as Rn-222, both normalized:

\[ 2\lambda_r(\text{Rn-222}) = \lambda_u U_{\text{chem}} \]

or a secular equilibrium of 0.5. Figure V-4 gives a graphic representation of this situation, and the lag of the uranium peak is a measure of the efficiency of the mining techniques being utilized. An unusually long lag time may indicate immediate adjustments in lixiviant composition, injection pressures, log term adjustments in well spacing or patterns in future drilling are required to optimize mining efficiency.

The ratio of the cumulative total effluent Rn-222 to the chemical uranium will yield valuable information in terms of future productivity (Figure V-5). Figure V-5 illustrates the hypothetical case of a 0.5 degree of secular equilibrium. By monitoring total effluent Rn-222 with a knowledge of the degree of secular equilibrium from gamma radiation counts, information is obtained which indicates how rapidly the ore is becoming depleted. Ideally, when the normalized Rn-222/U(U_{\text{chem}}) = 0.5 the ore will be depleted, but in general Rn-222 gas may diffuse into or out the ore body. This, however, may not be significant.

By knowing the state of an ore body as a function of the secular
FIGURE V-3

Graphical representation of the rapid rise and then decrease in Rn-222 as mining proceeds.
Total Effluent \( \text{Rn}_{222} \)

Duration of Mining
FIGURE V-4

Graphical representation of the lag time between uranium and Rn-222 in an in-situ leach due to the higher mobility of Rn-222.
FIGURE V-5

Hypothetical curve of the cumulative normalized Rn-222/U_{chem} ratio as mining proceeds in a uranium in-situ leach. At 0.5 the ore should be depleted if the degree of secular equilibrium is 0.5.
disequilibrium, it should be possible to use graphs such as Figures V-4 and V-5 to determine relative positions on investment vs. profit or injected solution vs. yield curves or any curve of this type. Secular equilibrium on the one hand limits conversion of gamma radiation counts to uranium concentration, but on the other hand may be a valuable tool in the location, evaluation, and determination of economic future of a uranium occurrence.

CONCLUSIONS:
1. It is possible to know the degree of secular equilibrium in the coarse evaluation stage of mining.
2. Variations in secular equilibrium make it difficult to convert gamma ray counts directly to uranium concentrations without knowledge of the disequilibrium factors in a specific area.
3. Rn-222 concentrations and gamma ray counts can be utilized to determine the degree of secular equilibrium, mining efficiency, future profitability, and evaluation.
VI. THE STABILITY OF UO\textsubscript{2} IN AQUEOUS SYSTEMS

Eh-pH diagrams for mineral stability have typically been drawn at a fixed total aqueous concentration of the species in question (for a discussion of Eh-pH diagrams see Garrels and Christ, 1965). This is not unreasonable since in the past most workers were concerned with emplacement mechanisms and the precipitation of mineral phases in the sedimentary environment. The question that implicitly was asked of an Eh-pH diagram was this: If a solution with X concentration of dissolved substance encounters varied Eh-pH situations what will precipitate and what will be the stable species in solution? This is not an unreasonable approach by any means. However, when concerned with the in-situ leaching of uranium or any material, more appropriate questions might be: If X amount of uraninite in a sedimentary system encounters various Eh-pH conditions in the presence of water and mixed complexing agents, what will be the thermodynamically predicted dissolved uranium species, where will they occur on the diagram, and what complexing agents generate the most soluble uranium species? Instead of asking when is it possible to precipitate uranium, the problem posed is what are the predicted dissolved species at the solution-solid interface?

A computer program "Eh-pH UR" was developed to analyze thermodynamic data from Langmuir (1978) in the context of dissolving uranium in a sedimentary system. As with most thermodynamic models, the kinetic relationships that exist within the systems are not taken into account, although the following discussion makes comparisons between existing kinetic data and predictions based on the model. With this kind of approach it is possible to gain insight into predicted dissolving uranium phases in the systems considered.

To determined oxidized (+6) uranium species in solution, equations of the following type were developed:

\[ \text{UO}_2^{2+} + 2\text{H}^+ + 2e^- = \text{UO}_2 + 2\text{H}_2\text{O}. \]
Free energy data (Langmuir, 1978) were used to calculate $E^0$ (reduction potentials) for the equations and these were then inserted into the Nernst Equation: 

$$E_h = E^0 - 0.05916/n \log_{10} \frac{\text{Products}}{\text{Reactants}}.$$ 

This equation could then be solved at Eh-pH values of interest to determine the concentration of oxidized aqueous species. The activity of uraninite was assumed to be 1 as were the activity coefficients for all other species. The effect of ignoring the ionic strength of the lixiviant solutions is not known, but is undoubtedly significant especially at high or low pH.

Reduced species (+4) of uranium in solution were determined from the equilibrium constant of that species with uraninite which was again calculated from free energy data by the equation:

$$\ln K = -\frac{\Delta G^0}{RT}.$$ 

Stable solid phases were determined from solubility products and electron activities at the Eh or pH of interest. A minimum acceptable concentration of the uranium in an aqueous phase was read in as data. Until this minimum acceptable value was obtained, solid phases are ignored and the aqueous phases are reported. Below this minimum value, the solid phases are recorded as output.

The program presently examines the following systems which may be of interest to solution mining: $\text{UO}_2\text{H}_2\text{O}-\text{O}_2\text{H}_2\text{O}-\text{CO}_2\text{H}_2\text{S}-\text{PO}_4$ or any combination of these at 25°C and 1 atm. The aqueous species and solid phases examined specifically in this analysis comprise Table VI-1. The chemical equations considered in the construction of the dissolution diagrams are shown in Table VI-2.

**DISCUSSION**

A typical Eh-pH diagram for the system $\text{UO}_2\text{H}_2\text{O}-\text{CO}_2\text{H}_2\text{O}$ is shown in Figure VI-1 (Langmuir, 1978). This diagram depicts the relationships of the $\text{UO}_2^{2+}$ in various Eh-pH situations with the sum of the uranium in solution held constant at a predetermined concentration (usually $10^{-6}$ M). It can be pointed out that
with the free energy of formation for each respective phase.

**TABLE VI-1.** The aqueous species and solid phases considered by the "M-PHI Win Computer Program"

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<th>Species</th>
<th>Free Energy (kJ/mol)</th>
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**Solid Phases**

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**Aqueous Species**

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<td>( \text{OH} )</td>
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</tbody>
</table>
1. $\text{UO}_2^{2+} + 2e^- = \text{UO}_2$
2. $\text{U}^{4+} + 2\text{H}_2\text{O} = \text{UO}_2 + 2\text{H}_2\text{O}$
3. $\text{UO}_2\text{OH}^+ + \text{H}^+ + 2e^- = \text{UO}_2 + \text{H}_2\text{O}$
4. $(\text{UO}_2\text{(OH)})_2 + 2\text{H}^+ + 4e^- = 2\text{UO}_2 + 2\text{H}_2\text{O}$
5. $(\text{UO}_2\text{(OH)})_3^{+} + 5\text{H}^+ + 6e^- = 3\text{UO}_2 + 5\text{H}_2\text{O}$
6. $\text{UO}_2(\text{CO}_3)_2^{2-} + 2e^- = \text{UO}_2 + \text{CO}_3^{2-}$
7. $\text{UO}_2(\text{CO}_3)_3^{4-} + 2e^- = \text{UO}_2 + 3\text{CO}_3^{2-}$
8. $\text{USO}_4^{2+} + 2\text{H}_2\text{O} = \text{UO}_2 + 4\text{H}^+ + \text{SO}_4^{2-}$
9. $\text{USO}_4^{2-} + 2\text{H}_2\text{O} = \text{UO}_2 + 4\text{H}^+ + 2\text{SO}_4^{2-}$
10. $\text{USO}_4^{0} + 2e^- = \text{UO}_2 + \text{SO}_4^{2-}$
11. $\text{USO}_4^{2-} + 2e^- = \text{UO}_2 + 2\text{SO}_4^{2-}$
12. $\text{UHPO}_4^{2+} + 2\text{H}_2\text{O} = \text{UO}_2 + 4\text{H}^+ + \text{HPO}_4^{2-}$
13. $\text{U}(\text{HPO}_4\text{)}_2^{0} + 2\text{H}_2\text{O} = \text{UO}_2 + 4\text{H}^+ + 2\text{HPO}_4^{2-}$
14. $\text{U}(\text{HPO}_4\text{)}_3^{2-} + 2\text{H}_2\text{O} = \text{UO}_2 + 4\text{H}^+ + 3\text{HPO}_4^{2-}$
15. $\text{U}(\text{HPO}_4\text{)}_4^{4-} + 2\text{H}_2\text{O} = \text{UO}_2 + 4\text{H}^+ 4\text{HPO}_4^{2-}$
16. $\text{USO}_4^{0} + 2e^- = \text{UO}_2 + \text{HPO}_4^{2-}$
17. $\text{USO}_4^{2-} + 2e^- = \text{UO}_2 + 2\text{HPO}_4^{2-}$
18. $\text{USO}_4^{2+} + 2e^- = \text{UO}_2 + \text{H}_2\text{PO}_4^{2-}$
19. $\text{USO}_4^{2-} + 2e^- = \text{UO}_2 + 2\text{H}_2\text{PO}_4^{2-}$
20. $\text{USO}_4^{0} + 2e^- = \text{UO}_2 + 3\text{H}_2\text{PO}_4^{2-}$
21. $\text{USO}_4^{2-} + 2e^- = \text{UO}_2 + 3\text{H}_2\text{PO}_4^{2-}$
22. $\text{USO}_4^{0} + 2e^- = \text{UO}_2 + \text{CO}_3^{2-}$
23. $\text{U}(\text{HPO}_4\text{)}_2^{+} 4\text{H}_2\text{O}^{(c)} = \text{UO}_2 + 4\text{H}^+ + 2\text{H}_2\text{O} + 2\text{HPO}_4^{2-}$
24. $(\text{UO}_2\text{(PO}_4\text{)}_2^{+} 6e^- = 3\text{UO}_2 + 2\text{PO}_4^{3-}$
25. $\text{H}_2(\text{UO}_2\text{(PO}_4\text{)}_2^{+} 4e^- = \text{UO}_2 + 2\text{PO}_4^{3-} + 2\text{H}^+$

TABLE VI-2 The chemical equations involved in the construction of the dissolution diagrams.
FIGURE VI-1

Eh-pH diagram with the sum of the uranium in solution held constant at $10^{-6}$ M (solid lines) and $10^{-4}$ M (dashed lines) for the system U-O$_2$-H$_2$O-CO$_2$, $T = 25^\circ$C, $P_{CO_2} = 10^{-3.4}$ atm (Modified after Hostetler and Garrels, 1962).
uraninite and coffinite have similar stability fields in conventional Eh-pH diagrams.

Figure VI-2 depicts the thermodynamically predicted dissolving uranium species and solid phases when it is assumed an infinite amount of UO$_2$(s) is dissolved in water (Figure VI-2) and with CO$_3^{2-}$ (Figure VI-3) as a complexing agent. The amount of uranium in solution is not fixed, but is allowed to vary according to thermodynamic predictions. Clearly these species in solution are stable only with respect to uraninite and will convert to other forms, (the forms predicted in the stability diagram of Figure VI-1) but these species (Figure VI-3) are the thermodynamically predicted phases at the dissolving interface. The differences between Figures VI-1 and VI-3 are immediately obvious and result from differences in the assumptions during preparation. Figures VI-2, VI-3, VI-4, and VI-9 of real interest in the regions adjacent to the uraninite field. The Eh of the system is not changed considerably until the reductants of the host medium are effectively oxidized. Although the lixiviant solution may contain large amounts of dissolved oxygen (Eh >0.8 v.) and this will create an unstable situation with respect to uraninite, the system itself is buffered at much lower Eh (<0.1 v.). The regions of interest in the diagrams, then, are at low Eh and adjacent to the uraninite field. Because of these assumptions in the construction of these diagrams, the name proposed for them here is "dissolution diagrams."

On the basis on the results of kinetic experiments, (Grandstaff, 1976 and Schortmann and DeSesa, 1958), the data presented here may more accurately predict the dissolution processes in operation. Grandstaff (1976) determined the reaction rate of the dissolution of uraninite decreases as the pH approaches 6.0, then levels off, then increases again at a pH greater than about 9.0. Figure VI-3 predicts the UO$_2^{2+}$ ion is the dissolving species from pH values of 3-6. However, at pH values from above 6-9 the predicted species is (UO$_2$)$_3$(OH)$_5^+$.
FIGURE VI-2

Dissolution Eh-pH diagram for uraninite in water. Minimum uranium in solution is $10^{-6}$ M before the solid phase is predicted.
FIGURE VI-3

Dissolution Eh-pH diagram for uraninite in water with $P_{CO_2} = 10^{-2}$ atm. Minimum uranium in solution is $10^{-6} \text{ M}$ before the solid phase is predicted.
FIGURE VI-4

Dissolution Eh-pH diagram for uraninite in water with $P_{CO_2} = 10^{-2}$ atm. and $P_{H_2S} = 10^{-2}$ atm.
and this species may be much slower to dissolve and subsequently convert to the carbonate, since it is a two-step process, which is consistent with the kinetic data of a decreased reaction rate in this pH region and with the hypothesis of the formation of an intermediate hydroxylated species. Grandstaff (1976) noted a slight buffering of the solution in his kinetic experiments at a pH of 6.1. It is proposed that \((\text{UO}_2)_3(\text{OH})_5^+\) may dissociate a \(\text{H}^+\) at a pH of about 6.1 to explain the buffering of the solutions at this pH encountered by Grandstaff (1978). The formation of an intermediate hydroxylated form \((\text{UO}_2)_3(\text{OH})_5^+\) may also explain the first order dependence of the dissolution rate on the carbonates at low carbonate concentration and the zero order dependence at higher carbonate concentrations. It is proposed that hydroxylated form dissociates from the uraninite at a rate independent of the carbonate concentration. At low carbonate concentrations the hydrated form reacts to form the carbonate, but at higher carbonate concentration the dissolution rate is controlled by the formation of the hydroxylated species. This explanation is consistent with Schortmann and DeSesa (1958) and with Grandstaff (1976). They predict an intermediate hydroxylated species which reacts in a two step process to form the carbonate. If the species \((\text{UO}_2)_3(\text{OH})_5^+\) does not exist practically in solution, the species in this field would be \(\text{UO}_2(\text{OH})_2^{2+}\) and the above arguments would still be valid.

At a pH of 9 or higher, the reaction rate would be expected to rise as the dicarbonate is the predicted dissolving species (Figure VI-3). If the dicarbonate forms as predicted, the conversion of uranium dicarbonate to the tricarbonate is kinetically fast (Grandstaff, 1978). This indicates the pH of an in-situ carbonate leach should be greater than 9.0. This is consistent with field data collected by Potter et al. (in press) who noted a substantial increase in uranium concentration in the lixiviant at a pH of 9.0. However, because bicarbonate dissociates at a pH of 10.34, the pH should be maintained at less than 10.0 to inhibit calcite
formation.

The first order dependence of the dissolution rate on the partial pressure of oxygen established by Grandstaff (1976) is a function of the intermediate dissolving uranium species, \((\text{UO}_2\text{)}_3\text{(OH)}_5^+\). The mechanism of dissolution which is consistent with thermodynamic data and the kinetic data must also be first order dependent on the hydrogen ion concentration in solution (Grandstaff, 1976). The model employed by Grandstaff (1976) to explain the first order dependence of the oxygen partial pressure is shown schematically as the adsorption of molecular oxygen onto the uraninite adsorption site:

\[
\text{UO}_2^+ + \text{O}_2 = \text{UO}_2\text{O}_2^-.
\]

The first order dependence of the hydrogen ion is not easily explained by existing models. The model proposed here is the surface oxidation site is also a site of formation as in the following equation:

\[
\text{UO}_2^{5+}/2\text{O}_2^- + 5\text{H}^+ = (\text{UO}_2\text{)}_3\text{(OH)}_5^+.
\]

Because the \((\text{UO}_2\text{)}_3\text{(OH)}_5^+\) seems to display the property of a dissociation constant due to the buffering of the solutions in the Grandstaff experiments at a pH above 6.1, the more correct structural formula may be \(\text{H}_5(\text{UO}_2\text{)}_3\text{O}_5^+\).

To give added insight into the dissolution diagrams, log concentration (M) vs. pH diagrams were constructed Eh values of 0.80, 0.00, and -0.20 v. (Figures VI-5, VI-6, VI-7, and VI-8). The diagrams of practical interest are those at Eh values of 0.00 and -0.20 because these are the regions in which in-situ leaching is accomplished. As stated earlier, lixiviant solutions may be at high Eh, but the system is buffered at low Eh. Figures VI-5–VI-8 describe the amount of uranium possible in solution for a given pH. Because of the kinetics of the dissolution process, however, the solutions are undersaturated as will be shown in the next chapter.

There is evidence to suggest that the dissolution reaction is half order
FIGURE VI-5

Log concentration vs. pH diagram for uraninite in water with $P_{CO_2} = 10^{-2}$ atm., $Eh = 0.80$ v.
Eh = 0.80 V.
FIGURE VI-6

Log concentration vs. pH diagram for uraninite in water with $P_{CO_2} = 10^{-2}$ atm., $Eh = 0.00$ v.
Eh=0.00v.
Log concentration vs. pH diagram for uraninite in water with

\[ P_{\text{CO}_2} = 10^{-2} \text{ atm.}, \quad P_{\text{H}_2\text{S}} = 10^{-2} \text{ atm.}, \quad \text{Eh} = 0.00 \text{ v.} \]
Log concentration vs. pH diagram for uraninite in water with $P_{CO_2} = 10^{-2}$ atm., $Eh = -0.20$ v.
Eh = -0.20v.
Dissolution Eh-pH diagram for uraniinite in water with $P_{CO_2} = 10^{-2}$ atm., $P_{H_2S} = 10^{-2}$ atm., and the $\Sigma PO_4 = 2.0 \times 10^{-5}$ atm.
dependent on the oxygen partial pressure (Hiskey, 1979 and Nichol and Needes, 1977). This would not effect the above arguments that dissolution diagrams more accurately describe the dissolution of uraninite in these systems.

An interesting note to Figure VI-3 is the large U$^{4+}$ field at a pH of 3 or less. If this solution phase exists in nature, it may be of great interest to those interested in the kinetics of acid leach systems. This would indicate that the oxidant concentration may be far less important than in the carbonate leach especially in the presence of a complexing agent (i.e. SO$_4^{2-}$). This is consistent with the observation of significant uranium mobilization in acid leach systems at low oxidant concentrations (Tweeton et al., 1979). Figure VI-4 depicts the dissolving species with the introduction of sulfate as a complexing agent. The kinetic relationships are not well known in the sulfate system, but a renewed interest in the sulfate acid leach (Tweeton, 1979) indicates this is a viable in-situ leaching technique. Figure VI-4 indicates the low pH values of 1 or less may not be needed and the technique may be viable at a pH as high as 3.0 due to the large U(SO$_4$)$_2$$_2^0$ field in this region. This is consistent with the data of Tweeton et al. (1979) who closely monitored the production and observation wells in an acid leach operation and noted a rapid increase in leached uranium at a pH of 3.0 or less. To complete the discussion Figure VI-9 is the dissolution diagram with the $\Sigma$PO$_4$ = 2.0 x 10$^{-5}$ M. It is unfortunate that not more is known about the kinetics of phosphate-uranium systems because of the soluble uranyl-phosphate complex at intermediate pH.

CONCLUSIONS:

1. Classical Eh-pH diagrams can be supplemented with the dissolution diagrams presented here to better describe the uranium leach process.

2. A hydroxylated species formed at the solution-solid interface which converts to the carbonate in a two-step process may account for the first order dependence
at low carbonate concentration and the zero order dependence at higher concentrations of carbonate.

3. The formation of $(\text{UO}_2)_3(\text{OH})_5^+$ may account for the decrease in the reaction rate as the pH approaches 6.0.

4. The first order dependence of the oxygen partial pressure and the hydrogen ion concentration may be explained by the formation of $(\text{UO}_2)_3(\text{OH})_5^+$.

5. Carbonate leach systems may be most efficiently operated at pH values between 9 and 10.0.

6. The dissociation of the hydroxylated species may explain the slight buffering of the solutions in the Grandstaff (1976) kinetic experiments.

7. Although detailed kinetic data are lacking, the sulfate acid leach may be operated at pH values as high as 3.0.
VII. OPTIMIZING IN-SITU LEACH OPERATIONS

The definition of in-situ leaching will be that of Larson (1978) as described earlier in this work. Optimizing an in-situ leach operation is a function of not only chemical, but also ecologic as well as economic considerations. The ore must be removed at some reasonable rate and at concentrations high enough to justify the expense of a mining operation. At the same time, the lixiviant cannot be allowed to migrate beyond the bounds of the well system to limit the waste of lixiviant in non-productive areas and the environmental impact. The stability of the gangue minerals should be maintained as well as the stability of the lixiviant to limit dissolution and reprecipitation of minerals which may detract from the overall permeability as mentioned earlier. The modeling considerations discussed within this chapter are exclusively for carbonate leach systems as kinetic data on acid leach reactions are unfortunately not available at this time.

Past interpretations of the in-situ leach problem have assumed the dissolution rate of the uranium is a function of the change in the hydrologic potential along a streamline (Bommer and Schechter, 1978). If this were so, uranium dissolution would be maximized at infinite flow rates and the only consideration would be bounding the leach pattern to limit lixiviant escape into the surrounding country rocks. The problem is considered by dividing it into two cases.

CASE I:

In Case I the assumption is made that the hydrologic parameters (the flux of the lixiviant, regardless of composition, through the ore) are the controlling factors in uranium dissolution and the reaction rate is of minimal importance.

CASE II:

In Case II the assumption is made that the reaction rate is the controlling factor and the hydrologic parameters are of minimal or no importance.
If Case I were the more accurate description of the system, this would indicate that the reaction is diffusion limited or the lixiviant becomes saturated with respect to uranium and the flux of the lixiviant through the ore is the controlling dissolution mechanism. Grandstaff (1976) determined an activation energy of 14 ±2 kcal/mole which is much higher than would be expected if the dissolution rate was diffusion limited. He also found in stirring experiments that uranium showed no increase in solution and he concluded that the reaction does not seem to be diffusion limited. Pearson and Wadsworth (1958) state, however, that at higher temperatures (greater than 175°C) the reaction was somewhat diffusion limited. If the reaction rate is diffusion limited, solution particle velocities at the surface of an ore mineral may cause an increase in the dissolution rate. Much more needs to be done in this area to determine quantitatively the influence of the flux of the lixiviant on the reaction rate of the ore minerals with respect to surface phenomena.

A computer program "WELSPECS" was devised to gain further insight into this problem. The program makes use of the La Place source and sink equation:

\[ p(x,y) = p_m - \frac{\mu}{4\pi k D} \sum_{i=1}^{n} q_i \ln \left\{ \frac{(x-x_i)^2 + (y-y_i)^2}{(x-x_i)^2 + (y-y_i)^2} \right\} \]  

(1)

which can be differentiated with respect to \(x\) and \(y\) to obtain equations for the \(x\) and \(y\) components of the particle velocity vector:

\[ v_x(x,y) = \frac{1}{2\pi \phi D} \sum_{i=1}^{n} q_i \frac{(x-x_i)}{(x-x_i)^2 + (y-y_i)^2} \]  

(2)

\[ v_y(x,y) = \frac{1}{2\pi \phi D} \sum_{i=1}^{n} q_i \frac{(y-y_i)}{(x-x_i)^2 + (y-y_i)^2} \]  

(3)

where \(p\) is the pressure, \(p_m\) is the mean pressure, \(\mu\) is fluid viscosity, \(k\) is permeability, \(D\) is the formation thickness, \(q\) is the flow rate, \(\phi\) is the porosity, \(x\) and \(y\) are position coordinates, \(n\) is the number of wells, and \(v_x\) and \(v_y\) are the \(x\) and \(y\) components of the velocity vector. The total solution particle
velocity can then be calculated by the equation:

\[ v(x, y) = (v_x^2 + v_y^2)^{\frac{1}{2}} \]  \hspace{1cm} (4)

Streamlines can be generated by considering the following equations which describe solution particle movement:

\[ x_{i+1} = x_i + v_x \Delta t \]  \hspace{1cm} (5)

\[ y_{i+1} = y_i + v_y \Delta t \]  \hspace{1cm} (6)

The program utilized typical hydrologic values in sandstone ore bodies (see Appendix A) to generate fluid particle velocities in a hypothetical five-spot well pattern (Figure VII-1). By considering the center symmetry of the interior cell only one-fourth of the cell need be considered after the particle velocities are determined using the entire grid. When streamlines and velocity contours are determined, a grid system extending 1.5 times the well pattern is considered to examine the migration of the lixiviant outside the system. The system considered this way is unbounded.

The solution particle velocities were found to range from about 0.5 to 0.01 m/day. Because the reaction does not appear to be diffusion limited at low temperatures, the assumption will be made here that the lixiviant particle velocities of these magnitudes will not effectively enhance the dissolution reaction rate.

Another consideration to be examined that would indicate Case I more accurately describes the system is the following: Is the rate of dissolution rapid enough such that the lixiviant moving at velocities of 0.5 to 0.01 m/day becomes saturated with respect to uranium? The reaction rate would then depend on the flux of the lixiviant.

The equation to describe the dissolution rate will be that of Grandstaff (1976) and is as follows:
FIGURE VII-1

Five spot well pattern analysed by the computer program "Umined".

Hatched area indicates area of mining rate calculations.
\[ R = - \frac{\delta(U)}{\delta(t)} = 10^{20.25} (SS)(RF)^{-1} (10^{-3.38} - 10^{0.8 \cdot \text{NOC}}) \times \]

\[ (a_{\text{CO}_2})(\text{D.O.})(a_{\text{H}^+}) \exp(-7045/T)/\text{day} \] (7)

where \( R \) is rate of the dissolution reaction, \( SS \) is the specific surface area, \( RF \) is the organic retardation factor, \( \text{NOC} \) is the mole fraction of the non-uranium cations in the uraninite, \( \text{D.O.} \) is the dissolved oxygen content of the water (ppm), \( \sum \text{CO}_2 \) is the total dissolved carbonate, and \( T \) is the absolute temperature. The values substituted in the model were as follows: \( \sum \text{CO}_2 = 3.6 \times 10^{-2} \text{M} \), \( a_{\text{H}^+} = 10^{-9} \text{M} \), \( RF = 1.0 \), \( \text{D.O.} = 500.0 \) ppm (to be described later), \( T = 298.15 \), and \( SS = 5.3 \times 10^{-4} \text{m}^2/\text{g} \).

The specific surface area was estimated by considering the uranium as typically associated with organics and clays and not being uniformly distributed. It has been reported (Larson, 1978 and others) that the uranium occurs principally as a paint on the sand grains around areas of high concentration or it was assumed to cover 25% of the sand grains in a cubic meter of rock. A medium sand is about 0.0375 cm. in diameter. The volume of 1 grain of sand is then 2.2761 x 10^{-5} cm³ (4/3 \( \pi r^3 \)); for a density 2.8 g/cm³, this would indicate 6.185 x 10^{-3} grams/grain or 1616 grains/gram multiplied by 1.0 minus the porosity, or 0.75, equals 1212.61 grains/grams. This multiplied by 0.25 (amount of sand covered) is equal to 303.15 grains/gr. From the diameter, the surface area (assuming a sphere) can be calculated (4\( \pi r^2 \)) to be 4.417 x 10^{-3} cm²/grain times 303.15 grains/gram or 5.35 cm²/gram or 5.36 x 10^{-4} m²/gram.

The specific surface area in practice should be a function of the emanating power of the ore with respect to Rn-222 (knowing the amount of secular disequilibrium). The more uranium that is exposed, the higher the emanation rate should be as the radon would not be contained within mineral grains. Experiments in the future could relate secular disequilibrium, specific surface
area and the radon emanation power. The retardation factor of Grandstaff's (1976) equation was assumed to be 1.0 for reasons which will become apparent as the discussion of this topic continues and a variable is introduced to account for total reductants. The amount of dissolved oxygen assumed in the equation will also be discussed further.

If equation 7 is solved using above variables the reaction rate is found to be:

\[ R = 7.894 \times 10^{-6} \text{ g/day}, \]

per gram of rock exposed. Assuming a density of rock of $2.8 \times 10^6 \text{ g/m}^3$, this indicates 7.894 g/day uranium mined. A cubic meter of rock of porosity 25% has a lixiviant content of 250 l at saturation, consequently:

\[ \frac{22.10 \text{ g(U)}}{250 \text{ l}} \times \frac{1 \text{ M}}{238 \text{ g(U)}} = 3.715 \times 10^{-4} \text{ M.} \]

The association constants for the carbonate complexes range from $10^{20}$ to $10^{25}$. This would indicate the solutions are far undersaturated with respect to uranium. Therefore, if the reaction rate is assumed to not be diffusion limited and the solutions are far undersaturated, there is nothing to substantiate Case I and it is therefore assumed that the flux of the lixiviant has no real effect on the reaction rate in the sense of the fluid dynamics of the system. It will shortly be shown, however, that the flow-rate is an important consideration in terms of oxidant replenishment to the system.

If Case I is not an accurate description of the system, then clearly Case II must be the more accurate description as one or the other must control the dissolution process. The sum of the carbonates is a problem in itself which must be considered in conjunction with the calcium concentration and the pH to limit $\text{CaCO}_3$ precipitation in the aquifer and in the recovery system. This problem will not be dealt with here, but since the bicarbonate ion dissociates at a pH
of 10.34 and the carbonate ion concentration significantly increases in this region, the pH of this type of leach should probably be less than 10.0. As stated in an earlier section a pH of less than 9.0 is not recommended and this seems to be verified in the field (Potter et al., 1980). The other variables are essentially constants, leaving only the dissolved oxygen to be manipulated. The reaction rate then is primarily a function of the chemical composition of the lixiviant (controlled by extremely complex parameters involving mineralogy and groundwater chemistry), the reducing capacity of the system, and the kinetic relationships that exist between the two. It may be aptly stated then that the reaction rate, \( R \), may be considered as:

\[
R = (A)(Ox),
\]

where \( Ox \) is the oxidant concentration used in the system, and \( A \) is a constant of proportionality relating the other kinetic and chemical factors.

Because of the instabilities inherent in hydrogen peroxide and its higher cost, many concerns have or are in the process of converting to oxygen dissolved in the lixiviant under pressure. Even though the dissolution rate is directly proportional to the amount of dissolved oxygen and it would be desirable in this respect to force as much oxygen into the ore as possible, there are adverse effects associated with this approach. When the lixiviant solution is released into the aquifer at the injection well, the pore pressure plus the well head pressure must be high enough such that the oxygen will remain in solution. If the pore pressure is too low to maintain the oxygen in solution, the oxygen will form aerated zones in the aquifer. The effect of this is detrimental and threefold: to lose effective specific surface area of ore being mined, to waste oxidant, and to decrease overall permeability.

An approach which might be suggested at this point is as follows: since the amount of oxidant decreases as the lixiviant migrates from the injection
well by reaction with various reductants, would it be possible to inject the lixiviant at a high enough flow rate to effectively increase the pore pressure around the injection well and allow an increase in the amount of dissolved oxygen introduced which would then decrease with the pressure away from the well? It will be shown shortly that 53.33 m$^3$/day (10 gal./min.) is in the range of flow rates in typical sandstone aquifers that are acceptable while maintaining confinement of the lixiviant to the system. (This is also typical of flow rates being used in in-situ leach operations.) The equation which would govern the new head in the aquifer due to the presence of injection and production wells in a source and sink situation is (Davis and De Wiest, 1966):

$$h = \frac{1}{4\pi KD} \sum \left\{ q_i \ln \left( \frac{(x-x_i)^2 + (y-y_i)^2}{(x+x_i)^2 + (y+y_i)^2} \right) \right\} + H, \quad (11)$$

where $h$ is the new value of the head, $K$ is the conductivity, $D$ is the height of the aquifer, and $H$ is the ambient head in the aquifer. For a system of two wells on the x-axis ($y_i=0$) at distances of $-x$ and $+x$ from the origin and with equal flow rates, equation 11 reduces to:

$$h = \frac{q}{4\pi KD} \ln \left( \frac{(x-x_0)^2 + y^2}{(x+x_0)^2 + y^2} \right) + H. \quad (12)$$

To consider the increase $(h-H)$ in the head at the injection well for an aquifer 10 m thick and a hydraulic conductivity of 1.0 m/day, equation 12 reduces to:

$$h = \frac{(53.33)}{4\pi (1.0) (10)} \ln(0), \quad (13)$$

or the increase in the head due to the presence of the well is:

$$h = 0.424 \text{ m.} \quad (14)$$

This results in an increase in the pore pressure of 0.041 atm. which is clearly insignificant in this discussion. For an increase in pore pressure of 0.5 atm. the
flow rate would need to be in excess of 649.81 m$^3$/day which would be entirely too high to confine the lixiviant as will be shown in a later chapter. It must therefore be assumed that increasing the pore pressure with increased flow rates is not an objective line of reasoning one would wish to pursue. One alternative might be to find a non-gasous oxidant that is not influenced by pore pressure, such as Fe(CN)$_6^{3-}$ or Cu(NH$_3$)$_4^{2+}$.

Another alternative is to increase the flow rate in order to deliver more lixiviant and consequently more oxygen to the system per unit time. Here again, however, one must deal with the problem of confining the lixiviant. Velocity contour diagrams were generated by the procedure described above for 32.73 m$^3$/day (6 gal./min.), 53.33 m$^3$/day (10 gal./min.) and 80.0 m$^3$/day (15 gal./min.) for a well spacing of 10.0 meters, a porosity of 25%, and a height of aquifer of 20m (Figures VII-2, VII-3, and VII-4) for this set of variables (only the outer contours are shown), a flow rate of approximately 53.33 m$^3$/day appears to be in the optimal range to confine the system for these parameters. It is interesting to note that the highest velocities occurred between the outer injection and production wells where the solution is not affected by the potentials from outside the pattern. It can be observed from Figure VII-2 that insignificant flow rates occurred within the well pattern for a flow rate of 32.73 m$^3$/day and this flow rate is insufficient to permeate an entire production cell. In the field this inability to permeate the cell may go unnoticed with the ultimate result of an inefficient mining system. It cannot be overemphasized that each systems' parameters and subsystems' parameters dictate optimum flow rates. Guard wells which can easily be added to this model can also be installed if necessary to inject water (not lixiviant) outside the ore body so that flow rates may be increased in the ore body and a high gradient maintained. Depending on the recharge rate of the host aquifer to maintain the pore pressure, the outer and/or
FIGURE VII-2

Velocity contour plot of the well pattern showing only outer contours. Hatched areas indicate insignificant interior velocities. Flow rate is $32.73 \text{ m}^3/\text{day}$ (6 gal./min.).
FLOW RATE = 32.73 m$^3$/day

- INSIGNIFICANT VELOCITIES
- 0.05 - 0.07 m/day
- INJECTION WELL
- PRODUCTION WELL
FIGURE VII-3

Velocity contour plot of the well pattern showing only outer contours. Flow rate is 53.33 m$^3$/day (10 gal./min.).
FLOW RATE = 53.33 m$^3$/day

- INSIGNIFICANT VELOCITIES
- 0.05 - 0.07 m/day
- 0.07 - 0.24 m/day
- INJECTION WELL
- PRODUCTION WELL
FIGURE VII-4

Velocity contour plot of the well pattern showing only the outer contours. Note the system is not well confined under these conditions. Flow rate is 80.0 m$^3$/day (15 gal./min.).
FLOW RATE = 80.00 m³/day

- 0.05 - 0.07 m/day
- 0.08 - 0.23 m/day

○ INJECTION WELL
X PRODUCTION WELL
inner production wells could pump at flow rates higher than the sum of the affected injection well flow rates to maintain a potential gradient toward the center of the well pattern.

An upper limit to the oxidation process occurs when the point is reached where increasing the oxidant concentration no longer affects the dissolution rate and more experimental work needs to be done to define this region. This limit as well as the economic feasibility of constructing an unlimited amount of injection wells to oxidize the ore body requires a new approach to gain more insight into the problem of optimizing leach parameters.

Through personal communications with in-situ leach operators, it became known to the author that the oxidant was in almost all cases expended by the time the lixiviant had reached the production well. To try and ascertain the locations in the ore where the oxidant in the lixiviant may have been expended, the moles of dissolved oxidant in the lixiviant was divided by the moles of uranium at the production well for various in-situ leach operations using data from Larson (1978). This produced fairly consistent values between 30 and 45. This number is certainly variable from operation to operation. This is an important value, however, because the reductants, for practical purposes, can be grouped together and considered as the number of moles of oxidant expended to mine one mole of uranium. This value should be derived without too much difficulty from leaching experiments using rock samples from different regions in the ore body.

A computer program "UMINED" was developed to model the in-situ leaching of uranium in a well pattern as described above (Figure VII-1). Because it has been assumed that the solution particle velocities are independent of the dissolution rate, the hydrologic parameters with the exception of the flow rate are not considered. (Flow rate is considered because increased flow rate implies an
increase in the amount of total oxygen delivered to the ore zone). It is implicitly assumed, however, that the host rock is permeable and porous enough to permit mining. The model will accept various well spacings, flow rates, moles of carbonate, specific surface areas, pH values, non-uranium mole percents in uraninite, and dissolved oxygen values. The model will also account for uranium that becomes fixed (by sorption etc.) onto the sediment after dissolution if this parameter is desired, although little is presently known regarding this phenomenon. The moles of oxidant per mole of uranium mined was set equal to 36.0. "UMINED" analyzes a grid of 2% of the well spacing distance as a unit length, this length squared times the height of the aquifer is calculated to obtain unit volumes and the program steps through the grid system. The kinetic equation described above is used and 36 moles of oxidant are subtracted for each mole of uranium mined. Results from "UMINED" are consistent with those of existing uranium leach systems (Larson, 1978 and Potter, in press).

The amount of uranium extracted per cubic meter of rock for the interior cell for various well spacings and flow rates are plotted in Figure VII-5. The ppm uranium at the production well for various well spacings and flow rates is shown in Figure VII-6. The ppm uranium converges because concentration is an intensive variable, i.e. at higher flow rates more uranium is mined per unit time due to the increase in the amount of oxidant introduced to the ore per unit time, but the concentration of the uranium in the production lixiviant converges as the oxidant is expended. It is interesting to note that the model predicts uranium in solution at the production well consistent with field data (Larson, 1978 and Potter, in press) Clearly it is desirable to maximize the amount of uranium produced per cubic meter of ore and to place the wells far enough apart so that the ppm curve (Figure VII-6) has converged, but this may be a closer spacing than is required. The distances from an injection well toward the
FIGURE VII-5

The grams of uranium extracted per cubic meter of ore in the interior cell for various well spacings and flow rates.
URANIUM MINED, g/m³ ROCK

WELL SPACING, m

q, m³/day

x 32.73
○ 53.33
□ 80.00

D.O. = 500 ppm
MIF = 36
FIGURE VII-6

The ppm uranium at the production well for various well spacings and flow rates.
URANIUM CONCENTRATION at PRODUCTION WELL, ppm

q, m³/day

- 32.73
- 53.33
- 80.00

D.O. = 500 ppm

WELL SPACING, m
production well to the point where the oxidant was expended for various flow rates is shown in Figure VII-7. An important parameter to ascertain is the amount of oxidant required to effectively oxidize the reductants in a typical volume of host rock in the ore. Knowing this parameter and the point at which the oxidant is expended at the beginning phase of mining, a well spacing pattern could be designed such that the point where the oxidant is expended migrates toward the production well at a rate comparable to the ore depletion near the injection well to allow the extraction of the ore in the vicinity of the production well. This would allow maximum spacing distances and minimize drilling and well costs. The optimum well spacing distance, then, is a function of the rate of extraction, maximum concentration, the amount of oxidant needed to oxidize the aquifer and migrate the oxidation front, and the time an organization would wish to spend mining one location depending on economic considerations. The duration a mining operation would be expected to produce uranium economically is an important consideration. Assuming a constant mining rate of uranium, the data obtained from the model is collected in Table VII-1 and presented graphically in Figure VII-8. Note the extreme influence of both ore grade and well spacing on mining duration.

As a final addition to the model, a computer program "WELSPACE" was designed to scan an ore body for grade and the "mobilization inhibiting factor" (MIF); the name was coined to describe the number of moles of oxidant to mobilize one mole of uranium. The program then analyzes these data and generates a well-spacing pattern to maintain an optimum well-spacing that was read in as input with respect to the grade and the MIF. The optimum distance is modified by a linear extrapolation to account for higher (more reducing) MIF values or lower (less reducing) MIF values. The grade is used to determine the boundaries of the ore. An example of a pattern generated by "WELSPACE" can
FIGURE VII-7

The distances from the injection wells toward the production well where the oxidant is expended for various flow rates.
<table>
<thead>
<tr>
<th>WELL SPACING (meters)</th>
<th>TOTAL HOST ROCK (cubic meters)</th>
<th>URANIUM MINED PER DAY (grams) (from UMINED)</th>
<th>TOTAL U 0.1% grade (grams)</th>
<th>TIME (years)</th>
<th>TOTAL U 0.3% grade (grams)</th>
<th>TIME (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>250</td>
<td>4103.2</td>
<td>$7.0 \times 10^5$</td>
<td>0.5</td>
<td>$2.1 \times 10^6$</td>
<td>1.4</td>
</tr>
<tr>
<td>5.0</td>
<td>1000</td>
<td>5486.4</td>
<td>$2.8 \times 10^6$</td>
<td>1.4</td>
<td>$8.4 \times 10^6$</td>
<td>4.2</td>
</tr>
<tr>
<td>10.0</td>
<td>4000</td>
<td>5508.5</td>
<td>$1.1 \times 10^7$</td>
<td>5.6</td>
<td>$3.4 \times 10^7$</td>
<td>16.7</td>
</tr>
<tr>
<td>15.0</td>
<td>9000</td>
<td>5508.5</td>
<td>$2.5 \times 10^7$</td>
<td>12.5</td>
<td>$7.6 \times 10^7$</td>
<td>37.6</td>
</tr>
<tr>
<td>20.0</td>
<td>16000</td>
<td>5508.5</td>
<td>$4.5 \times 10^7$</td>
<td>22.3</td>
<td>$1.3 \times 10^8$</td>
<td>66.8</td>
</tr>
</tbody>
</table>

TABLE VII-1. The Estimates of Quantities for an Ore Body 20 Meters in Height Used to Construct Figure VII-8.
FIGURE VII-8

Expected duration of mining as a function of well spacing. Flow rate = 53.33 m³/day, D.O. = 500 ppm, MIF = 36.
WELL SPACING, m

0  10  20  30  40  50  60  70
TIME, years

q = 53.33 m³/day
D.O. = 500 ppm
MIF = 36
FIGURE VII-9

An example of a well pattern generated by the computer program "WELSPACE" for an arbitrary ore body.
INJECTION WELL •
PRODUCTION WELL ×
be seen in Figure VII-8. The pattern generated by "WELSPACE" is a function of the chemical parameters of the ore and the geometry of the ore body with respect to the input of the optimum well-spacing. Because the program is equipped with averaging numerical iterative subroutines, very little in the way of input is needed in the way of grade or MIF at various points in the ore.

The optimum well-spacing which is fed in as input is not an easily calculated value. It is a function of the flow rate (oxidant introduction to the ore) which should be maximized, the MIF, and the ability of the system to confine the lixiviant to the ore body. The value should be arrived at by careful consideration of the streamline configuration, the distance from the injection well that the oxidant is expended, the effective oxidation rate of the primary reductants and how fast this effective oxidation zone migrates toward the production well, and the time one would expect to efficiently extract uranium.

CONCLUSIONS:

1. The reducing capacity of the ore and the kinetic relationships are primary considerations in determining the dissolution reaction rate.

2. The flux of the lixiviant through the ore has no significant effect on the dissolution rate, except that a higher flow rate will increase the total oxidant introduced to the ore.

3. Hydrologic parameters do not seem to have a significant effect on the dissolution rate, assuming an adequate permeability.

4. A non-gaseous oxidant which is not influenced by the ambient pore pressure may be more effective than hydrogen peroxide or oxygen.

5. Velocity contours in the ore should be analyzed to arrive at an optimum flow rate which should be maximized to introduce more oxidant.

6. The "mobilization inhibiting factor" (MIF) should be considered in leaching to account for the oxidant being used in other than uranium oxidation.
7. The rate of total oxidation of the aquifer at various points should be measured.
8. Well spacing and ore grade can dramatically change the time a mine can be economically operated.
VIII. SUMMARY

The Uranium deposits of SE Texas are highly variable with respect to host media and mechanisms to describe the emplacement of these deposits are extremely complex. It was the purpose of this work to consolidate radiometric, chemical, and hydrologic data concerning uranium deposition and subsequent leaching, and further, to propose mechanisms and models to optimize uranium ore evaluation and extraction.

The high degree of secular disequilibrium of these ores indicated their relatively recent emplacement and the mobility of the uranium and/or the decay products. The secular disequilibrium associated with many of these ores has been shown to limit direct conversion of gamma radiation counts directly to uranium concentrations, however utilizing disequilibrium data, it has been suggested here that it may be possible to predict the future profitability and the effectiveness of an in-situ leach operation. By monitoring radon-222/uranium ratios and knowing the degree of secular disequilibrium, a model was suggested to gain insight into mining effectiveness. The factors associated with this effectiveness are both hydrologic and chemical in nature. A technique was determined to predict future profitability of an in-situ leach by monitoring radon-222/uranium ratios.

Hydrologic and chemical parameters were selected as variables which can be manipulated to increase (or decrease) mining efficiency. These parameters were modeled in this work to determine those which are of primary importance and those of lesser importance.

Dissolution Eh-pH diagrams were constructed to gain insight into chemical variables and species which might be optimized to increase efficiency in an in-situ leach situation and to examine the possibility that predictions made from these diagrams would be in better agreement with kinetic models of uraninite dissolution than those from conventional stability diagrams. Dissolution Eh-pH
diagrams were shown to more closely agree with kinetic models. Information gained from these diagrams supported kinetic data that intermediate uranium species exist between uraninite and the uranium carbonate complexes in solution between pH values of 6-9.0 and that carbonate in-situ leach operations be operated at a pH of at least 9.0. The dissolution diagrams also were shown to be consistent with field data that acid leach systems may be operated at pH values as high as 3.0.

Hydrologic and chemical kinetic parameters were examined to determine their relative importance and it is suggested that the hydrologic parameters of primary interest are the flow rate and the well spacing which control oxidant replenishment to the system and mining longevity. It was proposed that the actual flux of the lixiviant solution through the ore was not important in increasing the uraninite dissolution rate, but that the chemical kinetics are the controlling factor. The kinetics of the dissolution process were shown to be proportional to the oxidant concentration in solution. The effective oxidant concentration was suggested to be a function of the pore pressure in the host aquifer and the flow rate of the lixiviant, however, the flow rate must be monitored to confine the lixiviant solution to the ore body. Because of the limiting relationship between oxygen partial pressure in solution and the ambient pore pressure in the aquifer, it was suggested that a non-gaseous oxidant, such as Fe(CN)\(_6^{3-}\) or Cu(NH\(_3\))\(_4^{2+}\), would be more useful as oxidants. The oxidant stoichiometry with respect to nonuranium substances as well as the capacity and rate of oxidant reaction with these substances was shown to be of extreme importance in relation to mining efficiency and profitability.
IX. RECOMMENDATIONS FOR FUTURE WORK:

1. The effect of the ionic strength on the dissolution rate of uraninite.
2. The speciation of soluble uranium complexes in the uraninite dissolution process to verify dissolution diagrams.
3. Experiments to better define the temperature dependence of the dissolution rate of uranium minerals.
4. The kinetic relationships between sulphate and phosphate complexes and uranium dissolution.
6. The stability and kinetics of dissolved uranium complexes in an in-situ leach situation in regions where the oxidant has been expended to protect against reprecipitation of the uranium.
7. The development of non-gaseous oxidants.
8. Monitoring effluent radon-222 and cumulative radon-222 to verify or deny the theoretical model presented in this work.
9. Experiments to verify the importance of the MIF.
10. Experiments to determine the reducing capacities and oxidation front migration from injection wells in individual ore bodies.


Faure, Gunther, 1977, Principles of Isotope Geology, John Wiley and Sons Publisher, pp. 52-53.


Hostetler, P.B., and Garrels, R.M., 1962, Transportation and Precipitation of Uranium and Vanadium at Low Temperatures, with Special Reference to Sandstone-Type Uranium Deposits, Econ. Geol., vol. 57, no. 2, pp. 137-167.


Pereira, Enio B., (in press), Reconnaissance of Radon Emanation Power of Pocos de Caldas, Brazil Uranium Ore and Associated Rocks, To Be Published in the Natural Radiation Environment III Symposium.


XI. APPENDIX A

The hydrologic parameters used in the "WELSPECS" computer program were as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity of the Sandstone</td>
<td>25%</td>
</tr>
<tr>
<td>Density of Water (25°C)</td>
<td>0.997048 g/cm³</td>
</tr>
<tr>
<td>Density of Rock</td>
<td>2.80 g/cm³</td>
</tr>
<tr>
<td>Height of Aquifer</td>
<td>20 meters</td>
</tr>
</tbody>
</table>
XII. APPENDIX B

The materials presented here are the computer programs EH-PH UR", "WELSPECS", "UMINED", and "WELSPACE". The programs themselves and their contemplation form a major and integral part of this research. The programs are written in Fortran IV and the work was done on a Fortran G compiler. The computing was accomplished at the Institute for Computer Sciences and Applications at The Rice University on an ITEL AS/6 computer system.
C THIS IS THE COMPUTER PROGRAM EU-PH UR
DIMENSION UNAMES(400), CARB(10), SULF(10), PHOS(10), UACT(10)
DIMENSION PHMAX(10), PHMIN(10), EHMAX(10), EHM(EUR(10), PH(10), TM(10), MS(15), IFMAT(7)
DIMENSION U(120), SYM(26), SYMBOL(120), CNTRL(150), ISP(14)
1 ' 17I', ' 14I', ' 13I', ' 11I', ' 10I', ' 9I', ' 8I', ' 7I', ' 6I', ' 5I', ' 4I', ' 3I', ' 2I', ' 1I', ' 0I'/
DATA ISP/1 (', 13 (', ' 14 ('/
DATA IFMAT/1 (', 13 ' 14('/
DATA SYM/1 'A', 'B', 'C', 'D', 'E', 'F', 'G', 'H', 'S', '+', 'K', '-', 'M', 'N'/
DATA CN'/1 /
READ(5, 1) UNAMES
C UNAMES ARE THE NAMES OF THE U SPECIES FOR LABELING
1 FORMAT(19(20A4), 20A4)
READ(5, 2) N, M, NM
C N=THE NUMBER OF JOBS
C M=THE NUMBER OF POSSIBLE U SPECIES TOTAL
C NM=THE NUMBER OF SOLID PHASES
2 FORMAT(3I2)
READ(5, 3) (CARB(I), I=1,N)
READ(5, 3) (SULF(I), I=1,N)
READ(5, 3) (PHOS(I), I=1,N)
C CARB IS THE PARTIAL PRESSURE OF CO2 GAS
C SULF IS THE PARTIAL PRESSURE OF H2S GAS
C PHOS IS THE TOTAL DISSOLVED PHOSPHATE IN CONCENTRATION UNITS
C UACT IS THE LOG10 OF THE TOTAL URANIUM ACTIVITY IN SOLUTION
READ(5, 5) (UACT(I), I=1,N)
READ(5, 5) (PHMAX(I), I=1,N)
READ(5, 5) (PHMIN(I), I=1,N)
C PHMAX AND PHMIN MUST BE UNIT PH NOS. I.E. 1.00, 9.00, ETC.
READ(5, 5) (EHMAX(I), I=1,N)
READ(5, 5) (EHMIN(I), I=1,N)
3 FORMAT(4E8.2)
5 FORMAT(4F5.2)
EHINT=0.02
DO1000 I=1,N
WRITE(6, 35)
35 FORMAT('1', '10X', 'EH-PH DIAGRAM PROGRAM')
DIFP=PHMAX(I)-PHMIN(I)
ISPACE=IPFX(126./DIFP)
SPACE=FLOAT(ISPACE)
PHINT=DIFP/SPACED(DIFPPH)
NEH=IPFX(((EHMAX(I)-EHMIN(I))/.02)+2.0)
NPH=IPFX(SPACE*DIFPPH)
NO=NPH+1
DO 7 J=1, NO
7 MS=IFMAT(4)=ISP(NOPH)
IFMAT(5)=IGIT(NOPH)
WRITE(6, IFMAT) (MS=J, NO)
EH(1)=EHMAX(I)
CO=CARB(I)
SU=SULF(I)
POS=PHOS(I)
DO 10 J=1,NEH
DO 45 II=1,NPH
45 CONT(II)=CN
PH(I)=PHMIN(I)
DO 8 K=1,NPH
IF(ER(J).LT.-0.059*PH(K).OR.ER(J).GT.1.23-0.059*PH(K))GO TO 40
DO 30 I=1,N
30 U(I)=0.0
CARB(I)=CO
SULF(I)=SU
PHOS(I)=PO
IF(CARB(I).EQ.1.0)GO TO 9
CARB(I)=-20.73+ALOG10(CARB(I))+2*PH(K)
9 IF(SULF(I).EQ.1.0)GO TO 11
SULF(I)=ER(J)-0.377+0.0295*ALOG10(SULF(I))+0.118*PH(K)
SULF(I)=ER(J)-0.17+0.0295*SULF(I)+0.118*PH(K)
11 IF(PHOS(I).EQ.1.0)GO TO 12
PHOS(I)=PHOS(I)/((EXP(-PH(K)/0.4343)**3)*0.524822+(EXP(-PH(K)/0.4343)**2)*0.398220+EXP(-PH(K)/0.4343)*0.251283+1.0)
PHOS(I)=ALOG10(PHOS(I))
12 U(1)=(ER(J)-0.4098)/0.0295
U(2)=4.637-4.0*PH(K)
U(3)=(ER(J)-0.5808+0.0295*PH(K))/0.0295
U(4)=(ER(J)-0.493+0.0295*PH(K))/0.0148
U(5)=(ER(J)-0.564+0.049*PH(K))/0.0098
IF(CARB(I).EQ.1.0)GO TO 25
U(6)=(ER(J)+0.092+0.059*CARB(I))/0.0295
U(7)=(ER(J)-0.223+0.0885*CARB(I))/0.0295
25 IF(SULF(I).EQ.1.0)GO TO 13
U(8)=SULF(I)-4.0*PH(K)+0.824
U(9)=2.0*SULF(I)-4.0*PH(K)+5.112
U(10)=(ER(J)-0.328+0.0295*SULF(I))/0.0295
U(11)=(ER(J)-0.284+0.0295*SULF(I))/0.0295
13 IF(PHOS(I).EQ.1.0)GO TO 14
U(12)=19.754-5.0*PH(K)+PHOS(I)
U(13)=42.154-6.0*PH(K)+2.0*PHOS(I)
U(14)=63.187-7.0*PH(K)+3.0*PHOS(I)
U(15)=83.621-8.0*PH(K)+4.0*PHOS(I)
U(16)=(ER(J)+0.2045-0.0295*PH(K)+0.0295*PHOS(I))/0.0295
U(17)=(ER(J)+0.1392+0.059*(12.40-PH(K)+PHOS(I)))/0.0295
U(18)=(ER(J)-0.320+0.0295*(19.6-2.0*PH(K)+PHOS(I)))/0.0295
U(19)=(ER(J)-0.248+0.059*(19.6-2.0*PH(K)+PHOS(I)))/0.0295
U(20)=(ER(J)-0.198+0.0885*(19.6-2.0*PH(K)+PHOS(I)))/0.0295
14 DO 15 MM=1,4
15 SYMBOL(MM)=SYM(MM)
LM=M-MM-1
DO 16 NN=1,LM
IF(U(NN).LT.U(NN+1).AND.U(NN+1).NE.0.0)GO TO 16
UTEMP(U(NN))=U(NN+1)
U(NN)=UTEMP
SYMT=SYMBOL(NN)
16
SYMBOL(NN) = SYMBOL(NN+1)
SYMBOL(NN+1) = SYMSTEP

16 CONTINUE
LM = LM + 1
IF(U(LM) .LT. UACT(I)) GO TO 60
CNTRL(K) = SYMBOL(LM)
GO TO 40

60 U(21) = (-EH(J) + 0.4098 + 0.0295*UACT(I))/0.0295
U(22) = UACT(I) + 2.0*PH(K) - 5.395
IF(CARB(I) .EQ. 0.0) GO TO 76
U(23) = UACT(I) + CARB(I) + 14.462

76 IF(PHOS(I) .EQ. 1.0) GO TO 77
U(24) = (-EH(J) + 1.066 + 0.0295*UACT(I) + 0.059*(12.40 - PH(K) + PHOS(I)) - 10.118*PH(K))/0.0295
U(25) = 3.0*UACT(I) + 2.0*PHOS(I) + 49.037
U(26) = 2.0*UACT(I) + 2.0*PHOS(I) - 2.0*PH(K) + 48.084

77 DO 57 MM = 1, M
57 SYMBOL(MM) = SYM(MM)
MP = M - 1
LM = M - MM + 1
DO 55 NN = LM, MP
IF(U(NN) .LT. U(NN+1) .AND. U(NN+1) .NE. 0.0) GO TO 55
UTEMP = U(NN)
U(NN) = U(NN+1)
U(NN+1) = UTEMP
SYMSTEP = SYMBOL(NN)
SYMBOL(NN) = SYMBOL(NN+1)
SYMBOL(NN+1) = SYMSTEP

55 CONTINUE
CNTRL(K) = SYMBOL(K)

40 PH(K+1) = PH(K) + PHINT

8 CONTINUE
WRITE(6, 17) EH(J), (CNTRL(K), K = 1, NPH)
17 FORMAT(' ', F5.2, 1X, 126(A1))
EH(J+1) = EH(J) - EHINT

10 CONTINUE
WRITE(6, IFMAT) (MScale(J), J = 1, NO)
WRITE(6, 20) PHMIN(I), PHMAX(I)
20 FORMAT(' ', 'PH INTERVALS MARKED BY (I). MIN. PH IS', F5.2, 1X,
     'MAX. PH IS ', F5.2)
WRITE(6, 50)
50 FORMAT(/, /)
READ(5, 21) WORDS
21 FORMAT(20A4/20A4)
WRITE(6, 22) WORDS
22 FORMAT(1X, 20A4/1X, 20A4)
WRITE(6, 23) UNAMES
23 FORMAT(20 (1X, 20A4/))

1000 CONTINUE
STOP
END

C$ENTRY
PH PLOTTED ON X-AXIS, EH (IN VOLTS) PLOTTED ON Y-AXIS
EH-PH DIAGRAM FOR U-H2O SYSTEM U DISSOLVED=10^-4

EH-PH DIAGRAM FOR U-H2O-CO2 SYSTEM WITH THE CO2=1.00E-02 ATM DISSOLVED U=10^-4
EH-PH DIAGRAM FOR U-H2O-CO2-H2S SYSTEM WITH CO2=1.00E-02 AND H2S=1.00E-02 ATM, DISSOLVED U=10^-4
EH-PH DIAGRAM FOR U-H2O-CO2-H2S-P04 SYSTEM WITH CO2=1.00E-02, H2S=U.00E-02, AND THE TOTAL DISSOLVED PHOSPHATE =2.00E-05, DISSOLVED U=10^-4
C THIS IS THE COMPUTER PROGRAM UMINEED.
DIMENSION XPOS(150,150), YPOS(150,150)
REAL NOC
READ(5,100) X, FOR, ZHGT, Q, SS, RF, M, N
READ(5, 101) NOC, OX, ACTH, CO, RHO, DEN
101 FORMAT(P5.3, F7.2, E10.3, E10.3, F6.6, F5.2)

XX = SQRT(X**2 + X**2)
DX = XX/50.0
DY = DX
YY = XX
DO 12 I = M, N
CTR = DX
DO 12 J = M, N
YPOS(I, J) = CTR
XPOS(J, I) = CTR
12 CTR = CTR + DX
RHO = RHO * 1000000.0
SS = SS * ZHGT * DX * DY / DEN * 1000000.0
RX = (1.77828E+20 * SS * CO * ACTH * 4.1687E-04 * 1.5849E-11 * NOC * EXP(-7045.0/
1298.15)) / RF
OX = OX * Q * 999.972/4
CONC = 0.0
L = 0
DO 40 K = 51, 74
CONC = 0.0
I = 50
J = 50
OXI = OX / Q / 999.972*4
RC = RX / OXI
CONC = RC
CONC = RC + CONC
CONC = CONC + CONC
OX = (OX / 1000.0 / 32.0 - (CONC / 238.0 + 35.0 * CONC / 238.0)) * 1000.0 * 32.0
IF (OX .LT. 0.1) OI = 0.0
IF (OX .NE. 0.0) GO TO 60
L = L + 1
IF (L .NE. 1) GO TO 60
WRITE(6, 61) XPOS(K, K), YPOS(K, K)
61 FORMAT('O', '5X', 'OXIDANT EXPENDED AT COORDINATES X=', F7.3, 'Z', 'Y=', F
17.3)
60 CONTINUE
41 I = I + 1
J = J + 1
IF (I .GE. K) GO TO 40
IF (J .GE. K) GO TO 40
CONC = 0.0
OXI = OX / Q / 999.972*4
RC = RX / OXI
CONC = RC
CONC = RC + CONC
CONC = CONC + CONC
OX = (OX / 1000.0 / 32.0 - (CONC / 238.0 + 35.0 * CONC / 238.0)) * 1000.0 * 32.0
GO TO 41
40 CONTINUE
CONCT=CONCT*4
WRITE (6,43) X, CONCT, OX
43 FORMAT ('0', 5X, 'WELL SPACING=', F6.2, 5X, 'AMOUNT OF URANIUM MINED IN 1GRAMS PER DAY=', E13.5, 5X, 'OXIDANT REMAINING=', F15.4)
PPM=CONCT/Q
CONCT=CONCT/(X*YY*ZHGT)
WRITE (6,50) CONCT, PPM
50 FORMAT ('0', 5X, 'URANIUM MINED PER CUBIC METER OF ROCK=', E13.5, 5X, 'P 1PM URANIUM IN SOLUTION AT PRODUCTION WELL=', E13.5)
STOP
END
C THIS IS THE COMPUTER PROGRAM WELSPECS

DIMENSION TIM (250, 250)
DIMENSION XPOS (250, 250), XINJ (4, 4), YPRO (3, 3), XINJ (4, 4), XPRC (3, 3),
YPOS (250, 250), VTOI (250, 250), XCOMF (250, 250), YCOMF (250, 250)
REAL NOC
READ (5, 100) X, POR, ZHGT, Q, SS, RF, M, N
100 FORMAT (F5.2, F4.2, F7.2, F7.2, E10.3, F6.2, E3, I3, I3)
READ (5, 101) NOC, OX, ACTH, CO, RHC, DEN
101 FORMAT (F5.3, F7.2, E10.3, E10.3, F8.6, F5.2)
XX = SQRT (XX**2 + YY**2)
DX = XI/50.0
DY = DXX
YY = YX
DO 10 I = 1, 4
CTR = 0.0
DO 10 J = 1, 4
XINJ (I, J) = CTR
XINJ (J, I) = CTR
10 CTR = CTR + DX*50.0
DO 11 I = 1, 7
CTR = 0.5*XX
DO 11 J = 1, 7
YPRO (I, J) = CTR
YPRO (J, I) = CTR
11 CTR = CTR + DX*50.0
DO 12 I = M, N
CTR = DX
DO 12 J = M, N
YPOS (I, J) = CTR
XPOS (J, I) = CTR
12 CTR = CTR + DX
C = -1/(2*3.14159*POR*ZHGT)
DO 13 I = M, N
CTR = 0.0
DO 13 J = M, N
YSTOR = 0.0
XSTOR = 0.0
QINJ = Q/4.0
XSTOR = 0.0
YSTOR = 0.0
QPRV = -Q
DO 14 K = 1, 4
DO 14 L = 1, 4
IF (XPOS (I, J) .EQ. XINJ (K, L) .AND. YPOS (I, J) .EQ. YINJ (K, L)) GO TO 15
IF (XPOS (J, I) .EQ. XINJ (K, L) .AND. YPOS (J, I) .EQ. YINJ (K, L)) GO TO 15
YSTOR = YSTOR + (((XPOS (I, J) - XINJ (K, L)) / (XPOS (J, I) - XINJ (K, L)) ** 2 + (YPOS
15 (I, J) - YINJ (K, L)) ** 2)) * QINJ
XSTOR = XSTOR + (((XPOS (J, I) - XINJ (K, L)) / (XPOS (J, I) - XINJ (K, L)) ** 2 + (YPOS
15 (J, I) - YINJ (L, K)) ** 2)) * QINJ
GO TO 14
14 CONTINUE
DO 16 K = 1, 3
16 GO TO 15
DO 16 L=1,3
   IF (XPOS (I,J).EQ. XINJ (K,L).AND. YPOS (I,J).EQ. YINJ (K,L)) GO TO 16
   IF (XPOS (J,I).EQ. XINJ (L,K).AND. YPOS (J,I).EQ. YINJ (L,K)) GO TO 16
   IF (XPOS (I,J).EQ. XPRO (K,L).AND. YPOS (I,J).EQ. YPRO (K,L)) GO TO 17
   IF (XPOS (J,I).EQ. XPRO (L,K).AND. YPOS (J,I).EQ. YPRO (L,K)) GO TO 17
   YSTOR=YSTOR+ ( ((YPOS (I,J)-YPRO (K,L))/(XPOS (I,J)-XPRO (K,L)) **2+(YPOS (I,J)-YPRO (K,L)) **2)) *QPRO
   XSTOR=XSTOR+ ( (IPOS (J,I)-XPRO (L,K))/(XPOS (J,I)-XPRO (L,K)) **2+(IPOS (J,I)-XPRO (L,K)) **2)) *QPRO
GO TO 16
17 XSTOR=0.0
   YSTOR=0.0
16 CONTINUE
   XCOMP (J,I)=C*XSTOR
   YCOMP (I,J)=C*YSTOR
   IF (XCOMP (J,I).GE.1.0) XCOMP (J,I)=0.001
   IF (YCOMP (I,J).GE.1.0) YCOMP (I,J)=0.001
   IF (XCOMP (J,I).LE.-1.0) XCOMP (J,I)=0.001
   IF (YCOMP (I,J).LE.-1.0) YCOMP (I,J)=0.001
13 CONTINUE
DO 18 I=M,N
   DO 21 J=M,N
18 VTOT (I,J)=SQR (XCOMP (I,J) **2+YCOMP (I,J) **2)
   DO 21 I=50,100
   DO 21 J=50,100
WRITE (6,20) XPOS (I,J), YPOS (I,J), XCOMP (I,J), YCOMP (I,J), VTOT (I,J)
20 FORMAT (' ',2X,'X=',F7.3,2X,'Y=',F7.3,2X,'X VELOCITY=',E11.4,2X,'Y VELOCITY=',E11.4,2X,'TOTAL VELOCITY=',E11.4)
21 CONTINUE
   DO 200 I=M,N
   DO 200 J=M,N
   TIM (I,J)=1.0
   XPOS (I,J)=XPOS (I,J)+XCOMP (I,J)*TIM (I,J)
   YPOS (I,J)=YPOS (I,J)+YCOMP (I,J)*TIM (I,J)
200 CONTINUE
   DO 202 I=M,N
   DO 202 J=M,N
WRITE (9,201) XPOS (I,J), YPOS (I,J), VTOT (I,J)
201 FORMAT (F8.3,2X,F8.3,2X,F12.4,2X)
202 CONTINUE
STOP
END
C THIS IS THE COMPUTER PROGRAM WELSPACE
DIMENSION COND(20,25),SWITCH(225,300),WELL(225,300),GRD(20,25),
1(20,100),DEPTH(100,25),FMT(20),RAD(20,25),DIP(20,25),
1RHO1(30),RTEST(30),ROI(225,300),GRADE(225,300),RF(20,25)
READ(5,1)Q,TIME,D,DY,DX,REFPLN,RADW,NY,NY
1 FORMAT(6FS.2,FS.4,2I2)
READ(5,2)(FMT(I),I=1,16)
2 FORMAT(16A4)
READ(5,FMT)((COND(I,J),J=1,NY),I=1,NX)
READ(5,FMT)((GRD(I,J),J=1,NY),I=1,NX)
READ(5,FMT)((DEPTH(I,J),J=1,NY),I=1,NX)
READ(5,FMT)((RF(I,J),J=1,NY),I=1,NX)
CALL AVERAGE(COND,NX,NY,20,25,DX,DY)
CALL AVERAGE(DEPTH,NX,NY,100,25,DX,DY)
CALL AVERAGE(REF,NX,NY,20,25,DX,DY)
CALL GRDISB(GRD,NX,NY,20,25,DX,DY)
A=(Q*TIME)/(3.141593*D)
B=(Q*TIME*ALOG(RADW))/(3.141593*D)
DO 26 I=1,NX
DO 26 J=1,NY
26 Z(I,J)=REFPLN-DEPTH(I,J)
NA=NX-1
NB=NY-1
DO 27 I=2,NA
DO 27 J=2,NB
DIP(I,J)=((DEPTH(I-1,J)-DEPTH(I+1,J))/(2*DX))**2+((DEPTH(I,J-1)
1-DEPTH(I+J+1))/(2*DY))**2
DIP(I,J)=ABS(DIP(I,J))
DIP(I,J)=SQR(DIP(I,J))
27 DIP(I,J)=ATAN(DIP(I,J))
DO 303 I=2,NA
DIP(I,1)=DIP(I,2)
303 DIP(I,NY)=DIP(I,NB)
DO 304 J=2,NB
DIP(1,J)=DIP(2,J)
304 DIP(NX,J)=DIP(NA,J)
DIP(1,1)=DIP(2,2)
DIP(1,NY)=DIP(2,NY-1)
DIP(NX,1)=DIP(NX-1,2)
DIP(NX,NY)=DIP(NX-1,NY-1)
CALL EDIP(DIP,NX,NY,20,25,DX,DY)
WRITE(6,201)
201 FORMAT('1D',2X,'AVERAGE CONDUCTIVITY,AVERAGE DEPTH TO ORE, AVERAGE
1RETARDATION FACTOR NORMALIZED TO 35.0, AND AVERAGE DIP ANGLE OF BE
10D'///)
DO 200 I=1,NX
DO 200 J=1,NY
DIP(I,J)=DIP(I,J)*57.296
WRITE(6,100)I,J,COND(I,J),DEPTH(I,J),RF(I,J),DIP(I,J)
100 FORMAT('1D',2X,'COND=',I3,2X,'DEPTH=',F7.3,2X,'
1RETARDATION FACTOR=',F7.3,2X,'
1DIP ANGLE=',F7.3)
DIP(I,J)=DIP(I,J)/57.296
200 CONTINUE
DO 28 I=1,NX
DO 28 J=1, NY
   RAD(I,J)=10.0*35.0/RF(I,J)
28 CONTINUE
   SUM=0.0
   DO 37 I=1, NX
      DO 37 J=1, NY
37 SUM=SUM+RAD(I,J)
   AVRAD=SUM/((NX*NY)
   DXX=FLOAT(IFIX(AVRAD/8))
   DYY=FLOAT(IFIX(AVRAD/8))
   XINT=DX/DXX
   YINT=DY/DYY
   M=IFIX(XINT)
   N=IFIX(YINT)
   XIN=(XINT-FLOAT(M))/XINT
   YIN=(YINT-FLOAT(N))/YINT
   KK=1
   LL=1
   DO 39 I=1, NX
      IF (I.EQ.1) GO TO 105
      KK=KK+IFIX(XINT)
      N=N+IFIX(YINT)
      LL=1
      N=IFIX(YINT)
105 DO 39 J=1, NY
      DO 38 K=KK, M
      DO 38 L=LL, N
         ROI(K,L)=RAD(I,J)
38 GRADE(K,L)=GRD(I,J)
      LL=LL+IFIX(YINT)
      N=N+IFIX(YINT)
39 CONTINUE
   XDIST=DX*FLOAT(NX)
   YDIST=DY*FLOAT(NY)
   NXI=IFIX(XINT)*NX
   NYI=IFIX(YINT)*NY
   DXX=IFIX(XDIST/DXX)/NX*NX
   DYY=IFIX(YDIST/DYY)/NY*NY
   WRITE(6,401)
401 FORMAT(*0*,3X,'NEW GRID PARAMETERS GENERATED WITHIN THE PROGRAM')
      WRITE(6,40) DXX, DYY, NX, NY
40 FORMAT(*0*,3X,'DX=',F6.2,2X,'DY=',F6.2,2X,'NO OF X*S=',I6,
     1 12X,'NO OF Y*S=',I6)
      CALL EROI(ROI,NXX,NYY,225,300,DXX,DYY)
      CALL ERDISB(GRADE,NXX, NYY, 225, 300, DXX, DYY)
      WRITE(6,206)
206 FORMAT(*0*,5X,'GRADE OF ORE AND RADII OF INFLUENCE AT EACH POINT (1
   COORDINATE LOCATIONS IN METERS FROM MAP ORIGIN'))
   DO 205 I=1, NXX
      DO 205 J=1, NY
         XI=FLOAT(I-1)*DIX+FLOAT(I-1)*XIN
         YJ=FLOAT(J-1)*DYY+FLOAT(J-1)*YIN
         IF (GRADE(I,J).LT.0.0) GO TO 205
         WRITE(6,400) XI, YJ, GRADE(I,J), ROI(I,J)
400 FORMAT(' ',2X,'X=',F6.2,2X,'Y=',F6.2,2X,'GRADE=',F7.3,2X,'RADIUS 0
1F INFLUENCE=',F7.3)
205 CONTINUE
   DO 42 I=1,NXX
   DO 42 J=1,NYY
   WELL(I,J)=0.0
   SWITCH(I,J)=0.0
   IF (GRADE(I,J).GT.0.0) GO TO 43
   SWITCH(I,J)=0.0
   GO TO 42
43 SWITCH(I,J)=1.0
42 CONTINUE
   NCTX=NXX-8
   NCTY=NYY-8
   DO 41 I=8,NCTX
   DO 41 J=8,NCTY
   IF (GRADE(I,J).LT.0.0) GO TO 41
   N=IFIX (ROI(I,J))
   NN=N
   SUMR=0.0
   M=0
48 LP=J+M
   IF (LP.LE.NYY) GO TO 110
   LP=NYY
110 L=J-M
   IF (L.GE.1) GO TO 111
   L=1
   INDEX=I-N
   IF (INDEX.GE.1) GO TO 112
   INDEX=1
112 KDX=I+N
   IF (KDX.LE.NXX) GO TO 113
   KDX=NXX
113 DO 44 K=INDEX,KDX
   44 SUMR=SUMR+SWITCH(K,L)
   IF (M.EQ.0) GO TO 46
   DO 45 K=INDEX,KDX
45 SUMR=SUMR+SWITCH(K,LP)
46 M=M+1
   IF (M.EQ.NN+1) GO TO 47
   IF (M.LT.5) GO TO 48
   N=N-1
   GO TO 48
47 TEST=0.90*2*(FLOAT(NN)+2)**2
   IF (SUMR.GE.TEST) GO TO 49
   GO TO 47
49 N=NN
   M=0
101 LP=J+M
   IF (LP.LE.NYY) GO TO 120
   LP=NYY
120 L=J-M
   IF (L.GE.1) GO TO 121
   L=1
121  INDX=I-N
     IF(INDX.GE.1) GO TO 122
     INDX=1
122  KDX=I+N
     IF(KDX.LE.NXX) GO TO 123
     KDX=NXX
123  DO 50 K=INDX,KDX
50  SWITCH(K,L)=0.0
     IF(M.EQ.0) GO TO 51
     DO 52 K=INDX,KDX
52  SWITCH(K,LP)=0.0
51  M=M+1
     IF(M.EQ.NN+1) GO TO 53
     IF(M.LE.5) GO TO 101
     N=N-1
     GO TO 101
53  WELL(I,J)=1.0
41  CONTINUE
     WRITE (6,57)
57  FORMAT (*1*,5X, 'INJECTION WELL COORDINATES')
     M=0
     DO 55 I=1,NXX
     DO 55 J=1,NYY
     IF(WELL(I,J).NE.1.0) GO TO 55
     M=M+1
     X=FLOAT(I-1)*DXX+FLOAT(J-1)*XIN
     Y=FLOAT(I-1)*DYY+FLOAT(J-1)*YIN
     WRITE(6,58) M, XI, YJ
55  CONTINUE
     DO 60 I=1,NXX
     DO 60 J=1,NYY
     IF(GRADE(I,J).GT.0.0) GO TO 61
     SWITCH(I,J)=0.0
     GO TO 60
61  SWITCH(I,J)=1.0
60  CONTINUE
     DO 160 I=1,NX
     DO 160 J=1,NY
     DEPTH(I,J)=0.0
160  Z(I,J)=0.0
     DO 62 I=8,NCTX
     DO 62 J=8,NCTY
     IF(WELL(I,J).EQ.1.0) GO TO 62
     IF(GRADE(I,J).LE.0.0) GO TO 62
     N=IP(M,ROI(I,J)*1.9)
     NN=N
     M=0
     SUMW=0.0
     MT=0
63  LP=J+M
     IF(LP.LE.NYY) GO TO 130
     LP=NYY
130  L=J-M
IF (L .GE. 1) GO TO 131
L = 1
131 END = I - N
IF (INDEX .GE. 1) GO TO 132
INDEX = 1
132 KDX = I + N
IF (KDX .LE. NXX) GO TO 133
KDX = NXX
133 DO 64 K = INDEX, KDX
SUMW = SUMW + SWITCH(K, L)
IF (WELL(K, L) .NE. 1.0) GO TO 64
MT = MT + 1
DEPTH(MT, 1) = K
DEPTH(MT, 2) = L
64 CONTINUE
IF (M .EQ. 0) GO TO 66
DO 67 K = INDEX, KDX
SUMW = SUMW + SWITCH(K, LP)
IF (WELL(K, LP) .NE. 1.0) GO TO 67
MT = MT + 1
DEPTH(MT, 1) = K
DEPTH(MT, 2) = LP
67 CONTINUE
66 M = M + 1
IF (M .EQ. NN + 1) GO TO 68
IF (M .LE. 5) GO TO 63
N = N - 1
GO TO 63
68 TEST = 0.40 * 2.0 * (FLOAT(NN) ** 2)
IF (MT .LT. 4) GO TO 62
IF (SUMW .LT. TEST) GO TO 62
XONE = (DEPTH(K, 1) + DEPTH(K + 1, 1)) / 2.0
YONE = (DEPTH(K, 2) + DEPTH(K + 1, 2)) / 2.0
XTWO = (DEPTH(K + 2, 1) + DEPTH(K + 3, 1)) / 2.0
YTWO = (DEPTH(K + 2, 2) + DEPTH(K + 3, 2)) / 2.0
XCO = (XONE + XTWO) / 2.0
YCO = (YONE + YTWO) / 2.0
ICO = IFIX(XCO)
JCO = IFIX(YCO)
WELL(ICO, JCO) = 2.0
M = 0
N = IFIX(FLOAT(NN) / 1.9)
76 LP = JCO + M
IF (LP .LE. NYY) GO TO 140
LP = NYY
140 L = JCO - M
IF (L .GE. 1) GO TO 141
L = 1
141 INDEX = ICO - N
IF (INDEX .GE. 1) GO TO 142
INDEX = 1
142 KDX = ICO + N
IF (KDX .LE. NXX) GO TO 143
KDX = NXX
143  DO 72 K=INDX,KDX
72   SWITCH(K,L)=0.0
       IF(M.EQ.0)GO TO 73
       DO 74 K=INDX,KDX
74   SWITCH(K,LP)=0.0
73   M=M+1
       IF(M.EQ.NW+1)GO TO 62
       IF(M.LE.5)GO TO 76
       N=N-1
       GO TO 76
62  CONTINUE
       M=0
67   WRITE(6,77)
77   FORMAT('1'5X,'PRODUCTION WELL COORDINATES')
       DO 75 I=1,NXX
       DO 75 J=1,NYY
       IF(WELL(I,J).NE.2.0)GO TO 75
       M=M+1
       XI=FLOAT(I-1)*DXX+FLOAT(I-1)*XIX
       YJ=FLOAT(J-1)*DYY+FLOAT(J-1)*YIX
       WRITE(6,78)M,XI,YJ
78   FORMAT('1'3X,I3,'1',2X,'X=',F6.2,3X,'Y=',F6.2)
75  CONTINUE
       M=M
       WRITE(6,92)
92   FORMAT('1'5X,'INJECTION WELL PRESSURES IN CU. METERS PER DAY')
       DO 80 I=8,NCTX
       DO 80 J=8,NCTY
       IF(WELL(I,J).NE.1.0)GO TO 80
       MM=MM+1
       N=IFIX(ROI(I,J)*1.75)
       NN=N
       M=0
       SUMI=0.0
       SUMP=0.0
91   LP=J+M
       IF(LP.LE.NYY)GO TO 150
       LP=NYY
150  L=J-M
       IF(L.GE.1)GO TO 151
       L=1
151   INDX=I-N
       IF(INDX.GE.1)GO TO 152
       INDX=1
152   KDX=I+N
       IF(KDX.LE.NXX)GO TO 153
       KDX=NXX
153  DO 85 K=INDX,KDX
       IF(WELL(K,L).NE.1.0)GO TO 86
       SUMI=SUMI+WELL(K,L)
86   IF(WELL(K,L).NE.2.0)GO TO 85
       SUMP=SUMP+WELL(K,L)/2.0
85  CONTINUE
       IF(M.EQ.0)GO TO 87
DO 88 K=INDX,KDX
   IF(WELL(K,LP).NE.1.0) GO TO 89
   SUMI=SUMI+WELL(K,LP)
89 IF(WELL(K,LP).NE.2.0) GO TO 88
   SUMP=SUMP+WELL(K,LP)/2.0
88 CONTINUE
87 M=M+1
   IF(M.EQ.NN+1) GO TO 90
   IF(M.LE.5) GO TO 91
   N=N-1
   GO TO 91
90 SUMI=(O*SUMP)/SUMI
   WRITE(6,93) MM,SUMI
93 FORMAT(1' ','3X,I3,' ','3X,F7.3)
80 CONTINUE
STCP
END
SUBROUTINE AVERAGE(AV,KI,KJ,KL,DDX,DDY)
   DIMENSION AV(IJK,JKL),TEST(225,300),AHOLD(225,300)
   DO 12 I=1,KI
      DO 12 J=1,KJ
   12 AHOI(I,J)=AV(I,J)
      GO TO 317
   ENTRY EDIP(AV,KI,KJ,IJK,JKL,DDX,DDY)
      DO 315 I=1,KI
         DO 315 J=1,KJ
   315 AHOI(I,J)=0.0
      GO TO 317
   ENTRY EBOI(AV,KI,KJ,IJK,JKL,DDX,DDY)
      DO 316 I=1,KI
         DO 316 J=1,KJ
   316 AHOI(I,J)=0.0
317 M=0
   KXX=KX-1
   KYX=KY-1
   DO 3 I=1,KI
      DO 3 J=1,KJ
   3 TEST(I,J)=AV(I,J)
      DO 4 I=2,KXX
         DO 4 J=2,KYX
   4 IF( (AHOI(I,J),NE.0.0) GO TO 4
      AV(I,J)=((AV(I+1,J)-AV(I-1,J))/(2.0*DDX)+AV(I-1,J)+(AV(I,J+1)-
1AV(I,J-1))/(2.0*DDY)+AV(I,J-1))/2.0
   CONTINUE
      DO 5 I=1,KX
         IF( (AHOI(I,1).GT.0.0) GO TO 312
            AV(I,1)=AV(I,2)
   312 IF( (AHOI(I,KY).GT.0.0) GO TO 5
            AV(I,KY)=AV(I,KY-1)
   5 CONTINUE
      DO 6 J=1,KY
         IF( (AHOI(1,J).GT.0.0) GO TO 313
            AV(1,J)=AV(2,J)
   313 IF( (AHOI(KX,J).GT.0.0) GO TO 6

AV(KY,J) = AV(KX-1,J)

6 CONTINUE
M = M + 1
COV1 = 0.0
COV2 = 0.0
DO 7 I = 1, KX
DO 7 J = 1, KY
IF (AHOI(I,J) .EQ. AV(I,J)) GO TO 7
7 COV1 = COV1 + ((AV(I,J) - TEST(I,J))**2 / AV(I,J)**2)
COV2 = FLOAT(KX*KY)
COV1 = ABS(COV1)
COV1 = SQRT(COV1)
COV1 = COV1 / COV2
IF (COV1 .LT. 0.0005) GO TO 8
IF (M .GT. 25) GO TO 10
GO TO 9

10 WRITE (6,11)
11 FORMAT ('-', 'HAS NOT CONVERGED IN SUBROUTINE AVERAGE')
GO TO 311

8 WRITE (6,310) M, COV1
310 FORMAT ('-', 'CONVERGENCE OBTAINED IN SUBROUTINE AVERAGE IN ITERATION
1 NO. ', I3, ' (', 2X, E10.3)
311 CONTINUE
RETURN
END

SUBROUTINE GBRDSB(AV, KX, KY, IJK, JKL, DDX, DDY)
DIMENSION AV(IJK, JKL), TEST(225, 300), AHOI(225, 300)
DO 13 I = 1, KX
DO 13 J = 1, KY
13 AHOI(I,J) = AV(I,J)
GO TO 323
ENTRY EBRDSB(AV, KX, KY, IJK, JKL, DDX, DDY)
DO 322 I = 1, KX
DO 322 J = 1, KY
AHOI(I,J) = AV(I,J)
IF (AV(I,J) .LT. 0.0) GO TO 324
IF (AV(I,J) * 10.0 .EQ. FLOAT(IPIX(AV(I,J) * 10.0))) GO TO 322
AHOI(I,J) = 0.0
GO TO 322
324 AHOI(I,J) = -1.0
322 CONTINUE
323 M = 0
KXX = KX - 1
KYY = KY - 1
23 DO 14 I = 1, KX
DO 14 J = 1, KY
14 TEST(I,J) = AV(I,J)
DO 15 I = 2, KXX
DO 15 J = 2, KYY
IF (AHOI(I,J) .NE. 0.0) GO TO 15
IF (AHOI(I-1,J) .GE. 0.0) GO TO 16
AV(I,J) = AV(I+1,J)
GO TO 15
16 IF (AHOI(I,J-1) .GE. 0.0) GO TO 17
AV(I,J) = AV(I,J+1)
GO TO 15
17 IF(ABOLD(I+1,J) .GE. 0.0) GO TO 18
   AV(I,J) = AV(I-1,J)
   GO TO 15
18 IF(ABOLD(I,J+1) .GE. 0.0) GO TO 19
   AV(I,J) = AV(I,J-1)
   GO TO 15
19 AV(I,J) = ((AV(I+1,J) - AV(I-1,J)) / (2.0*DDX) + AV(I,J-1) + (AV(I,J+1) - AV(I,J-1)) / (2.0*DDY)) / 2.0
15 CONTINUE
   M = M + 1
   N = 0
   COV1 = 0.0
   COV2 = 0.0
   DO 20 I = 1, XI
   DO 20 J = 1, KY
   IF(AV(I,J) .LT. 0.0 OR. TEST(I,J) .LT. 0.0) GO TO 20
   IF(ABOLD(I,J) .EQ. AV(I,J)) GO TO 20
   N = N + 1
   COV1 = COV1 + ((AV(I,J) - TEST(I,J)) ** 2 / AV(I,J) ** 2)
20 CONTINUE
   COV2 = FLOAT(N)
   COV1 = ABS(COV1)
   COV1 = SQRT(COV1)
   COV1 = COV1 / COV2
   IF(COV1 .LT. 0.0005) GO TO 21
21 WRITE(6,24)
   GO TO 23
24 FORMAT('1-1, \'HAS NOT CONVERGED IN SUBROUTINE GRDISB\'
   GO TO 321
21 WRITE(6,320) M, COV1
320 FORMAT('1-1, \'CONVERGENCE OBTAINED IN SUBROUTINE GRDISB IN ITERATION
   1 NO. 13,5X, \'COV1=\', 2X, E10.3)
321 CONTINUE
   RETURN
   END