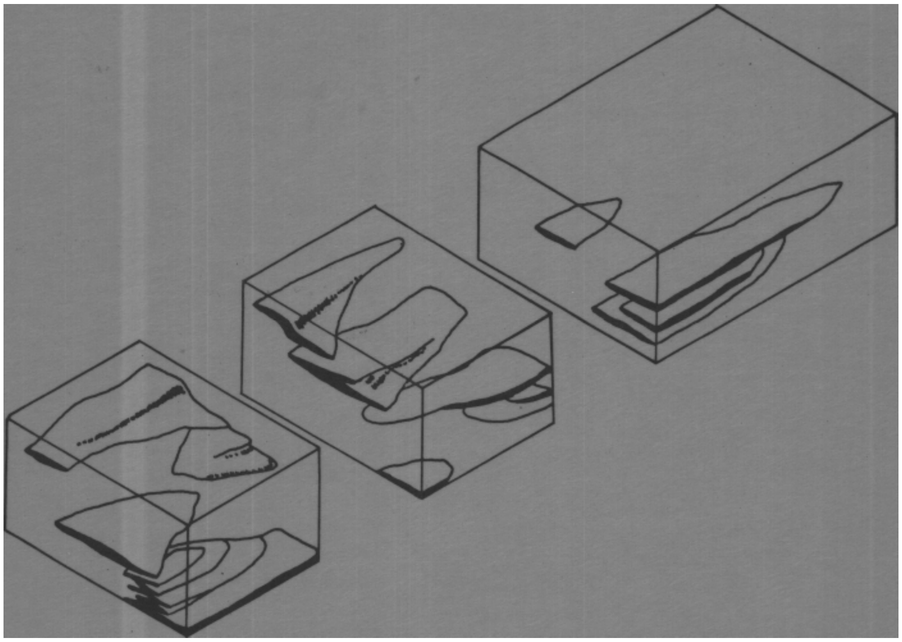
CIRCULAR 118

Selected Papers from 1970 Uranium Symposium at Socorro, New Mexico

1971



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New Mexico State Bureau of Mines and Mineral Resources

Circular 118

SELECTED PAPERS FROM 1970 URANIUM SYMPOSIUM AT SOCORRO, NEW MEXICO

compiled by

Ronald J. Roman
and
Don H. Baker, Jr.
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CONTENTS

Page

HYDROMETALLURGICAL ASPECTS OF MINERAL EXPLORATION

by Dale C. Matthews
The Anaconda Co.

This talk is the viewpoint of a metallurgist in which he suggests that those fundamentally involved with mineral exploration take under consideration. It demands their assuming more responsibility in selectively supplying representative samples of any given mineral deposit. The chief purpose is to provide, for amenability testing, realistic composites that will more closely simulate commercial mill feeds that will produce the greatest achievable economic return.

There is no intent to give you specific examples of second guessing nor recipes guaranteeing success. Nonetheless, certain historical facts are reviewed in general.

It is felt that specialization can be too much of a good thing, particularly in regard to exploration, mining and metallurgy.

My discussions with engineers specializing in these three phases of the mineral industry generally defend their positions by stating that precedent limits their becoming more closely involved with the other two phases. This seems to have been especially the case in my discussions with those specializing in exploration.

It is believed that there are times when too much emphasis is placed just on the potential ore zones and their respective tonnages, and not enough on the variables within and immediately adjacent to the orebody. In other words, more samples rather than necessarily larger samples.

Although Klaproth (clopp'rote) is credited with the discovery of uranium in 1789, Ebelmen (able'men) may be considered the father of uranium hydrometallurgy for his dissolution of uranium minerals and precipitation to what he correctly claimed to be hydrated uranyl hydroxides and/or uranic oxides in the late 1830's.

Ceramic use of uranium salts in coloring and glazing pottery dates back well over 1,000 years and in glass making many hundreds of years. Of course, fissionable application dates back a mere 25 years.

Some find it surprising that uranium minerals were mined, processed and marketed here in the United States even prior to 1900. A survey covering the last 70 years disclosed no record that uranium ever sold for less than 50 cents per pound. Taggart quotes in his 1945 edition handbook that ceramic grades of uranium oxide, yellow and black, were marketable at $1.75 and $2.65 per pound of U_30_8 at the close of 1939 with $900,000.00 worth of uranium being produced in the United States during 1938.

History further informs us that pitchblende was first found in the United States on the dump of the Wood Mine, Central City, Colo., in 1871.

Domestic uranium production amounted to about 2 million pounds between 1913 and 1923, and contained one-half (202 grams) of the world's radium production.

It is generally accepted that "hydrometallurgy" is the treatment of minerals by wet processes, and "exploration" is the act of searching into possible economically minable deposits.

Hydrometallurgical processes do not eliminate pyrometallurgical applications, but quite to the contrary often incorporate heat treatments such as roasting and fusion.

Hydrometallurgy may incorporate such preparational procedures as boring into a mineral deposit for in situ leaching, blasting or ripping for heap leaching, crushing for vat leaching and grinding for agitation leaching.

In regard to the formation of sedimentary orebodies involving erosion, metamorphism, leaching primary minerals, migration, concentration and precipitation, it probably took a few hundred thousand years to come to pass. To be commercial, hydrometallurgy must perform a near parallel in a few years at the most for in situ and heap leachings and in a few hours for agitation leaching.

It will always remain that an ore is worth no more than the sum of its economically recoverable values. Too many monuments to ignorance have been left to posterity simply because mineral deposits were evaluated by assays alone without adequate concern for their amenableness to the existing economic hydrometallurgical processes.

Some deposits may contain minerals uneconomically extractable due to excessive mining, chemical or other involved costs. Still others may contain impurities that may make marketable concentrates and precipitates uneconomical to produce or be weighted down so heavily with surcharges that a profit may not exist.

The gangue constituents may present mechanical problems that could add dollars to the per ton of ore treatment costs, particularly when accompanied with excessive clay.

Not only are there current uranium deposits that contain refractory minerals in combination with clay gangues that make them uneconomical to process, but throughout the world for centuries there has been gold in clay deposits uneconomical to recover, even though their assays per cubic yard are manyfold that of the profitable more amenable gravel deposits.

It could very well be that future uranium ore deposits will be increasingly refractory to hydrometallurgical processing, just as other minable orebodies have become more complex and refractory. For example, the remaining highly amenable Dakota sandstone uranium deposits are apparently exhausted, just as the free-gold placer mines that can be worked by hand at a profit are practically nonexistent.

Before exploration costs become out of line, the amenableness of the prospective ore should be ascertained. The number of shafts and strippings of overburden, considered at the time to be costs of development, has too numerously been charged back to nonproductive exploration when the mineral deposit was found nonamenable.

Extensions of the originally found, explored, developed and mined orebody could be less amenable or even nonamenable to the initially designed hydrometallurgical process. Hence, hydrometallurgical evaluations can never cease until full extremities of the mineral deposit have been explored.

In situ leaching of uranium bearing mineral deposits has had varied degrees of activity over the past 20 years or more. Too many were doomed to failure because they had no chance of success in the first place; that is, the values required roasting to commercially solubilize or were not exposible to the lixiviant due to being encased in gilsonite-type organics or intergrown within the host gangue. Permeability tests too often bypass the mineral values as a result of solution shortcircuiting.

Consequently, exploration must give due consideration to proposed mining methods in regard to selectivity and/or separation of the ores into metallurgical intervals and provide ample representative samples for the metallurgist to blend and composite to simulate potential mill feeds. By all means, samples of possible contaminating adjacent waste rock and debris should be provided for investigation by the metallurgist to determine such ill effects as slowing of flow, settlement and/or filtration rates, having a direct influence on process throughput and ultimate uranium production.

# # #

URANIUM EXPLORATION IN SOUTHWEST TEXAS

by Leonard M. Taucher
Atlantic Richfield Co.

INTRODUCTION

Southwest Texas is rapidly developing into a prominent uranium producing province. Intensive exploration is being carried on along an arcuate band parallel to the Gulf Coast some 50 miles wide and 400 miles long, extending from the Mexican border at the Rio Grande River northeastward to the Trinity River north of Houston (fig. 1).

Attention was first focused on this area in the mid-1950's. A small oil company from San Antonio discovered a radioactive anomaly near Tordilla Hill while making radiometric surveys with an airborne scintillation counter in the search for halos around prospective oil fields. Subsequent AEC airborne work outlined a rather extensive area of anomalous radioactivity, prompting Susquehanna-Western and others to prospect the area near these anomalies. This early work resulted in several small prospects and indicated updip from the Butler-Weddington deposit presently being operated by Susquehanna-Western.

After the initial exploration, there was little activity until late 1967. At this time, the uranium industry was revitalized by surging demand to supply nuclear power plants, and Southwest Texas again began to see significant exploration activity. This activity still appears to be on the increase, and the results have been gratifying for those who have been diligent. Southwest Texas has a very bright future in the uranium industry, and an increasing discovery rate can be expected as the genetics of ore emplacement are more fully understood.

The author acknowledges the contributions of G. L. Fletcher and also thanks him for his critical review of the paper and providing helpful suggestions.

GENERAL GEOLOGY

Stratigraphy . Sediments outcropping within the area of most intense exploration interest include the Whitsett Formation of the Jackson Group, Upper Eocene in age; and Frio and Catahoula Formations of the Geuydan Group, Oligocene in age; the Oakville and Lagarto Formations of the Fleming Group, Miocene in age; and the Goliad Formation or Citronelle Group of Pliocene age (fig. 2). Radioactive anomalies and/or mineralization have been reported in these sediments throughout the area of interest.

The rock groups listed above all exhibit unconformable relationships with one another and exhibit a regional dip toward the Gulf of Mexico. The older Upper Eocene beds dip southeast at 90 feet per mile, and there is a gradual decrease in dip through the Oligocene and Miocene beds with the Pliocene beds dipping 45 feet per mile. Locally, this dip will vary because of faulting as will be illustrated in discussing the various uranium deposits.

Sediments of the oldest sequence of interest, the Whitsett Formation are littoral shallow water deposits interstratified with continental and beach deposits (fig. 4). These sediments consist of tuffaceous sandstones commonly interbedded with lignitic material, bentonitic clay, tuff, and tuffaceous clay. Erosion of highlands to the west along with volcanic ash from igneous activity in northwest Mexico, West Texas, and New Mexico is believed to have provided the granitic and volcanic detritus for these sediments.

Within the Whitsett Formation, the Hasse-Steimann, Stones Switch, and Tordilla sand members are the host for uranium found in this stratigraphic sequence. As is illustrated in fig. 4, the Butler-Weddington and Hobson deposits appear to be associated with fault controlled "back bay" facies of these sands.

The Frio Formation consists of dark-colored clays believed to be of continental origin. Detritus for these sediments was derived from erosion of older sediments to the west and, includes material from the underlying Whitsett Formation. A poorly developed stray sand in the upper part of this formation is considered to be the host sand for the depleted Mabel-New deposit in northwest Live Oak County.

The Catahoula Formation is composed of primarily pyroclastic sediments consisting of light-colored ash, tuff, and tuffaceous clays interbedded with fluviatile sand and clay. An increase in volcanic activity during Oligocene time along the Rocky Mountains to the west is evidenced by the abundance of volcanic material found in this stratigraphic sequence. Petrographic studies show an abnormally high uranium content in volcanic material interbedded with the Catahoula and also the Whitsett Formations. This has led many geologists to speculate the source for uranium found in the Southwest Texas Province is the volcanic material associated with these sediments.

The Oakville Formation is of continental origin. The sediments consist of conglomerates, sandstone, and silt interbedded with clay. The conglomerates, massive sands, and lack of lignitic material suggest rapid deposition from a nearby source for this sedimentary sequence. This influx of sediment was probably a result of rejuvenation of the Balcones fault zone along the Llano uplfft. Reworked fossils, calcareous sediments, volcanic material, and arkosic sands described in this formation were derived from erosion of the older Tertiary, Cretaceous, and Paleozoic sediments. This was augmented by the pre-Cambrian granites and schists from the Llano area.

Sands in the Oakville Formation are the host rock for uranium found in the Ray Point area and along the so-called Oakville trend. This trend has become the most active exploration area in Texas, and the Oakville sands promise to be a major uranium producing sequence in Southwest Texas.

The Goliad Formation of Pliocene age, overlying the Oakville, consists of interbedded sands and clays of continental origin. Material for these sediments was provided by continued erosion of older sediments around the Llano uplift area and to the area west. The basal unit of this formation provides the host sands for uranium found at Palangana Dome. Little is known to date of its regional uranium potential; however, it certainly has similar stratigraphic and structural attributes to the Whitsett and Oakville formations where uranium deposits do exist.

Structure - Within the area of exploration interest are two major flexures or hinge lines; namely, a Cretaceous flexure along the west margin of the trend and the Wilcox flexure through the middle of the trend (fig. 3). As is the case throughout the Gulf Coast, these hinge lines more or less define the shelf break in past geologic time where downdip, the rate of dip and thickening of sedimentary beds, is accentuated. This has provided both uranium and petroleum geologists with an area of interest for exploration.

Associated with these major flexures are complex normal fault systems. These faults are of the gravity flow variety formed by the overloading of sediments basinward and exhibit down-to-the-coast movement. Associated with these faults are small relief faults which are up-to-the-coast. The Fashing fault system is associated with the Cretaceous flexure, and the Mirando-Golke fault zone is associated with the Wilcox flexure (fig. 3). It is believed faults in these systems had considerable bearing on uranium accumulation, as will be illustrated later.

ORE TRENDS

JACKSON - The first ore trend to be reviewed is the Jackson trend located in southwest Karnes County. Pl. I is an aerial view of this trend looking north. The Galen deposit, initially discovered by Susquehanna-Western can be seen in the background. On the southern continuation of the trend is the Butler-Weddington deposit. The drill pattern in the foreground is on Tenneco's Weddington property and is being stripped at the present time. This trend continues southward to the properties held by Continental and Pioneer Nuclear.

Ore along the Jackson trend is found in the Stones Switch and Tordilla sand members of the Whitsett Formation. The block diagram (fig. 4) illustrates the geological environment during deposition of the Stones Switch sand member. The sands were laid down in a deltaic environment with back bay bars developed contemporaneously with slumping or faulting. The Tordilla sand member is considered to be a similar type deposit only higher in the section. The conduit for this material appears to have been the ancestral San Antonio River drainage.

The source of the uranium for Jackson trend deposits is postulated to be the volcanic material comprising the bulk of the Whitsett and Catahoula Formations. Meteoric waters percolating through the volcanic material probably leached uranium out of the sediment and carried it in the ground water until it encountered a reducing environment where it precipitated. This reducing environment in tuffaceous sandstone host rocks of the Whitsett Formation was set up by decay of carbonaceous matter formed in the lagoons. The hydrogen sulfide generated from this decay probably concentrated in the host sands much like hydrocarbon in a stratigraphic trap. These accumulations precipitated uranium from the pregnant ground water and formed ore bodies which are described as roll-front types. Fig. 5 shows the distribution of known uranium deposits associated with this type of geologic environment.

OAKVILLE

The genetic emplacement of ore bodies along the Oakville trend is well illustrated in the paper on the Felder deposit in Live Oak County, Texas (fig. 6). This paper was presented at the 1970 National AIME Convention in Denver by M. L. Klohn and W. R. Pickens. The Felder mineralization is found in point bar and over bank sediments of the Oakville Formation and is described as a roll-type deposit. However, faulting adjacent to the Felder and other deposits along this trend had much to do with the ore emplacement (fig. 7). Minor reversals and local changes in dip developed in fault blocks probably controlled ground water movement and also provided shallow lower pressure traps for hydrogen sulfide gases migrating up the fault planes from deeper hydrocarbon pools. In my opinion, the Felder ore body is not a true roll-type deposit when compared to a typical Wyoming type roll. The so-called barren zone does not exhibit alteration as described in a typical roll, nor does the host sand have sufficient disseminated uranium to enrich the roll front as it migrates downdip. I believe the uranium found in ore deposits along the Oakville trend is a result of surface waters leaching volcanic material from the exposed portions of the Whitsett and Catahoula Formations updip. These waters were subsequently altered into alkaline solutions forming the solvents which carried the uranium into the subsurface. Migration of these pregnant waters into the channel sands of the Oakville brought them in contact with the reduced environment formed by trapped hydrogen sulfide which precipitated the uranium. This precipitation appears to have been more prevalent along the margin of the channels or adjacent to faults where a reduction in permeability promoted accumulation of hydrogen sulfide. Fluctuations in the ground water level in the fault blocks probably kept the uranium moving and promoted downdip concentration of uranium.

To illustrate ore emplacement along the Oakville trend, let us look at a schematic diagram of a portion of the Clay West deposit (fig. 8). The simple block diagram shows one of the major down-to-the-coast faults in the Mirando-Golke fault zone referred to earlier and an up-to-the-coast relief fault associated with the larger down-to-the-coast fault. The shaded section represents a sand body in the Oakville. Slumping in the down-thrown block along the major down-to-the-coast fault would form a structure capable of trapping hydrocarbons. Continued movement along this fault would develop the up-to-the-coast relief fault. Drag along this fault formed a so-called microstructure,, a structure with 10 to 20 feet of relief in the up-thrown block. Subsequent movement on the up-to-the-coast relief fault enabled hydrocarbons to migrate from the original trap into the upper sand producing a long narrow reducing zone along the fault. Uranium from percolating uranium bearing waters, discussed above, apparently precipitated upon contact with this reducing environment. Generally speaking, uranium concentration at Clay West and other Oakville deposits along this trend may be explained by this mechanism. There are many geologic variables which tend to mask basic ore controls, and it will take much more detailed knowledge to fully evaluate these features.

EXPLORATION METHODS

The geologist involved in uranium exploration in an area such as Southwest Texas is indeed fortunate. This area is unique in that the present uranium exploration trend roughly coincides with the petroleum Wilcox exploration trend. Exploration and development oil wells drilled along this trend give the geologist access to a wealth of subsurface data for working out potential shallow host sand depositional trends. Exploration methods employed in Southwest Texas (in addition to subsurface study) include gamma ray logging of wildcat, development and workover wells, water sampling, radon sampling, airborne radiometrics, photogeology, etc. Of course, the drill is also used for exploration. In addition, an inexpensive means of exploration used by many oil companies is to probe seismic shot holes throughout the area of interest. The drill, of course, is the final answer; and in Southwest Texas where drilling is inexpensive, it is the most widely used exploration tool.

CONCLUSION

Results of exploration and development drilling in Southwest Texas and the high level of current activity indicate the potential of this area becoming a major uranium producing province.

The method of entrapment of uranium deposits in Southwest Texas is not fully understood. It is apparent that many accumulations are fault controlled, whereas others appear to be deposited in channel sands. As far as depositional mechanism is concerned, hydrogen sulfide probably played a leading role where it was present in small structures and along faults. Reducing environments created in coaly sedimentary sequence undoubtedly promoted precipitation of uranium, and unquestionably, other parameters also entered the picture.

From the above statements it is apparent there is a great deal to be learned about Southwest Texas uranium deposits. As these deposits become more thoroughly understood, additional reserves will be found, and Southwest Texas should take its place beside New Mexico and Wyoming as a major producing region.

Figures and plates follow

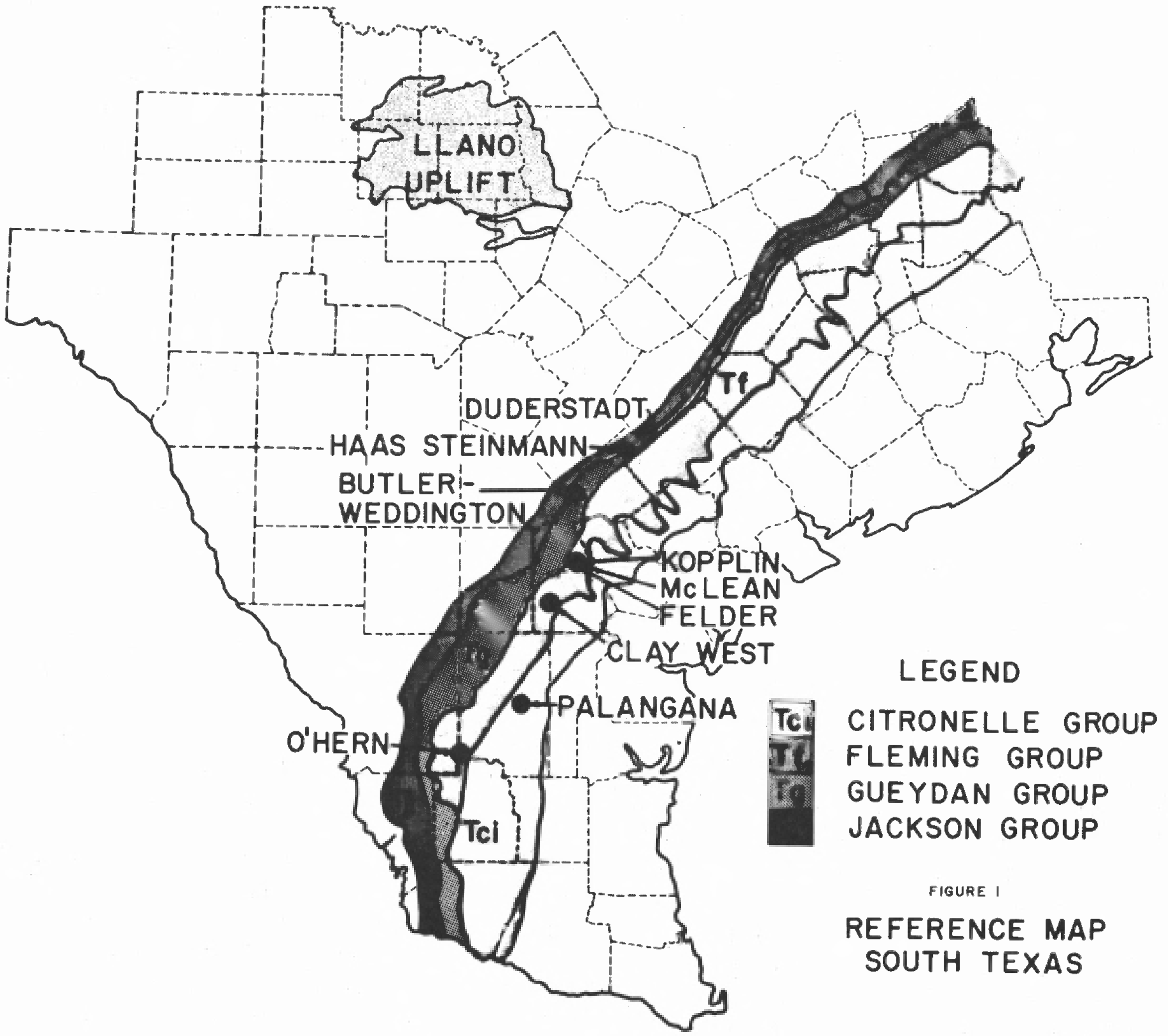
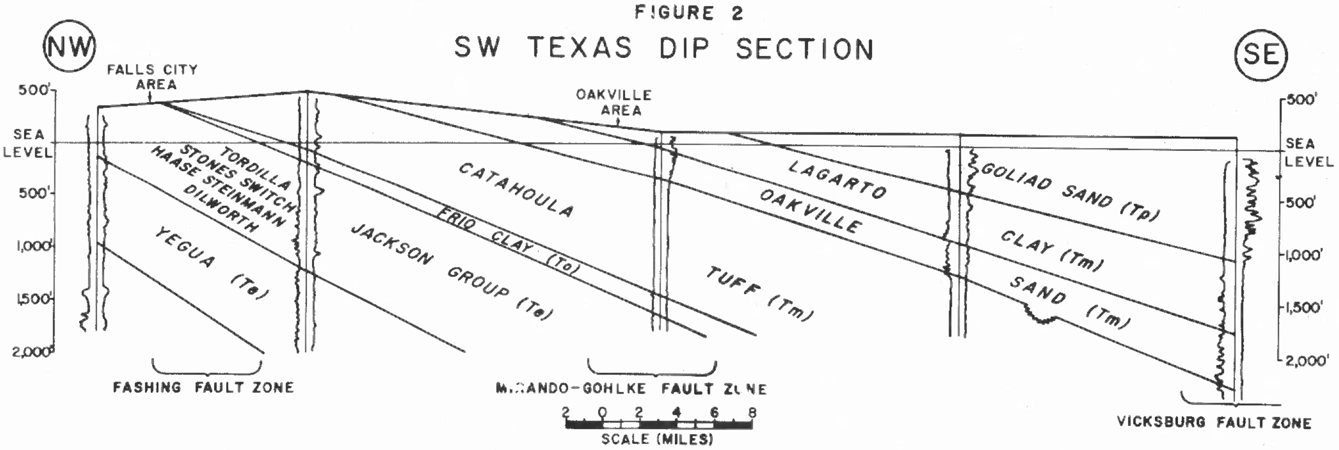


FIGURE 1

REFERENCE MAP SOUTH TEXAS

FIGURE 2

SW TEXAS DIP SECTION



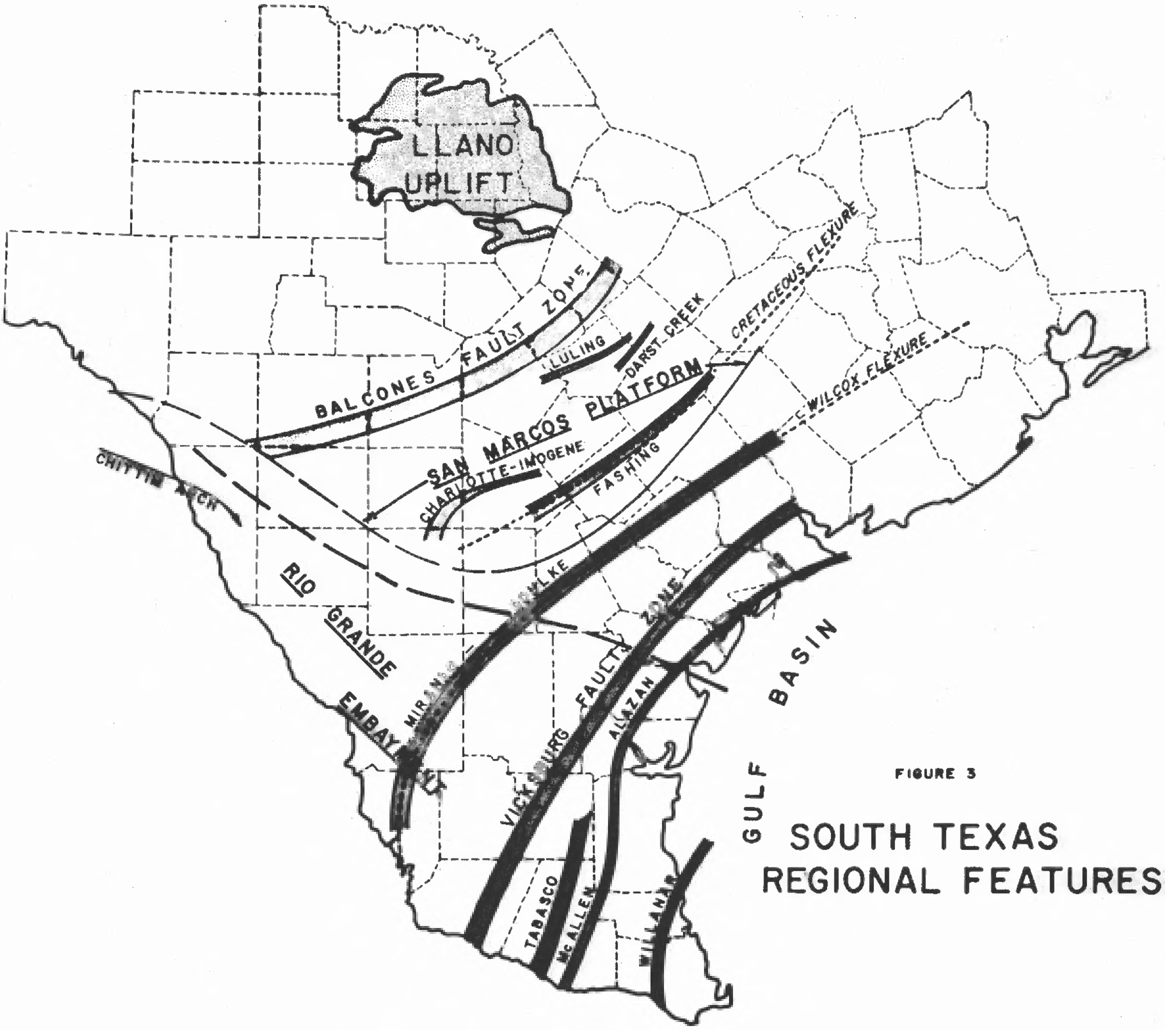
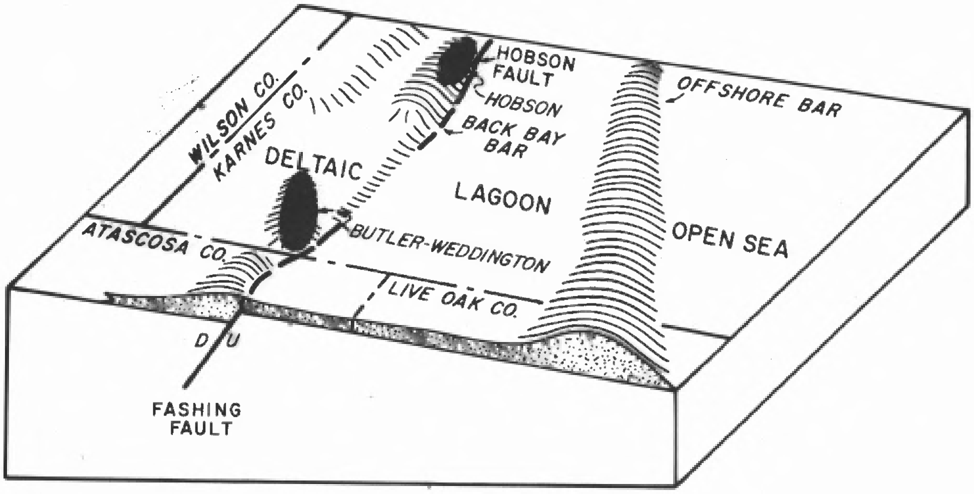


FIGURE 3

SOUTH TEXAS REGIONAL FEATURES



BLOCK DIAGRAM
STONES SWITCH DEPOSITION

FIGURE 4

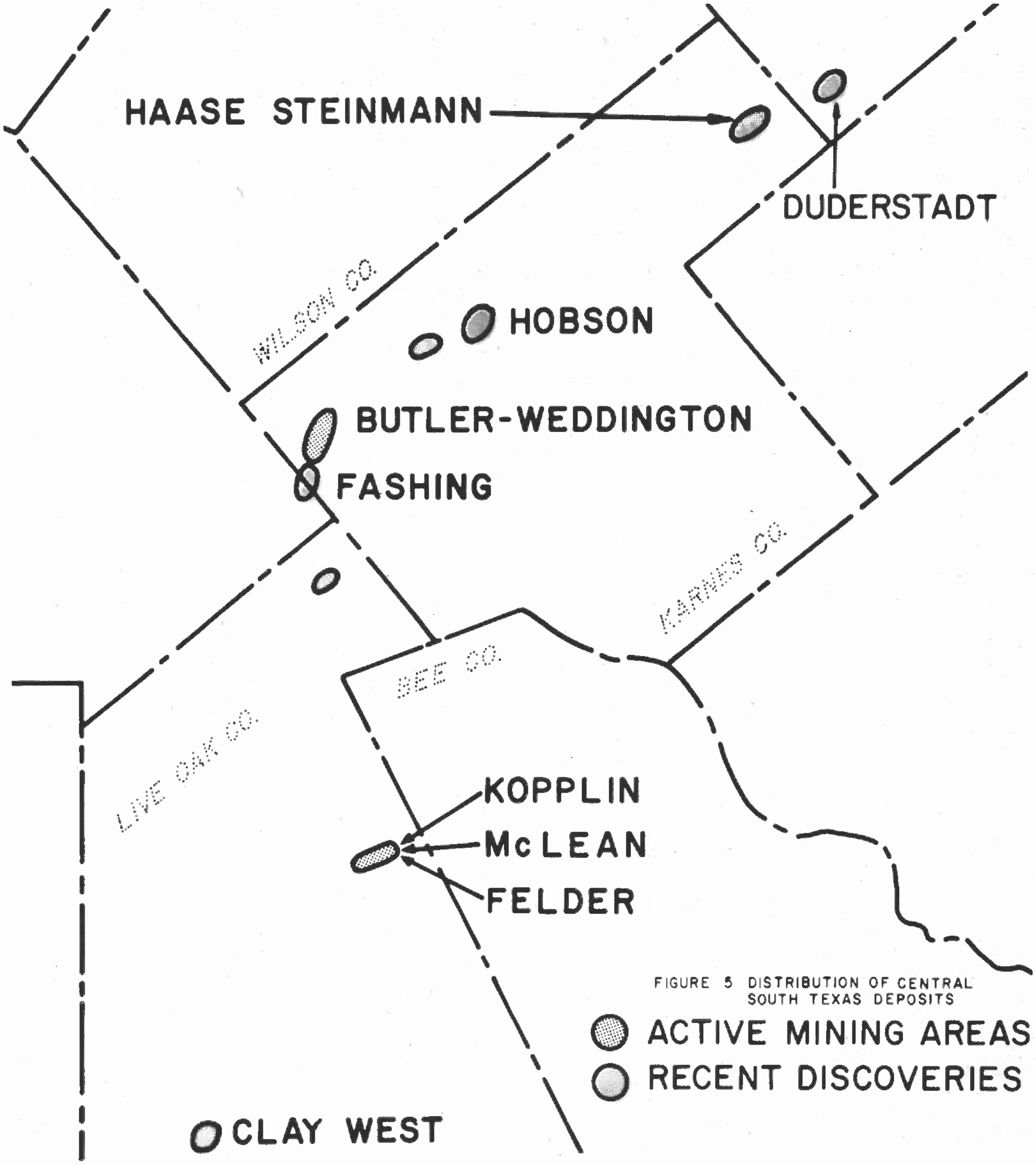


FIGURE 5 DISTRIBUTION OF CENTRAL SOUTH TEXAS DEPOSITS

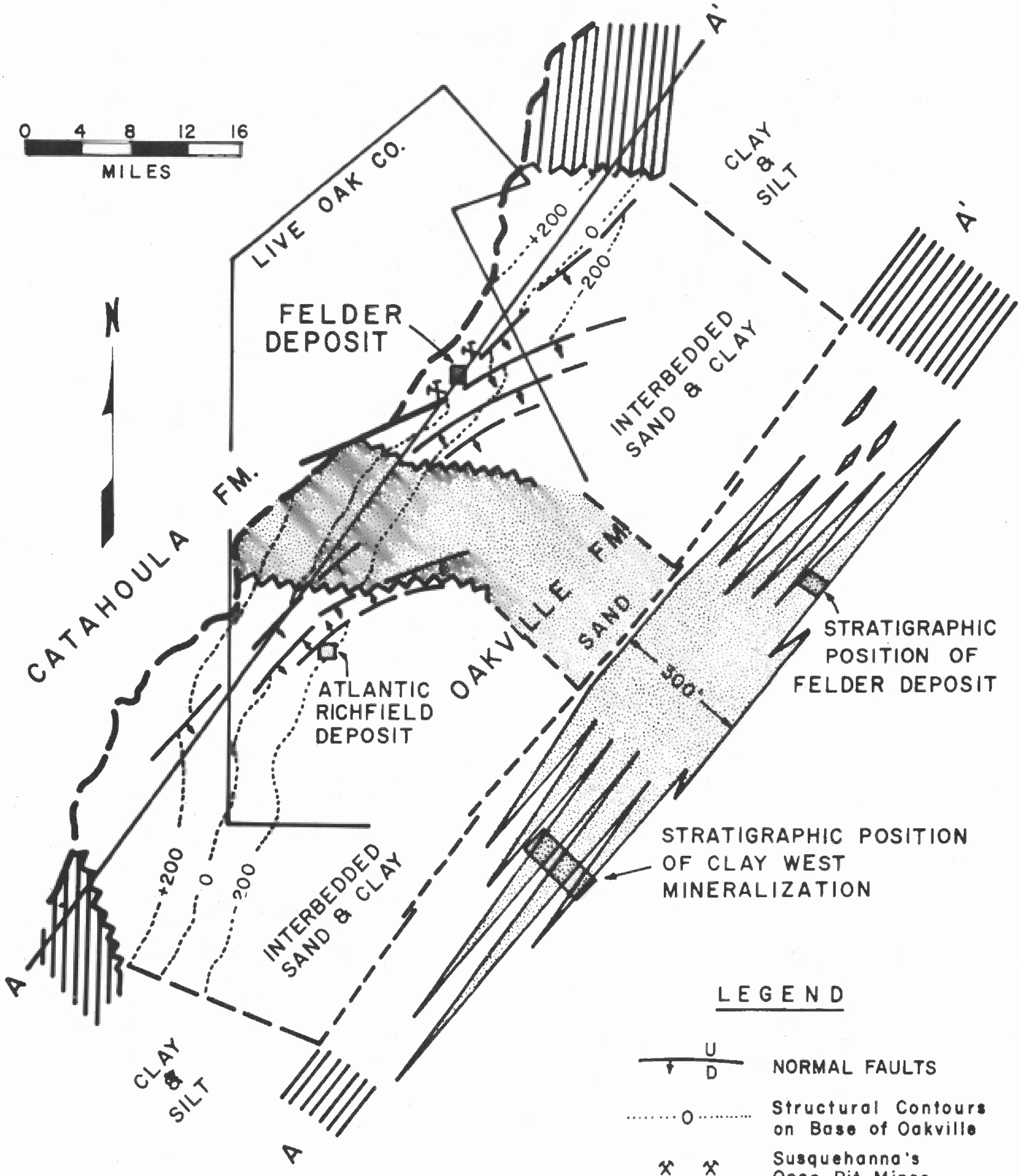


FIGURE 6 Generalized Geologic Map and Diagramatic cross-section of the Ore-Bearing Alluvial System Centered in Live Oak County, Tex. after M.L. Klohn and W.R. Pickens.

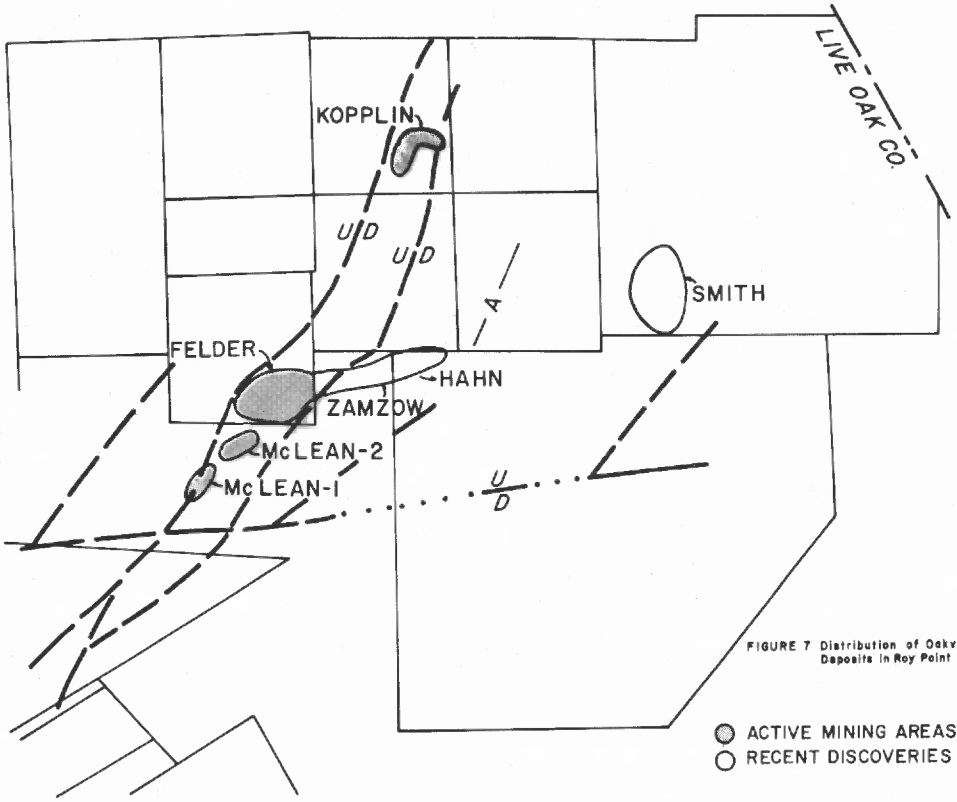


FIGURE 7 Distribution of Oakville Deposits in Ray Point Area.

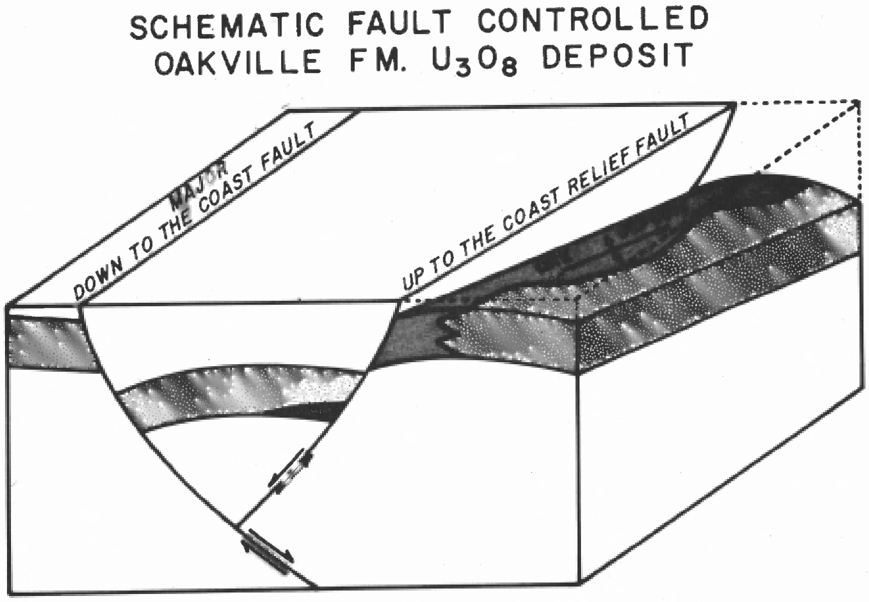


FIGURE 8 GENERALIZED BLOCK DIAGRAM OF FAULT RELATED CLAY WEST MINERALIZATION.

PLATE I. Aerial view of Jackson Trend.

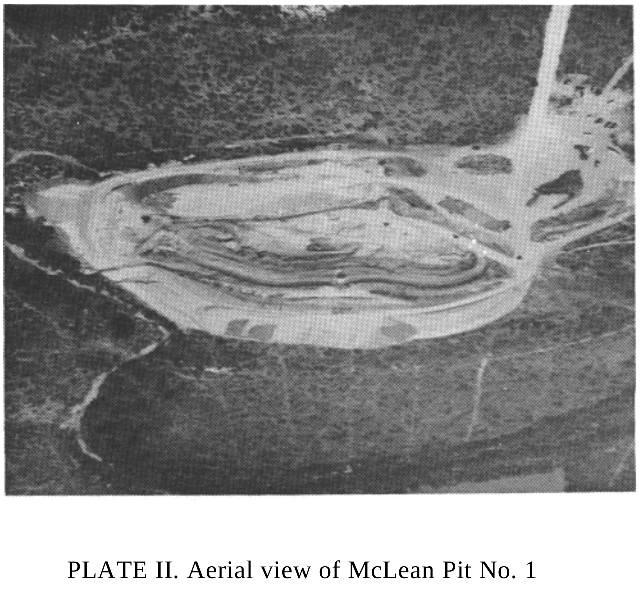


PLATE II. Aerial view of McLean Pit No. 1

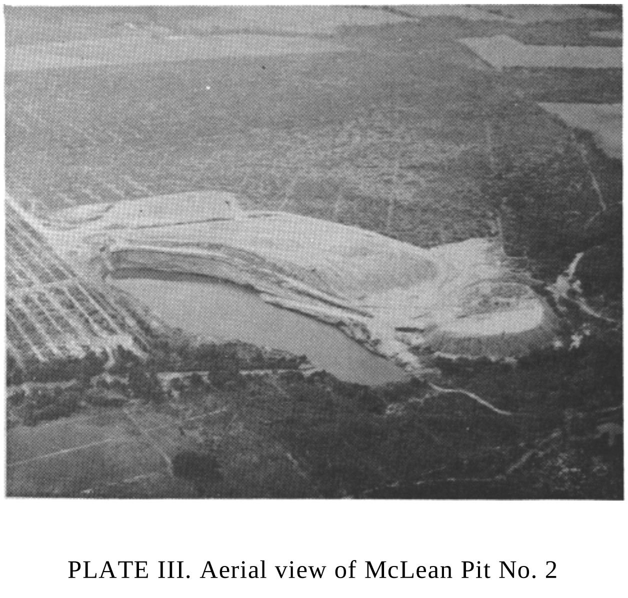


PLATE III. Aerial view of McLean Pit No. 2

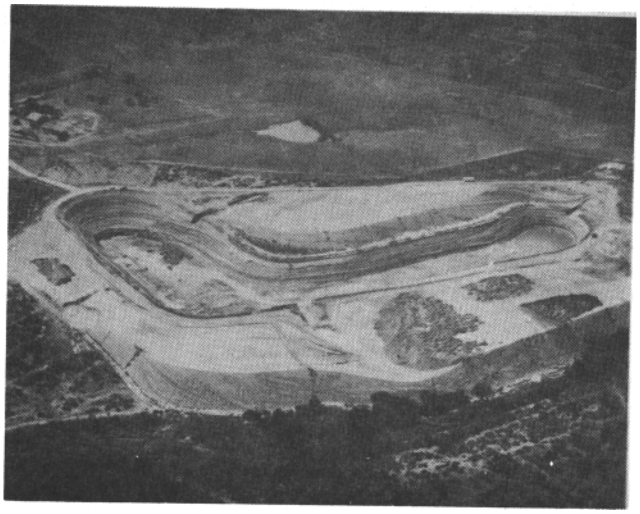


PLATE IV. Aerial view of Kopplin Pit.

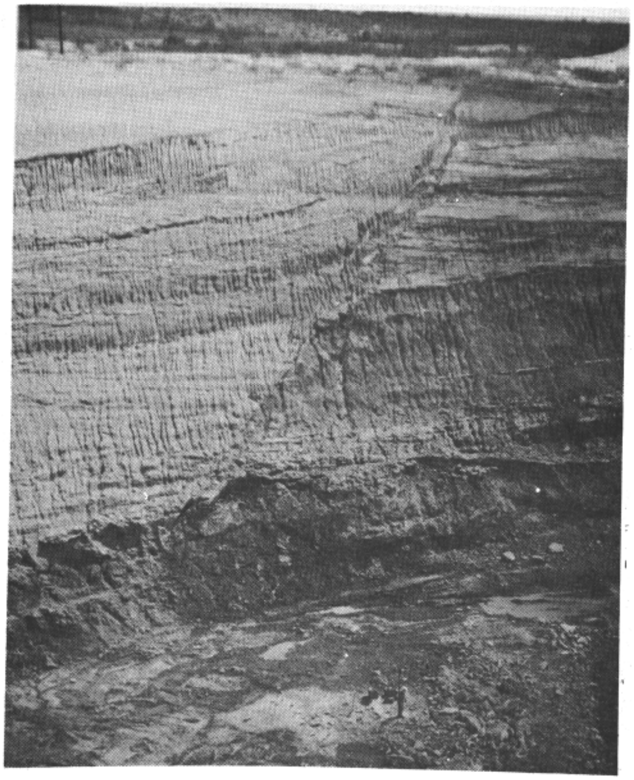


PLATE V. Photograph of fault controlling Kopplin Deposit.

EXPLORATION GEOLOGY METHODS IN THE GRANTS MINERAL BELT

by David C. Fitch
Ranchers Exploration and Development Co.

This paper summarizes uranium exploration methods currently being used in the Grants mineral belt, and is intended for those of you not familiar with these methods. The following remarks will be directed toward exploration for ore deposits in sandstone in the Morrison Formation. Ore deposits that occur in other rocks, mainly the Todilto Limestone and Dakota Sandstone will not be discussed.

The Grants mineral belt extends from several miles east of Laguna to the Gallup area (fig. 1) and includes the deposits in the Laguna, Ambrosia Lake, Smith Lake, and Church Rock- districts. Mines in the Grants mineral belt have yielded most of New Mexico's uranium production which totals more than 158 million pounds of U_30_8 to January 1, 1970. The Atomic Energy Commission reports New Mexico uranium reserves of 34.9 million tons at 0.25% U308, containing a total of 172 million pounds of U308 as of January 1, 1970. Nearly all of these reserves, which represent about 42% of the nation's total reserves reported by the A.E.C., are located in the Grants mineral belt. From 1950 to the present, more than 95% of the total tonnage of uranium ore produced in northwestern New Mexico was from fluvial sandstone in the Jurassic Morrison Formation. Similarly, most of the uranium reserves are in the Morrison sandstones. Other, less important producing formations are the Todilto Limestone and Entrada Sandstone of Jurassic age, and the Dakota Sandstone of Cretaceous age.

The Morrison Formation was deposited in a continental environment and in the Grants mineral belt consists of three members (fig. 2). These are, in ascending order, the Recapture Member which contains several minor orebodies, the Westwater Canyon Member which contains the largest orebodies in the Ambrosia Lake, Smith Lake, and Church Rock districts, and the Brtishy Basin Member which includes the Jackpile Sandstone, host rock for the large orebodies in the Laguna district.

The Recapture Member consists mostly of alternating beds of grayish-red siltstone, claystone, and thin sandstone, however in the Gallup area the Recapture contains large amounts of sandstone and conglomerate. The Recapture ranges in thickness from less than 50 feet in the Laguna district to more than 250 feet in the Gallup area.

The Westwater Canyon Member consists of gray, light-yellow brown, and reddish-brown, fine-to coarse-grained, arkosic sandstone with interbeds of greenish-gray and reddish-gray claystone. The Westwater thickens northward from 0 to a maximum of about 300 feet. Thickness of the Westwater is about 50 to 100 feet in the Jackpile area, about 150 to 250 feet in the ore-bearing Ambrosia Lake area, and about 220 feet in the Church Rock area.

The Brushy Basin Member consists mostly of greenish-gray claystone and ranges up to 300 feet thick. The Brushy Basin Member contains local channel sandstone beds, including the Jackpile Sandstone which reaches a maximum thickness of 220 feet.

Orebodies in the Grants mineral belt range in size from a few to several million tons. They are irregular in shape, are roughly tabular and elongate, and range from thin pods a few feet in width and length, to bodies several tens of feet thick, several hundred feet wide, and several thousand feet long (figs. 3, 4, and 5). The orebodies are roughly parallel to the enclosing rock, but in many places form rolls that cut across bedding. Many of the deposits occur in more than one layer (fig. 6) and most occur in clusters that form district trends as in the Ambrosia Lake district (fig. 7). Individual orebodies in the Ambrosia Lake area are commonly elongate parallel to sedimentary depositional trends. Post-fault ore, also termed redistributed or stack ore, is related to faults, joints and oxidation features. Most workers state that postfault ore is nearly always in close spatial association with prefault or primary ore. The larger primary ore deposits tend to occur in, but are not restricted to, the areas containing thickest sandstones. The Jackpile and Paguate orebodies for example, occur near the axis of a large Jackpile Sandstone channel that is 100 to 220 feet thick (fig. 8).

Primary ore in Morrison sandstones in the Grants mineral belt consists mostly of extremely fine grained coffinite contained in dark-gray or brown carbonaceous material that coats sand grains and impregnates the sandstone. The abundance of organic carbon correlates well with the abundance of uranium (Moench and Schlee, 1967, p. 75, and Squyres, p. 111). Abundant carbonized wood is present in many of the deposits and commonly contains large concentrations of uranium. Pyrite is commonly more abundant in and near ore than in barren ground some distance from ore, however large areas of barren rock contain detectable amounts of pyrite.

The host rock in the vicinity of primary ore is bleached to a light color ranging from white to medium gray. Claystone galls in and near ore and claystone beds adjacent to the bleached host rock are commonly bleached greenish-gray. The claystone galls in many places near ore consist of a red core and a bleached rim.

These geologic relationships have been developed into ore guides early in exploration in the Colorado Plateau.

The ore guides currently in general use in the Grants mineral belt for Morrison Sandstone ore deposits consist of:

1. Anomalous mineralization (0.01 - 0.03 percent $_eU_3O_8$ in sandstone is generally felt to be encouraging) .
2. Color of host rock (gray or bleached rock is considered favorable, buff-colored, limonitic rock is considered by several to be oxidized favorable, reddish, hematitic rocks are considered unfavorable except near primary ore deposits.
3. Position of area with respect to mineralized trends.
4. Presence of carbonaceous material and pyrite.
5. Bleaching of mudstone at base of host rock.
6. Relative thickness of host rock.
7. Stratigraphic environment of host rock.

Current exploration practices involve using the above criteria to outline favorable areas by drill data, and to a lesser extent, outcrop studies. Early exploration in the Grants mineral belt was concentrated near the outcrops, but has moved into deeper areas following intense exploration of outcrops and shallow areas.

Most of the present exploration is by drilling in several stages. During the first stage, holes are drilled• on a wide spacing ranging from about ih mile to several miles to obtain geologic information. The information acquired during this stage is used to designate favorable areas that merit further drilling. In the second stage, holes are drilled on a closer spacing, perhaps as many as 5 to 10 holes per section of land in the more favorable areas. It is hoped that significant mineralization is encountered during the second stage. In the third stage, holes are drilled on a close spacing to extend mineralization intersected during previous drilling and to "block out" ore. Drill hole spacing in the third stage is geared to drill depths, continuity and grade of ore, and approximate size of the orebodies. Small Brushy Basin Member orebodies at depths of 80-120 feet have been drilled on 12$_1$%-foot spacings, while large, continuous Westwater Canyon Member orebodies at depths of greater than 2,000 feet have been drilled on 200 to 500-foot spacings. Large orebodies at 650-900 feet are often drilled on a 50-200-foot spacing. At depths of 1,400 to 1,500 feet the holes are commonly spaced at 75 to 200 feet.

The geologic setting of an area, and a concept of the origin of sandstone uranium deposits often influences the over-all exploration program and may be useful to rank broad favorability of areas during the first and second stages of drilling. Because the first requirement for favorability is at least the presence of a host rock, channel sandstones that pinch out laterally narrow the target somewhat. However, narrow and thin channel sandstones often contain only small orebodies. The Jackpile Sandstone is an example of a large channel 15 miles wide and over 35 miles long that provides a finite target (fig. 8). The Westwater Canyon Member, however, is tabular and occurs throughout the Grants mineral belt. The Westwater Sandstones are favorable-looking by color and lithology over a large part of the belt and prove to be an enormous target by specific favorability criteria alone. The main Westwater Member orebodies in the Ambrosia Lake district occur in a zone of relatively thicker sediments (figs. 7 and 9). The position of an area with respect to the regional outline of the mineral belt is another concept used to evaluate broad favorability.

Because of its exploration significance, a brief outline is given of the origin of the Morrison Sandstone deposits in the Grants mineral belt. There are many theories and much data has been gathered over the past 20 years regarding the origin of sandstone-type uranium deposits and the subject is still controversial. However, there appears to be some agreement that the deposits were formed by dilute, uraniferous ground-water solutions moving through or into the host sandstones to zones of precipitation either during or relatively soon after deposition of the host sediments. Specific data supporting a pre-Dakota age for the deposits have been reported by several workers (Nash and Kerr, 1966, p. 1283-1290; Squyres, 1970, p. 135-143). Theories of the source, transportation, and precipitation of the uranium, associated elements, and carbonaceous material are in controversy.

Current theories of the source of uranium propose that the uranium was (1) derived from hydrothermal solutions, (2) leached from volcanic constituents of the sedimentary rock during or following sedimentation, or (3) leached from granitic terrain or the sediment derived from granite (arkosic .sandstones). It is generally agreed that the carbonaceous material associated with ore is humate, derived from humic acids which are formed during the decay process of plants.

Current literature tends to support the hypothesis that the uranium was transported in very low concentrations in weakly alkaline, slightly reducing solutions. Some feel that the uranyl ions were carried as the carbonate or sulfate, or as a humic acid complex. Many geologists feel that the humic solutions bleached the rock through which they passed.

Several theories state that the uranium was precipitated in an area having an acidic, reducing environment. The precipitating environment is believed to be caused by (1) vegetal and humate accumulations along sedimentary stream channels, or (2) a zone of stagnation in the ground-water flow caused by impedance of basin-ward flowing solutions (this zone being related to stratigraphic features and Jurassic tectonic features), or (3) the paleo-ground water table.

The most common method of evaluating drill hole information is by geophysical logging and lithologic logging of drill cuttings. Many companies have studied or are studying specialized techniques to obtain drill hole information. Among these techniques are trace element determination of drill samples, uranium determination of formation water, and down-the-hole radon determination. These techniques are not in general use.

Nearly all of the drilling is by truck-mounted rotary rigs capable of drilling 4-3/4 or 5-inch diameter holes to depths ranging from 200 to 3,000+ feet (fig. 10). The upper part of a hole is drilled by air as far as possible and the remainder of the hole is drilled by water and mud. A tri-cone rock bit is used for drilling. Occasionally certain zones are cored with a diamond core bit to obtain chemical assay samples or stratigraphic information. Generally samples are caught at 5-foot intervals, washed and either placed in sample bags or placed on the ground in rows of 100 feet of samples. Considerable experience is required by the drillers to obtain representative samples. The lithology of samples is logged by a geologist using a hand lens or binocular microscope. The data recorded (fig. 11) include rock type, color, and grain size. Special attention is given to determine if carbonaceous material or pyrite are present in the Morrison Formation. The presence and amounts of hematite and limonite are given special attention, but are also indicated by the rock color. Notes are generally made of accessory minerals. However detailed notes are not usually made of the percentage of the common minerals.

After a drill hole is completed it is logged by a company-owned or logging service company probe truck. The geophysical log generally in use consists of gamma-ray, resistivity, and self-potential curves plotted by depth (fig. 12). The resistivity and S P curves provide bed boundaries and are mainly used for correlation. The resistivity curve, calibrated in ohms, is largely a measure of the formation water resistivity. Generally sandstones show a deflection to the right, or a greater resistivity than claystones and shales. The spontaneous, or self-potential curve indicates the natural potential differences in millivolts, between an electrode at the surface and an electrode in the drilling fluid that is pulled up past different beds. This potential depends on a number of factors, but generally indicates the permeable zones, or sandstones, as a deflection left from the shale base line.

The gamma-ray log is used to interpret the amount of equivalent U_30_8 in a zone by measuring the gamma radiation of radioactive uranium decay products. The instruments in common use can delineate anomalous mineralization down to about 10 or 15 parts per million ${}_eU_3O_8$. Uranium is therefore easily detected by inexpensive means in contrast to other metals. Ore values derived by gamma-ray log interpretation are relatively accurate in the Grants mineral belt. The exact method of interpretation varies among mining companies in the area. The method described by Linton (1963, p. 223-233) is relatively accurate for interpretation of Century Geophysical logs, and yields results within about 5 - 9 percent of A.E.C. calculations. For thick ore zones (5 ft. or more), the procedure consists of determining ore boundaries to the nearest foot, at a point about halfway between background and peak of the gamma-ray curve. Readings of the counts per second (CPS) are made at the boundaries and at each 1-foot interval within the ore zone. These readings are totaled and divided by the number of readings, resulting in an average cps for the curve. This average cps value is then corrected for instrument lag (dead time) by a conversion chart, and the corrected value divided by a constant to obtain grade in percent ${}_eU_3O_8$. Thin ore zones (4% ft. and less) are figured similarly, however, boundaries and readings are taken at each half-foot interval and the total uncorrected cps for the zone is divided by one less than the number of readings to account for tail effect.

Several companies are using digital print-outs of the gamma intensity, and some are using punch-tapes, made in the field, that speeds up the process of computer analysis of ore reserves. Ore holes and adjacent holes are generally surveyed for drift by a probe that determines drill hole inclination and azimuth at 100-foot intervals (fig. 13), The data are plotted to show the map position of the ore intercept, and the elevation of the ore zone is calculated. Drill holes 1,000 to 1,500 feet deep generally drift less than 30 or 70 feet, but it is not uncommon for holes 2,500 feet deep to drift 100 to 400 feet or more. Other logging techniques such as spectral radiation analysis, temperature logs, and caliper logs are in less common usage.

The cost of exploration drilling programs in the Grants mineral belt varies somewhat by area, but a discussion of typical costs may serve as a guideline. The major cost items are direct drilling and related costs such as water purchase and moving charges, geophysical logging costs, drill roads and sites, and land acquisition costs.

Most of the drilling is by contract drillers on a fixed price-per-foot basis with provision for abnormal drilling conditions and moving between widely spaced locations. Some of the drill rigs operate on an hourly rate basis plus drill materials cost to the mining company. Most rigs operate 24 hours per day. The hourly rate costs are often similar to the price-per-foot cost, but are not always predictable. A summary of typical price-per-foot costs is shown in (fig. 14). These costs apply to normal drilling conditions, and if lost circulation is encountered, the driller is paid an hourly rate generally ranging from $25 to $35 per hour, plus circulation materials until either the hole is completed, circulation is regained, or the hole is abandoned. Lost circulation charges or difficult drilling conditions can significantly increase the cost of a drill hole, particularly at greater depths. Rig standby rates, ranging from about $15 to $35 per hour, generally go into effect if the rig is requested to remain at a location for the convenience of the mining company, except for a reasonable time allowance to log a hole. Standby costs can usually be avoided by planning and are seldom incurred.

The cost of building drill sites varies greatly, depending on the topography. Easily accessible areas with drill depths less than 600 feet may require no expense, yet sites in rough terrain may require expensive road building and large drill pits. Most of the site preparation is done by independent contractors by hourly rates. Equipment rental rates (with operator) range from $9 to $12 per hour for a small backhoe, to $18 to $27 per hour for equipment capable of building roads. These rates are also generally charged to move the equipment into the area. The range of cost per location shown in fig. 14 applies to relatively accessible areas and drill depths of 1,000 to 2,600 feet.

Commercial logging services at the present time are available at a typical cost of 10 cents per foot plus $10 per setup. Typical mileage charges from a base to the drill hole and return are 25 to 30 cents per mile in excess of 50 miles. Drill hole drift survey costs range from 10 to 15 cents per foot. Several companies own and operate their own logging trucks.

Land acquisition costs vary as to the status of the available land. Mineral ownership in the Grants mineral belt falls into 4 general categories: (1) Federal land upon which claims may be staked, (2) Private or fee land, including Railroad land, and land grants, (3) State land, and (4) Indian alloted or tribal land. The cost of staking claims ranges from a low of about 50 cents per acre to about $2.50 per acre or much more in rough, tree covered country. Terms of acquisition of fee land, Railroad land, and State land are generally negotiable with the owners, and costs vary according to the nature of the land and other factors. The Santa Fe Pacific Railroad, the Bureau of Indian Affairs, and the State offer land for competitive bonus bid from time to time. Bids may reach as high as the winning bid of $302.78 per acre for a railroad section in the Ambrosia Lake district, September 1968.

In conclusion, the future potential of the Grants mineral belt to contain large amounts of uranium ore is considered fair to excellent by many geologists. In a recent U.S. Geol. Survey Prof. Paper, Hilpert stated (1969, p. 1) that undiscovered and potential uranium reserves in northwestern New Mexico probably are several times production plus reserves and may be as great as 200 million tons at 0.25 percent U_3O_8 (1 billion pounds U_3O_8) expected to be mostly in the Morrison Formation in the Grants mineral belt. There are, of course, economic limits to these estimates and a large part of the estimated reserves may be expected to occur at depths of 2,500 feet and much greater, and in areas of difficult drilling such as near Mt. Taylor. However, even by conservative estimates the future potential of the Grants mineral belt appears very good.

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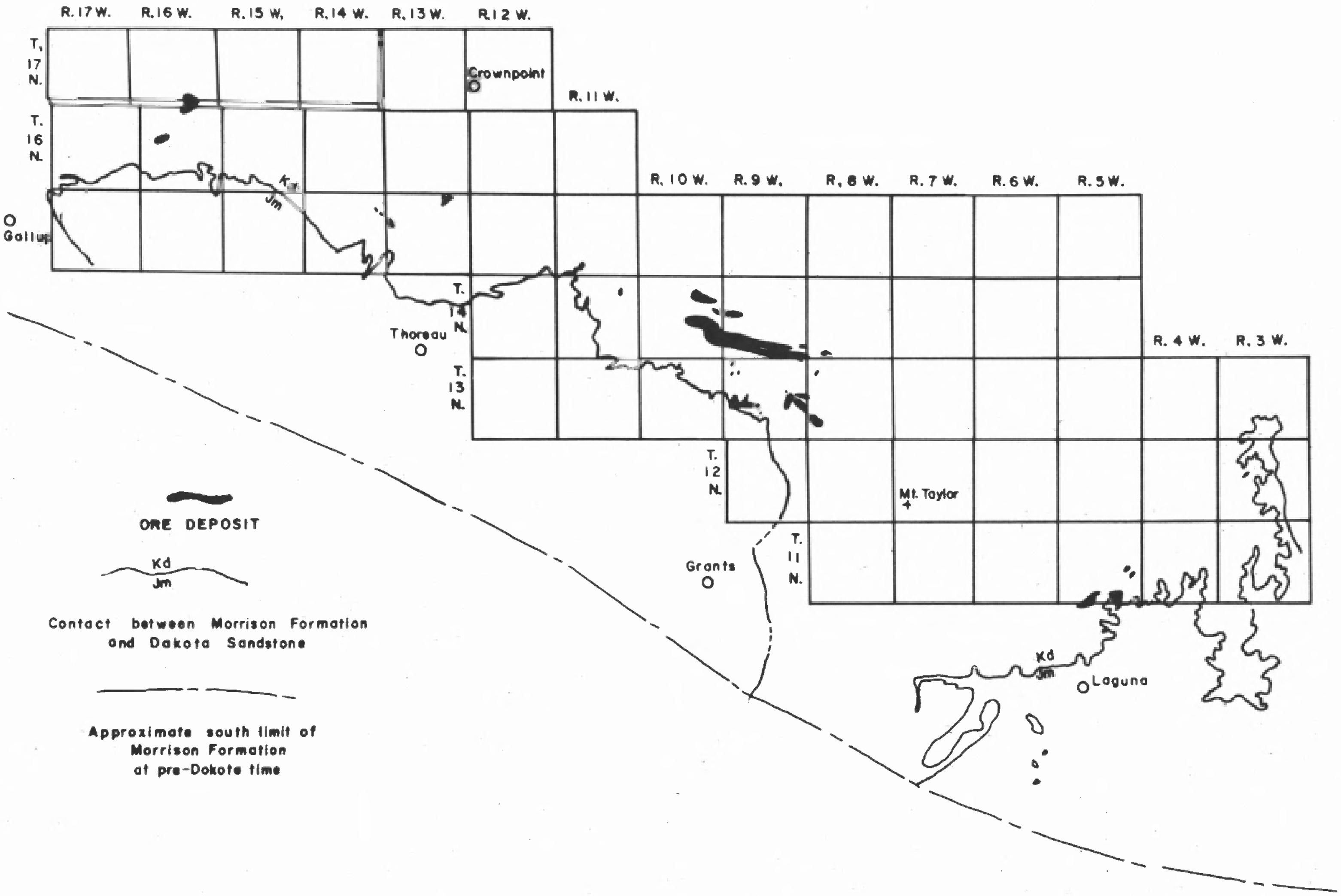
Figures follow



GRANTS MINERAL BELT
Figure 1.

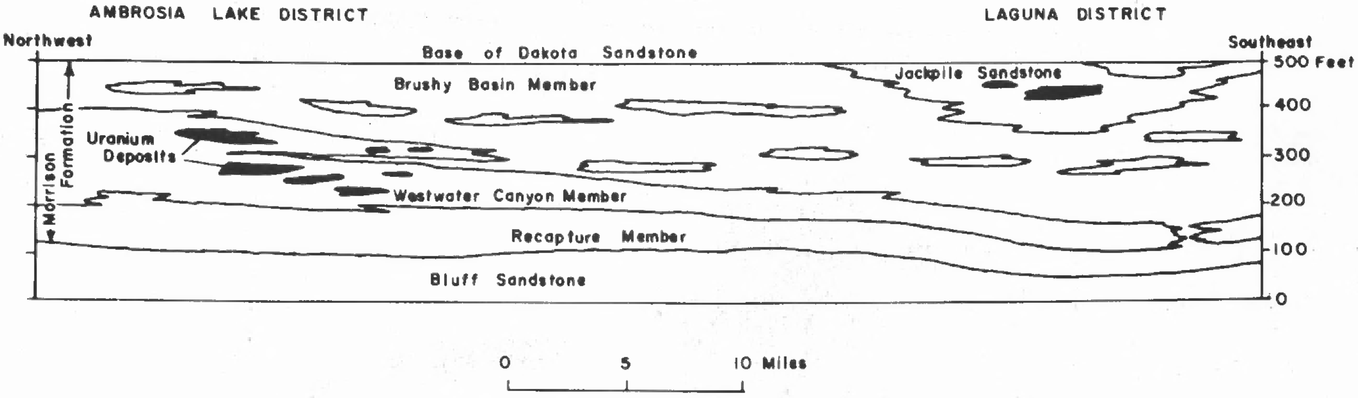


Figure 2. - Generalized geologic section showing the stratigraphic relations of the Morrison Formation between Ambrosia Lake and Laguna. From L.S..Hilpert (1963, p. 16).

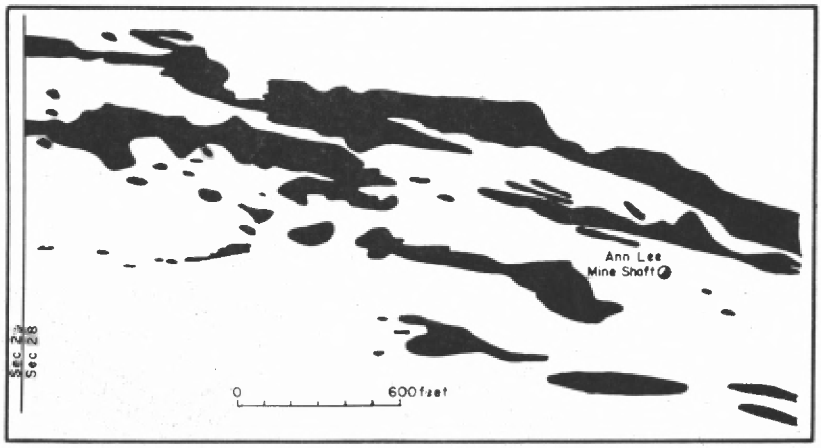


Figure 3. - Map of the west side Ann Lee ore deposit in Sec. 28, T. 14 N., R. 9 W. Ambrosia Lake district. Modified from J.B. Squyres (1963, p. 95).

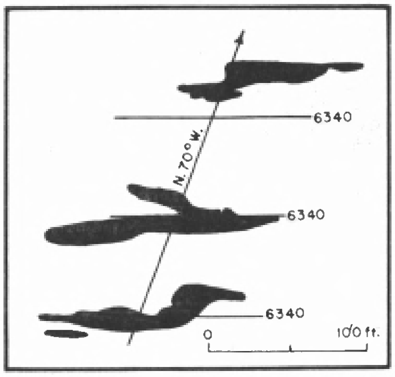


Figure 4. - Three sections across the main Ann Lee orebody representing a length of about 800 feet along ore trend. Modified from J.B. Squyres (1963, p. 93).

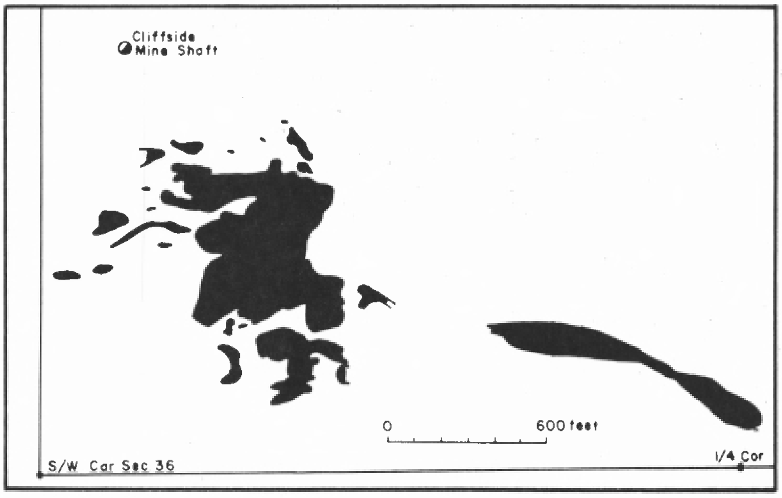


Figure 5. - Map of Cliffside ore deposit in Sec. 36, T. 14 N, R. 9 W, Ambrosia Lake district. Modified from D.S. Clark and S.R. Havenstrite (1963, p. 109).

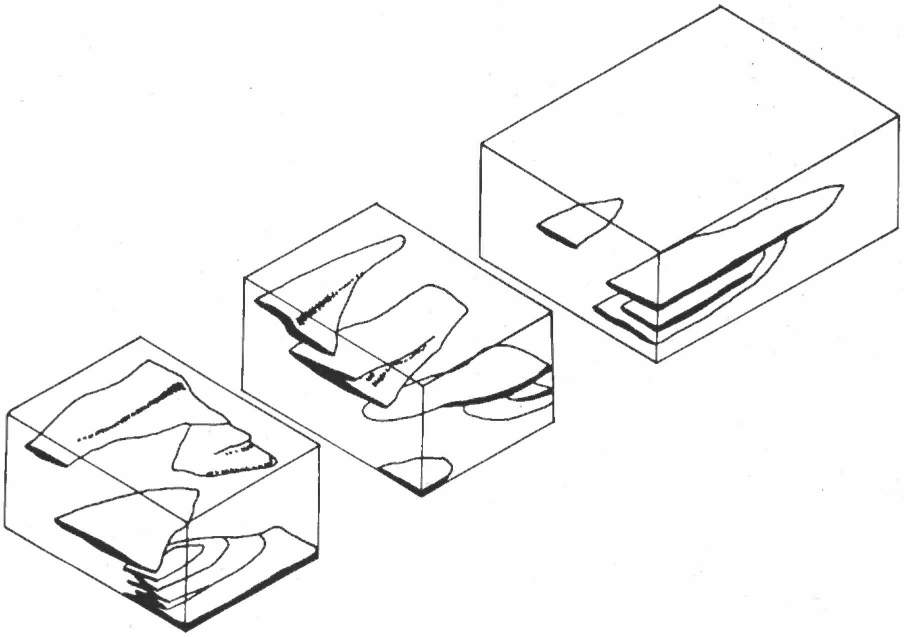


Figure 6. - Idealized exploded block diagram showing typical relationships of prefault orebodies in the Ambrosia Lake district. From Granger, et. al. (1961, p. 1189).

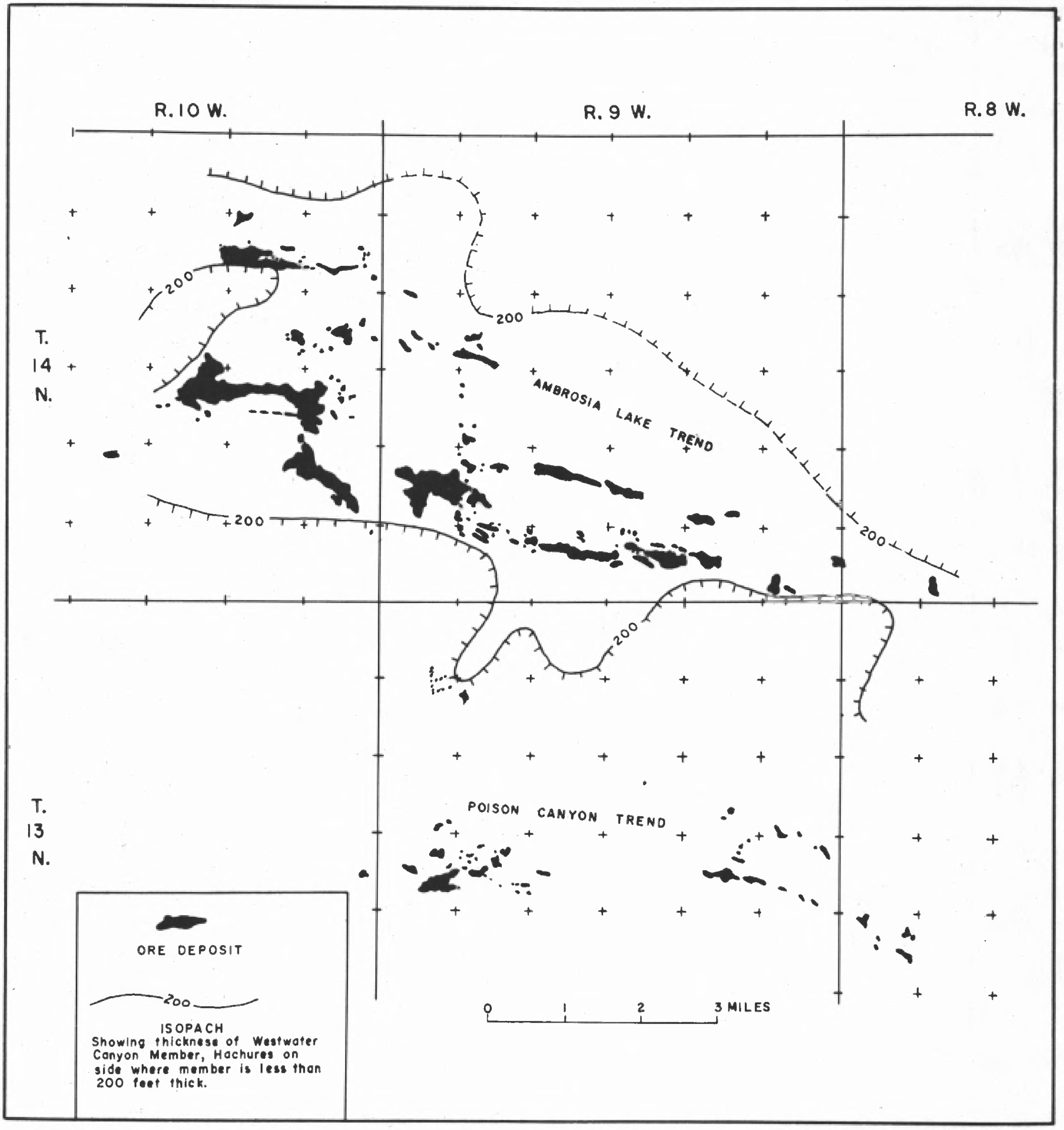


Figure 7. - Ore deposits in the Morrison Formation, Ambrosia Lake district. Modified from E.S. Santos (1963, p. 56) and L.S. Hilpert (1969, p. 67).

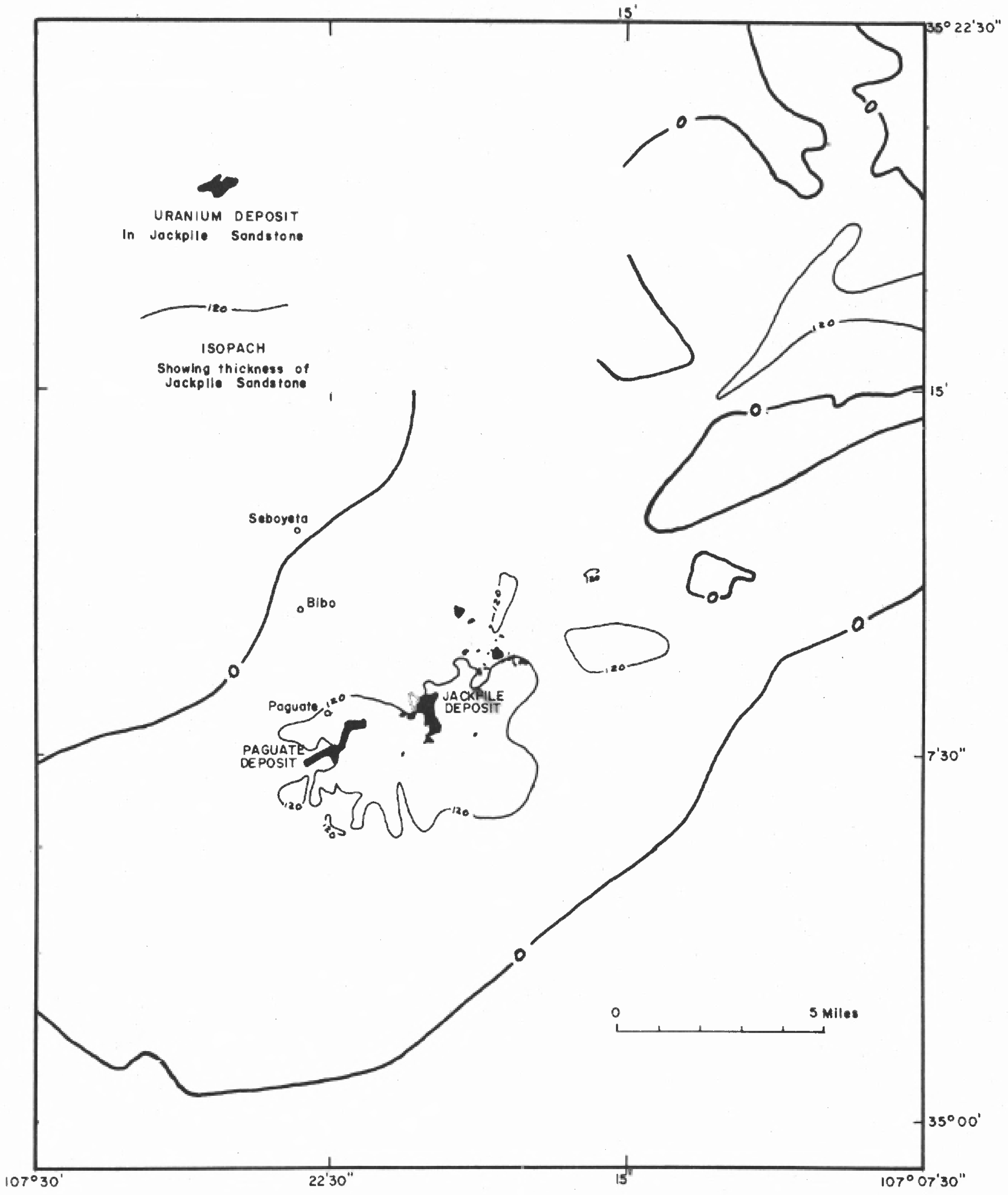


Figure 8. - Map of ore deposits in the Jackpile sandstone in the Laguna district, showing thickness of the Jackpile sandstone. Generalized from R.H. Moench and J.S. Schlee (1967, pl. 3).

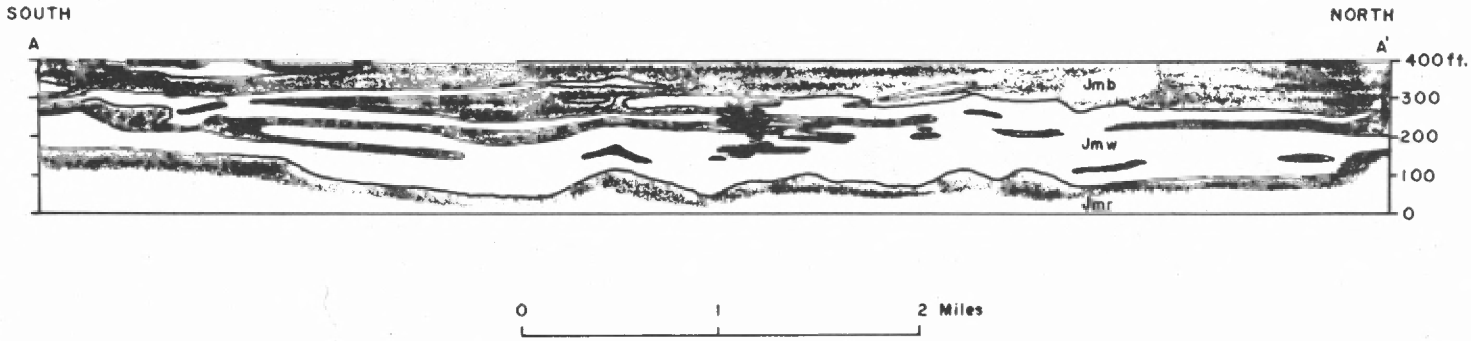


Figure 9. - Geologic section of the Morrison Formation showing stratigraphic relationships of the ore deposits. Section crosses Ambrosia Lake trend and extends from Sec. 8, T. 13 N. R. 9 W. to Sec. 8, T. 14 N. R. 9 W. Modified from L.S. Hilpert (1969, pl. 4).

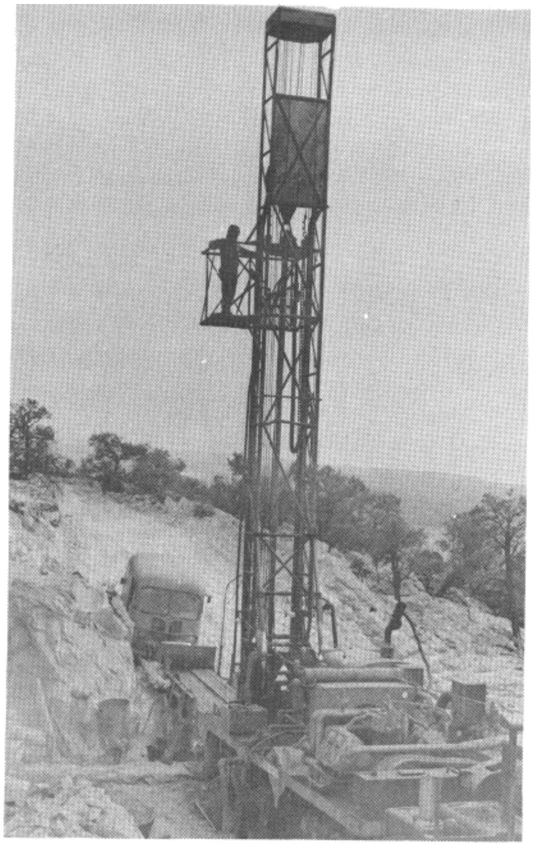


Figure 10. Above; photo of typical drill rig used in uranium exploration. Below; photo of drill samples.

DRILL LOG

Hole No. __________ Section __________ T. ______ R. __________ County __________________ State ________________

Started ______________ Completed ______________ Collar Elevation ________________ Bottom Elevation _____________

Total Depth _______________ Driller ____________________ Logged By _____________________ Date ______________

Depth Probed ____________________

Formation	From	To	Thickness	Rock Type	Color	Grain Size	Carbon	Accessory Minerals	Remarks

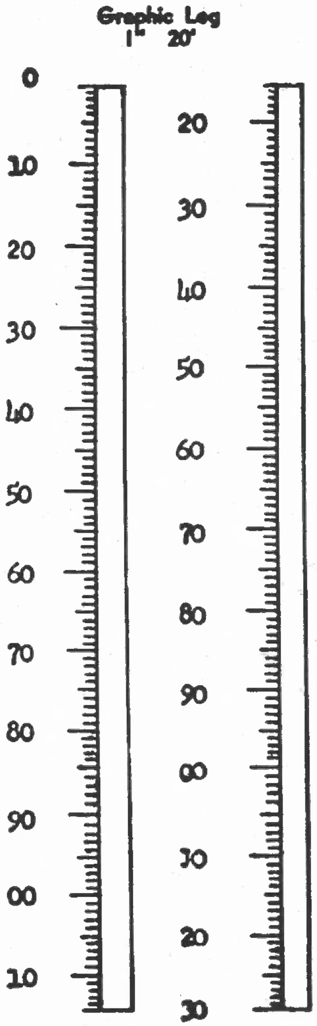


Figure 11. - Lithologic drill log.

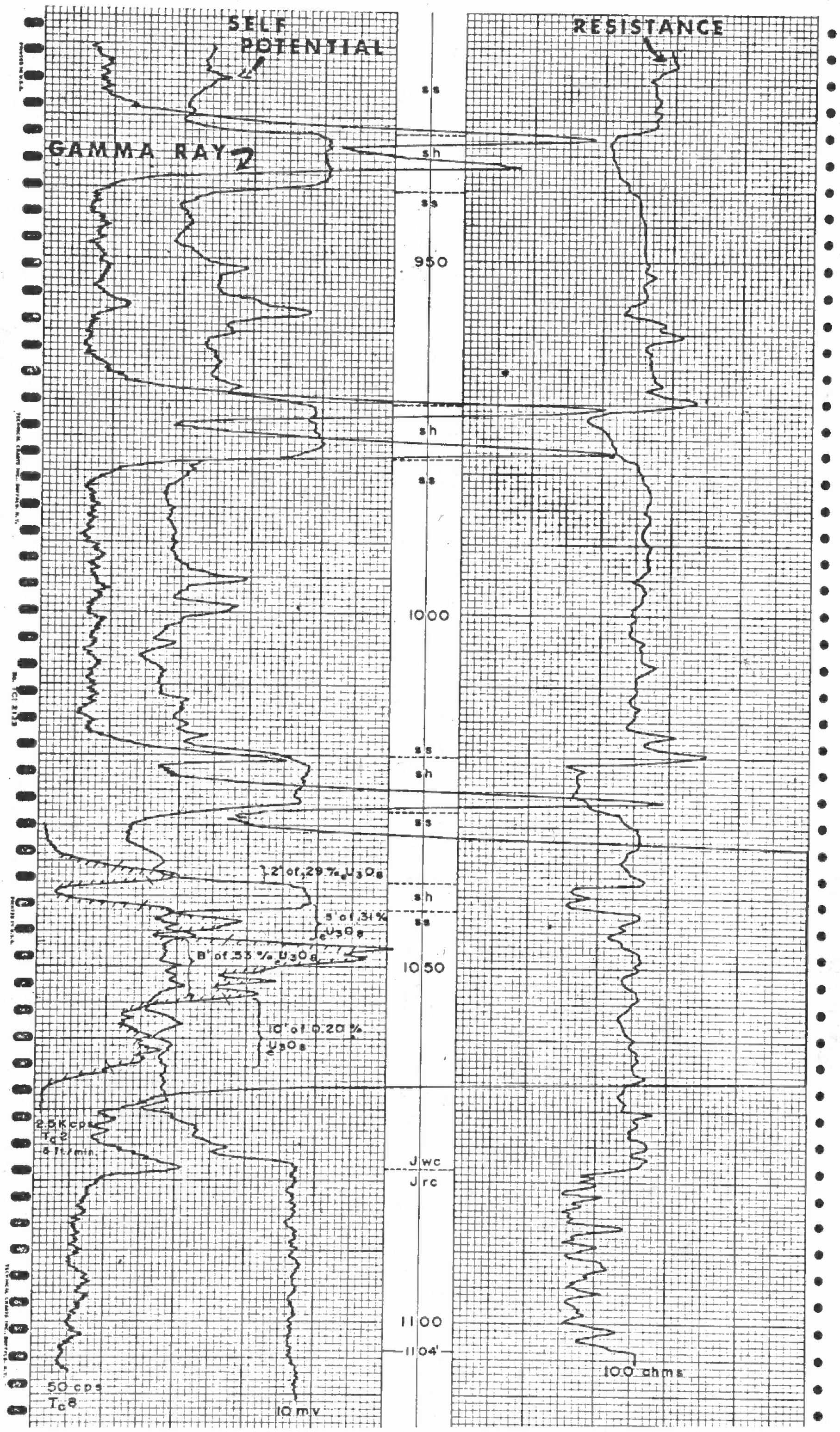
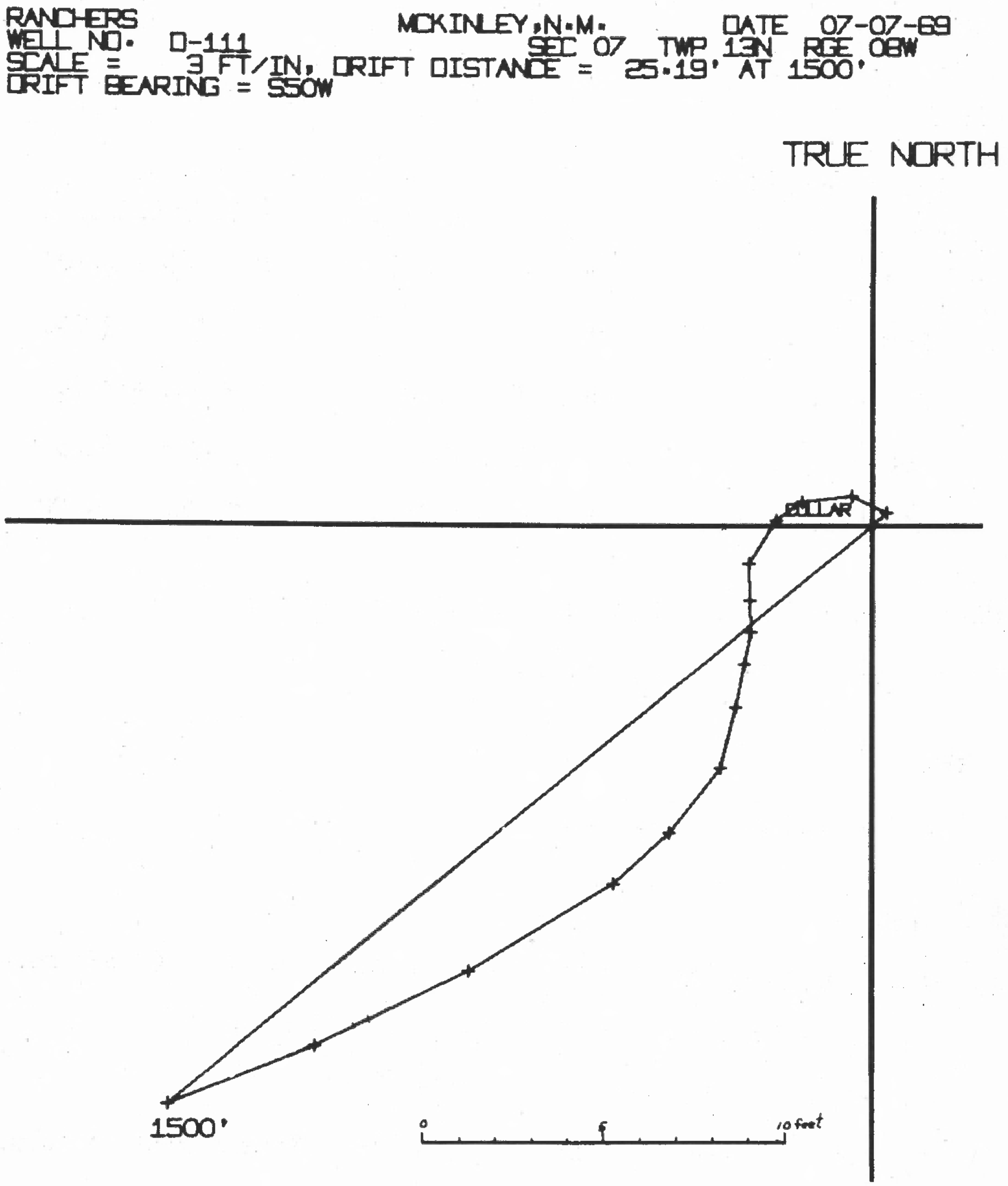


Figure 12. - Part of a geophysical drill log.



RANCHERS MCKINLEY,N.M. DATE 07-07-69
WELL NO. D-111 SEC 07 TWP 13N RGE 08W
SCALE = 3 FT/IN, DRIFT DISTANCE = 25.19' AT 1500'
DRIFT BEARING = S50W

Figure 13. - Printout map of drill hole drift survey.

SOME TYPICAL EXPLORATION COSTS IN THE GRANTS MINERAL BELT

DRILLING:

Total Depth Of Drill Hole	Cost Per Foot	Cost Of Drill Hole
1000 ft.	$ .95 - 1.20	$ 950 - 1,200
1500 ft.	$ 1.05 - 1.50	$ 1,575 - 2,250
2000 ft.	$ 1.30 - 1.90	$ 2,600 - 3,800
2500 ft.	$ 1.75 - 2.50	$ 4,375 - 6,250
3000 ft.	$ 2.35 - 3.50 +	$ 7,050 -10,500 +

Lost Circulation:	$ 25 - $ 35 per hour plus materials.
Standby Rates:	$ 15 - $ 35 per hour.

Roads and Sites:

$ 5 -$ 200 per drill hole.

Geophysical Logging:

1) Gamma-ray Resistivity: 10¢ per foot plus $ 10.00 per set-up.
2) Drift Hole Survey: 10 - 15 ¢ per foot.
3) Mileage: 25¢ per mile over 50 miles.
4) Contract Probe Truck: $ 2,500 - $ 3,000 per month + 2¢ per foot.

Figure 14.

THE BENEFICIATION AND REFINING OF URANIUM CONCENTRATES

by N. R. Leist
National Lead Co. of Ohio

ABSTRACT

The tributyl phosphate (TBP) liquid extraction process used for the purification of uranium concentrates at the National Lead Company of Ohio has been modified drastically during the past two decades. The present high-productivity flowsheet employed for the purification of domestic concentrates is described in this paper. Although the modified TBP system has a greater tolerance for the impurities in concentrates, some maximum impurity limits must be specified. The purification capabilities of the modified system are discussed in terms of the impurities normally found in various types of concentrates.

PROCESS FUNDAMENTALS

Uranium trioxide (UO_3, orange oxide) is produced from uranium concentrates at the National Lead Company of Ohio Refinery using a three-step process (fig. 1). The uranium values of the concentrates are first converted to uranyl nitrate by dissolution in nitric acid. By preferential extraction using an organic extractant, TBP in kerosene, the uranyl nitrate is removed from the feed slurry in a fairly pure form. The organic extract is scrubbed with water and/or nitric acid to achieve the desired product quality. Following a water re-extraction from the scrubbed extract organic phase, the aqueous uranyl nitrate is evaporated to dryness and calcined to yield a pure uranium trioxide. The uranium-depleted slurry from the extraction process (raffinate) is neutralized and discarded. Nitric acid vapor and NO_x fumes are recovered in a nitric acid recovery system and returned to the digestion system. This process has been in use at the National Lead Company of Ohio at Fernald, Ohio, since about 1954;[1] however, the hardware used for the process has changed during the last 16 years.

PROCESS EQUIPMENT

DIGESTION

The uranium concentrate is received at the digestion area in 55-gallon drums which have been sampled previously for assay and weighed. On the receiving pad, the concentrate is segregated into batches, each containing sufficient uranium for a continuous digestion operation of about 75,000 uranium pounds. The concentrate drums are transferred by roller conveyor to the bucket elevator where they are dumped manually on a given time schedule. A schetnatic diagram of this operation is presented in fig. 2. The bucket elevator carries the concentrate to the top of the digestion building; from there, it is conveyed by a screw conveyor to a surge hopper. From the surge hopper, the material is carried again by a screw conveyor to the first of three 3500-gallon digesters. There is essentially no solids holdup in the feed system.

The required volume of dilute acid is metered into the first digester tank simultaneously with the dry feed. The rates of the liquid addition and of the digestion reaction are controlled by the rate of solid feed addition and the temperature maintained in the three digestion tanks. Each digester is equipped with internal coils which can either be used for heating or cooling and with heavy-duty agitators and recirculation pumps. Any water vapor, nitric acid, or oxides of nitrogen evolved during the digestion reaction are conveyed through a vent line system to the nitric acid recovery area. Dust collectors located in the vent lines trap any fine solid material carried from the digesters. The slurry product from this system is continuously pumped to a slurry storage system for subsequent use in the extraction area.

EXTRACTION

The digest slurry is received from the digestion area in a feed hold tank. The feed system is designed to handle slurries containing a relatively high solids content and which have a high settling rate. Slurries containing up to 15 percent solids by settled volume have been handled successfully in this feed system. The feed tank is equipped with an agitator and a recycle loop extending to the top of the extraction columns. A high velocity centrifugal pump continuously recirculates the slurry through the loop at a rate sufficiently high to keep the solid particles suspended, thereby supplying a relatively homogeneous feed stream to the columns. The slurry is fed to the extraction columns through Omega Rotodip Liquid Feeders located at the top of the recycle loop. The feed slurry is dipped from the Rotodip recirculation tank into gravity downcomers which feed the primary extraction columns. The speed of the dipper wheel (and consequently the aqueous feed rate) is controlled by density measurement of the extract stream from the column. A gamma-counting monitor is used for this service. This system is illustrated in fig. 3.

The uranium extraction system is composed of four perforated-plate pulse columns, a single mixer-settler unit, and ti pump mixer-settler unit which consists of four mixers and four settlers. Two pulse columns operating in a parallel connection are used for the preferential extraction of uranium into the organic phase. These 18-inch diameter units are 36 feet high with a plated height of 25 feet. The stainless steel plates which are 1/16-inch thick have a free area of 23 percent and a 3/16-inch hole diameter. The holes of the plate are spaced in an equilateral triangular configuration. Plate spacings in the columns themselves are two inches; consequently, each column contains 150 plates. One Teflon bellows-type pulse generator serves both of the primary extraction columns. This generator produces a modified sine wave-form cycle of about 3/4-inch amplitude with a frequency of about 60 cycles per minute.

The single mixer-settler unit (called the "raffinate mixer-settler system") is used in series with the two primary extraction columns to completely remove the uranium from the aqueous waste stream leaving the primary extraction columns. This mixer-settler unit was also designed to handle aqueous streams containing solid materials.'

The uranium contained in the extract stream is further purified by a scrubbing operation which is accomplished in the previously mentioned 4-stage countercurrent mixer-settler system. A typical stage of this mixer-settler unit is illustrated in fig. 4. The organic and aqueous phases are pump-mixed and maintained in a dispersed condition in the mixer tank by a high-velocity recycle system. Each mixer tank is 3 feet in diameter by about 4 feet high, and the liquid level in the mixer tank is maintained constant by an air dip-tube control system. The dispersion is pumped to the 3-foot diameter, 6-foot high settler tank by the mix pump. This stream enters the settler through a swirl chamber which aids phase disengagement. The separated organic phase flows by gravity from the settler unit to the next mixer, while the separated aqueous phase also flows by gravity from the settler to the proper mixer unit. The dispersion interfaces in the settler units are controlled by a weir level in the aqueous gravity flow piping.

Re-extraction of the uranium into an aqueous phase is accomplished in two perforated-plate pulse columns which are very similar to the primary extraction columns. These columns are also operated in parallel, but they are slightly larger in diameter (26 inches) than the primary extraction columns. The larger columns accommodate a higher liquid flow rate than is normally experienced in the primary extraction operation. The plate geometry of the re-extraction columns is similar to that of the primary extraction columns; however, the hole diameter of these plates is larger (i.e., 3/16-inch compared with 1/8-inch for the primary extraction system). The free area of the plates is the same in both sets of columns (i.e., 23 percent). The re-extraction columns are also served by bellows-type pulse generators which produce an amplitude of about 1/2-inch in the column and a frequency of about 70 cycles per minute. These pulse conditions yield a pulse power of about 35 inches per minute, which is critical[3] for good re-extraction operations.

The purified uranyl nitrate stream from the extraction system is pumped to a large auxiliary decant chamber where additional phase separation is accomplished. From the decant tank, the aqueous product passes through a 20-micron cotton cartridge filter to remove any last traces of suspended solid impurities. The combination of the auxiliary decant tank and filter is a vital part of the purification system, and the product uranyl nitrate from these units constitutes the feed for the denitration operations. The stripped organic phase from the re-extraction columns normally contains many impurities which have been introduced during the extraction process and which must be removed prior to the recycling to the primary extraction columns. Also, some uranium remains in the organic phase and must be removed to prevent its later loss through the raffinate stream from the primary extraction columns. In addition, the hydrolysis products of the tributyl phosphate—namely, the di- and mono-butyl phosphates and tramp organic impurities (such as lubricating oils) — must be removed to insure satisfactory extraction system operation.

Tramp organic materials are periodically removed from the solvent system by an acid-saturation, charcoal-treatment process.[4] The solvent is pumped into a large decant tank where it is saturated with nitric acid and mixed with powdered charcoal. A rotary drum vacuum filter is used to separate the charcoal from the solvent. The solvent treated in this manner is normally returned to the extraction system through a carbonate treatment system to insure that di- and mono-butyl phosphate impurities are kept to a minimum.

The carbonate solvent treatment system consists of a mixer system for washing the solvent with aqueous sodium carbonate. All solvent from the pulse column system normally is treated in the carbonate system prior to reuse in the extraction columns. After the solvent has been mixed with the aqueous sodium carbonate, phase disengagement is accomplished with a high-speed centrifuge unit which also removes residual entrained solids from the system. A mixer-settler unit is then used to acid-treat the solvent. The total organic stream after treatment in the carbonate solvent treatment system is pumped into an organic hold tank from which it is recycled to the extraction column system.

DENITRATION

The aqueous uranyl nitrate product from the extraction system is stored in large tanks located in the denitration area. The solution is pumped from these tanks at a constant rate through a preheater to a vertical-tube evaporator where it is concentrated at a constant temperature. The evaporator is located on the roof of the denitration building to permit the concentrated solution to flow by gravity to a steam-heated boildown tank (fig. 5) in which the solution is further evaporated to an essentially molten uranyl nitrate hydrate. The boildown operation is monitored by product density measurements. From the boildown tank, the molten salt cascades to a hold tank which is now used only as a surge tank. Up to this point, the operation is continuous. The vapor stream from the evaporator is condensed and recycled to the extraction area as a make-up water for re-extraction. The vapor stream from the boildown tank is condensed, cooled, and sent to a uranium recovery sump..

The denitration operation itself is conducted batchwise in a series of gas-fired denitration pots. During denitration, the pot charge is continuously stirred to prevent caking. Caking on the walls is prevented by setting the agitator blades close to the inner surfaces of the pot. This prevents conversion of the UO_3 to U_3O_8 by overheating. The oxides of nitrogen evolved during the process pass through an entrainment separator to remove uranium oxide dust and are then sent to the nitric acid recovery area.

After cooling and degassing, the UO_3 powder is removed from the pots by a vacuum "gulping" system. The UO_3 is vacuumed from the pot using a flexible metal hose. Cyclones remove the solids from the air stream and convey them to a surge hopper. The fine material is removed by dust collectors and, finally, a plate-and-frame air filter. These fines are contaminated and are subsequently returned to the digestion area. From the surge hopper, the product UO_3 powder is sent by a screw conveyor to a hammer mill where it is ground to meet particle size specifications, sampled for purity analysis, and charged to mobile hoppers. The hoppers are weighed, sealed, and stored, pending shipment to another plant for UF_4 production.

OPERATING CONDITIONS

The digestion of the uranium concentrates is accomplished at a temperature of approximately 150˚F. Normal retention times for the continuous digestion system range from 3-5 hours, and uranium digestion efficiencies of greater than 99.9 percent are normally achieved.' The concentrates are digested to produce a "low-acid" feed slurry[6] containing 400 grams per liter uranium, 0.5 M free HNO_3, and 0.5 M NH_4NO_3. The NH_4NO_3 is obtained by the addition of an extra 0.5 M of HNO_3 in the first digester and by an NH_3 addition in the third or last digester.

The aqueous feed slurry (generally 2-4 wt. percent solids) is fed at a variable rate to the top of the primary extraction columns after it has been mixed with the aqueous raffinate from the scrubbing system (fig. 6). The uranium is extracted into the solvent (30 vol. percent TBP in kerosene) as the aqueous flows by gravity through the columns. The extraction operation is accomplished at 100˚F, and the 0.5 M HNO_3 and 0.5 M NH_4NO_3 produce a sufficient salting strength to yield a final aqueous raffinate stream containing less than 0.05 g/l soluble uranium. The TBP extractant is fed at a fixed rate to the system through the "raffinate mixer-settler system." The use of this system in series with the columns permits a high uranium loading of the extract stream (i.e., 90 percent of theoretical) while only a minor quantity of uranium is lost in the aqueous raffinate. The uranium loading in the organic extract stream is important from the standpoint of impurity decontamination, and loadings of from 90-92 percent are desirable. Normally, the primary extraction system is operated with an organic continuous phase; consequently, the aqueous phase is pulsed through the plates and falls from plate to plate by gravity.

Since the nitric acid and other impurities which follow the uranium into the organic phase contribute little to the specific gravity of the extract stream in comparison to that contributed by the extracted uranium, it is possible to maintain a constant uranium saturation level in the product stream by monitoring and controlling its specific gravity. Therefore, the drive motors of the Rotodip feeders are controlled by a signal from the gamma-counting density instruments, and uranium saturation of the extract stream is maintained within close limits (i.e., — 2 percent of saturation).

Although in the TBP extraction system, as outlined, the TBP is relatively specific toward uranium, other compounds (nitrates) do extract or are physically entrained in the organic product stream. Therefore, while the extraction columns do eliminate practically all of the impurities with the exception of nitric acid, an additional purification step is required to bring the contamination level to within the imposed product purity specifications. This operation is performed, as was described previously, in a 4-stage countercurrent scrubbing unit. Deionized water or dilute HNO_3 can be used as the aqueous phase for extract scrubbing, and the 0/A used in the system can be varied from the normal 20/1 ratio. Both of these variables—as well as the temperature of the scrubbing operation—must be changed periodically as the extracted impurities vary with changing feed sources. The scrubbing conditions illustrated in fig. 7 are normally used for most of the currently generated concentrates. The temperature of the scrubbing operation is normally about 100˚F.

The re-extraction operation is similar to the operation in the primary extraction system except that uranium is transferred from the organic stream to the descending aqueous phase. In the re-extraction column, the aqueous-to-organic flow ratio is increased to the point where essentially all of the uranium values can be removed from the scrubbed extract stream. A higher operating temperature (i.e., 150°F) and a lack of HNO_3 in the system reverses uranium distribution preference in favor of the aqueous phase. Condensate from the denitration area evaporator and deionized water are used to strip the uranium from the organic, and an 0/A of 1.1/1 is usual for this operation.

The stripped organic from the re-extraction columns is normally carbonate-treated (with a 3 wt percent Na_t CO_3 solution at an 0/A of 12/1) and subsequently reacidified with a 1 M HNO_3 solution (0/A of 12/1) prior to reuse in the extraction system. This treatment removes residual uranium and the TBP degradation products from the solvent. This operation is illustrated in fig. 8. The operating conditions used in the acid-saturation are illustrated in fig. 9, charcoal-solvent treatment which is periodically administered to portions of the solvent inventory to remove tramp organic materials. This treatment is only required periodically since great care is taken to prevent lubricating oils and other tramp organics from entering the extraction system. The solvent is saturated with HNO_3 in this operation, and the decanted aqueous phase is subsequently used in the digestion area. Charcoal is added to the saturated solvent, and the now relatively insoluble tramp materials are adsorbed on the solid material which is separated from the solvent on a rotary vacuum drum filter. Charcol usage for this treatment is about 0.0834 lb/gal.

The aqueous uranyl nitrate product from the re-extraction columns contains approximately 0.08 M HNO_3. NH_3 is added to this product stream to neutralize the acid prior to the uranium concentration operations. The uranium content of the product stream is a nominal 110 g/l. This concentration is increased to about 400 g/1 in the 220-230°F evaporation step and is further increased to about 1300 g/1 in the boildown operation (fig. 10). The batch denitration operation is conducted at a temperature of about 1,300°F during a 5- to 7.5-hour period. Sulfuric acid is added to each denitration pot charge so that the product UO_3 will contain about 1,500 ppm SO_4 (uranium basis). This quantity of SO_4 in the product has been shown to be helpful during the manufacture of uranium tetrafluoride.

URANIUM PURIFICATION

During 1962 the Uranium Concentrate Committee of the Atomic Energy Commission formulated purchase specifications for uranium concentrates. The specifications are presented in table 1.

Generally, these specifications have been met easily and routinely by the concentrate producers. Typical AEC receipts from all western mills f6r the period of July through September 1968, are presented in table 2.

The improved refining process described in this paper has consistently produced a higher quality material than was produced by the TBP process as initially designed.' The changes, which are fully described in References 2 through 7, have brought about extraction results as listed in table 3. These results are typical of the last concentrate refining campaign conducted in the Refinery of the National Lead Company of Ohio. Although some maximum impurity limits must still be specified, the results shown in table 3 and other Refinery considerations indicate that some relaxation of the concentrate specifications might be warranted if required by concentrate producers for special reasons:

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[4] Leist, N. R., and Krekeler, J. H., 1963, *Removal of foreign organic materials from TBP-kerosene solvent:* AEC report NLCO-882.

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Figures and tables follow

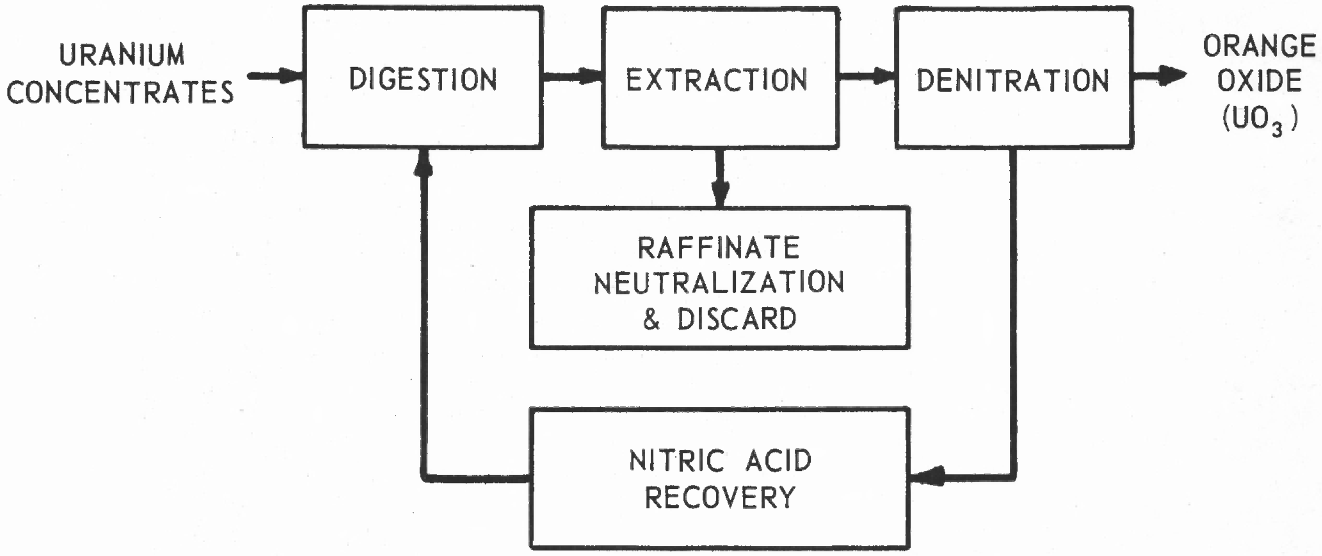


FIGURE 1 Uranium Refinery Process Flowsheet

DWG. NO. 179-61

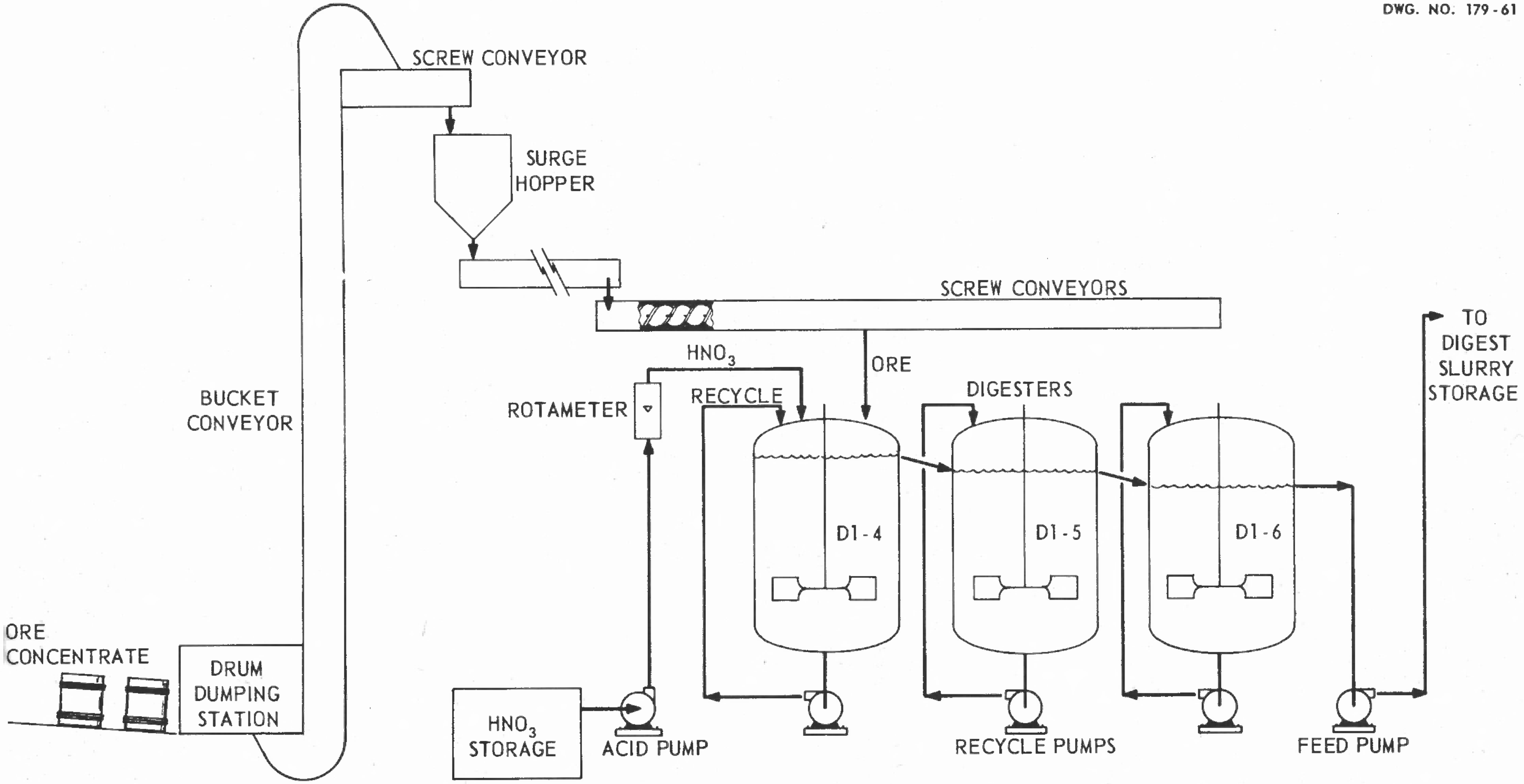


FIGURE 2 Continuous Digestion System

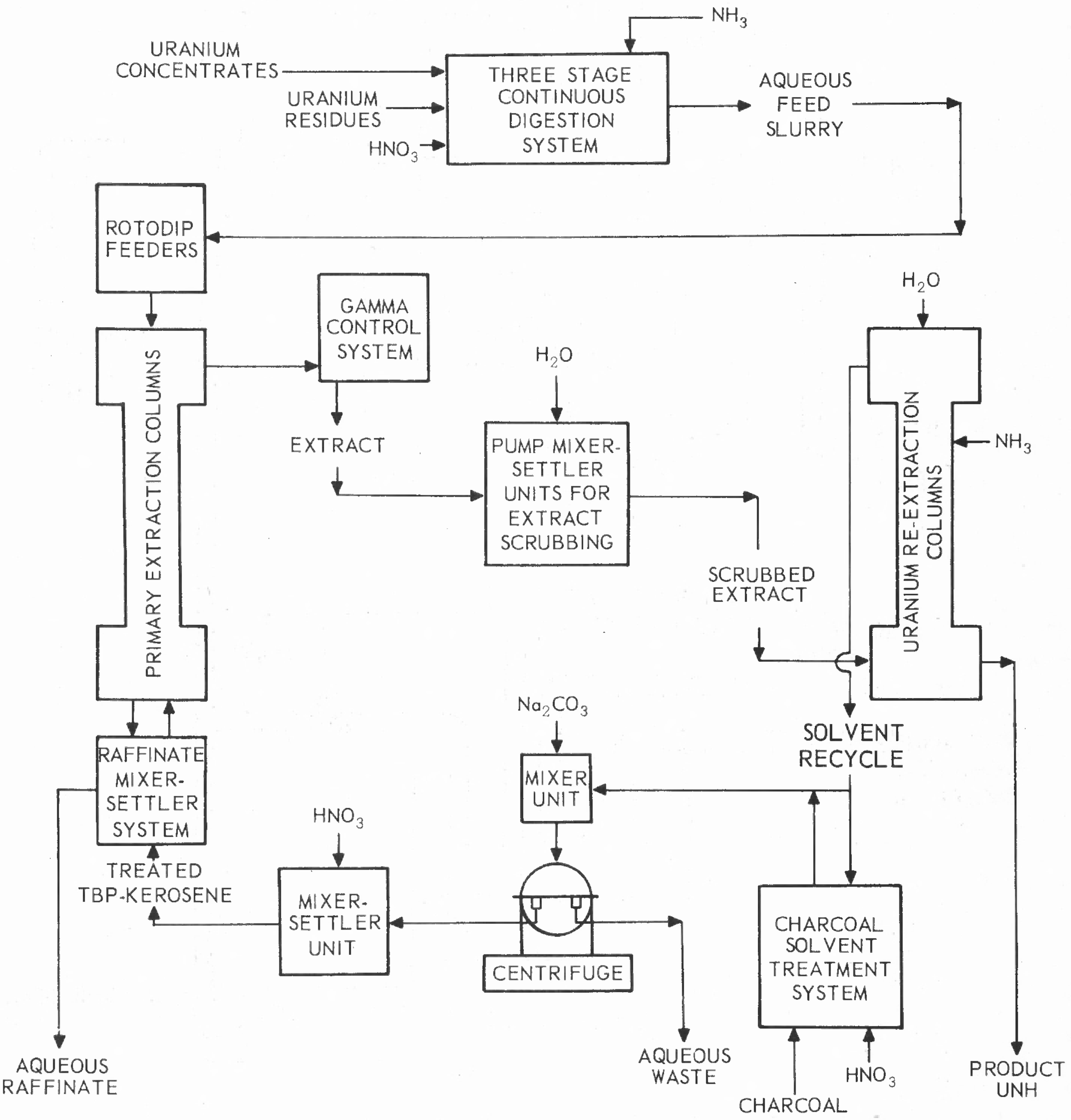
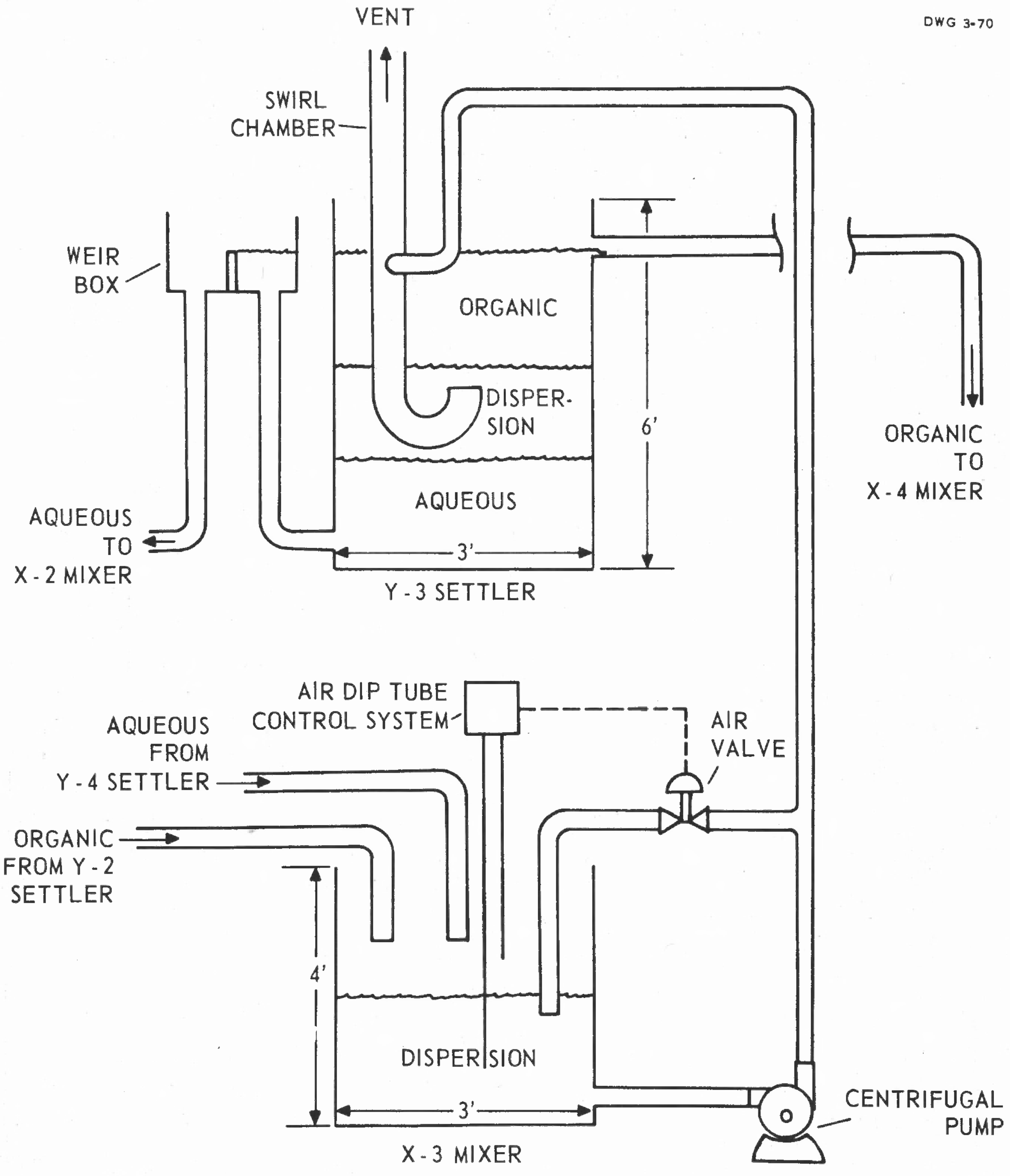


FIGURE 3 Concentration Extraction Process



NOTE: 4 MIXER-SETTLER UNITS CONSTITUTE A SCRUBBING UNIT

FIGURE 4 Pump M-S Unit for Scrubbing

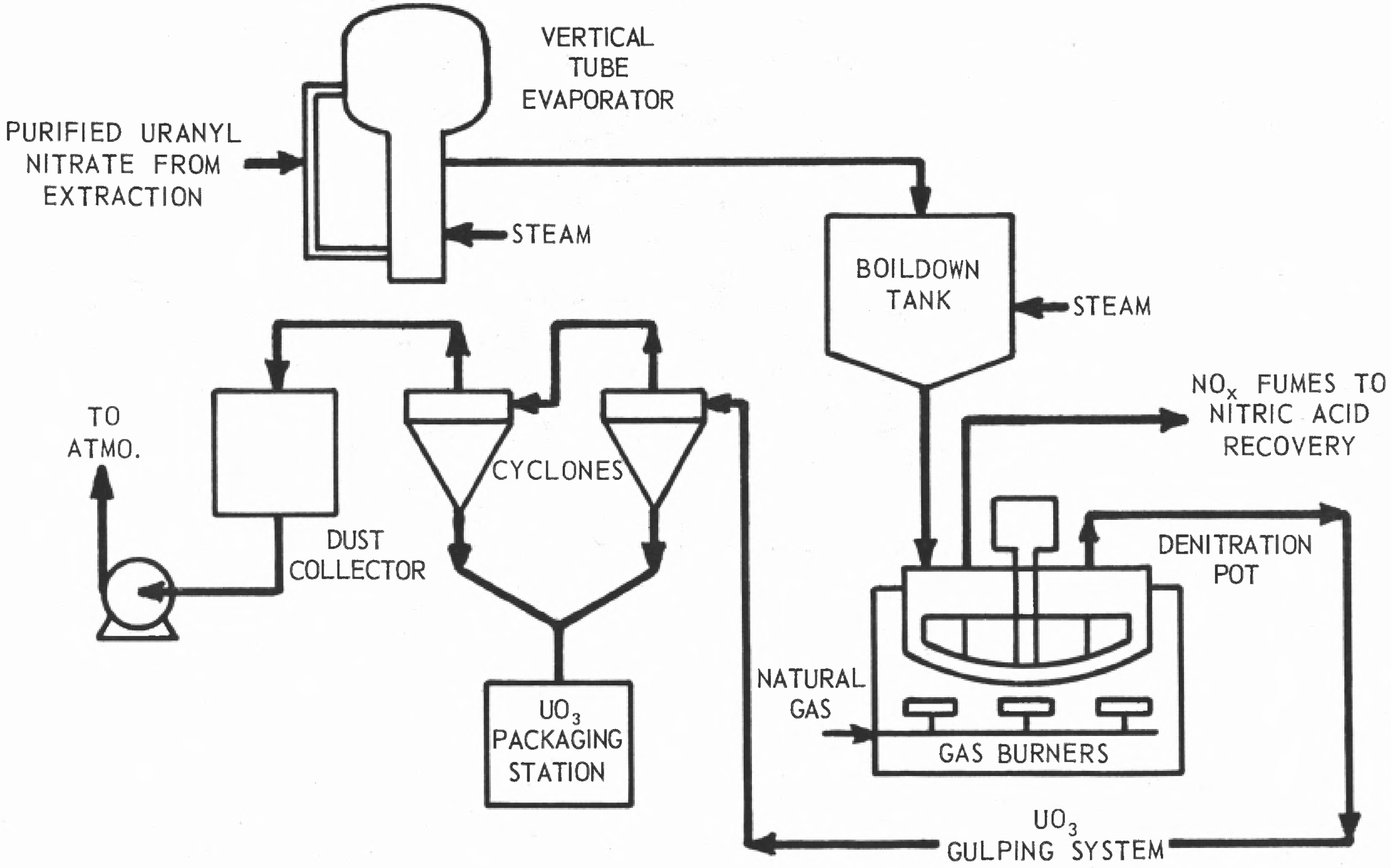


FIGURE 5 Denitration System

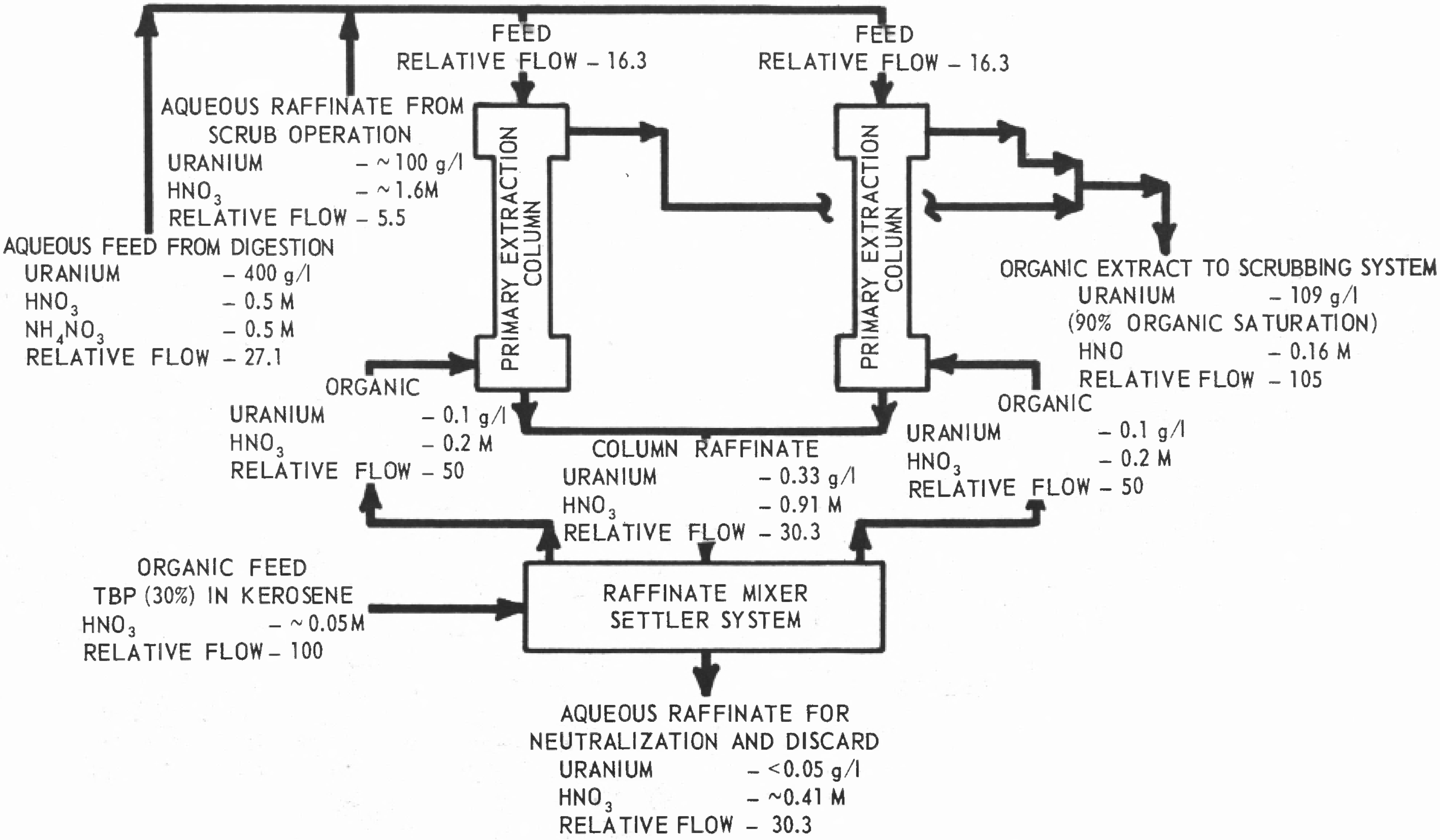


FIGURE 6 Primary Extraction Operating Conditions

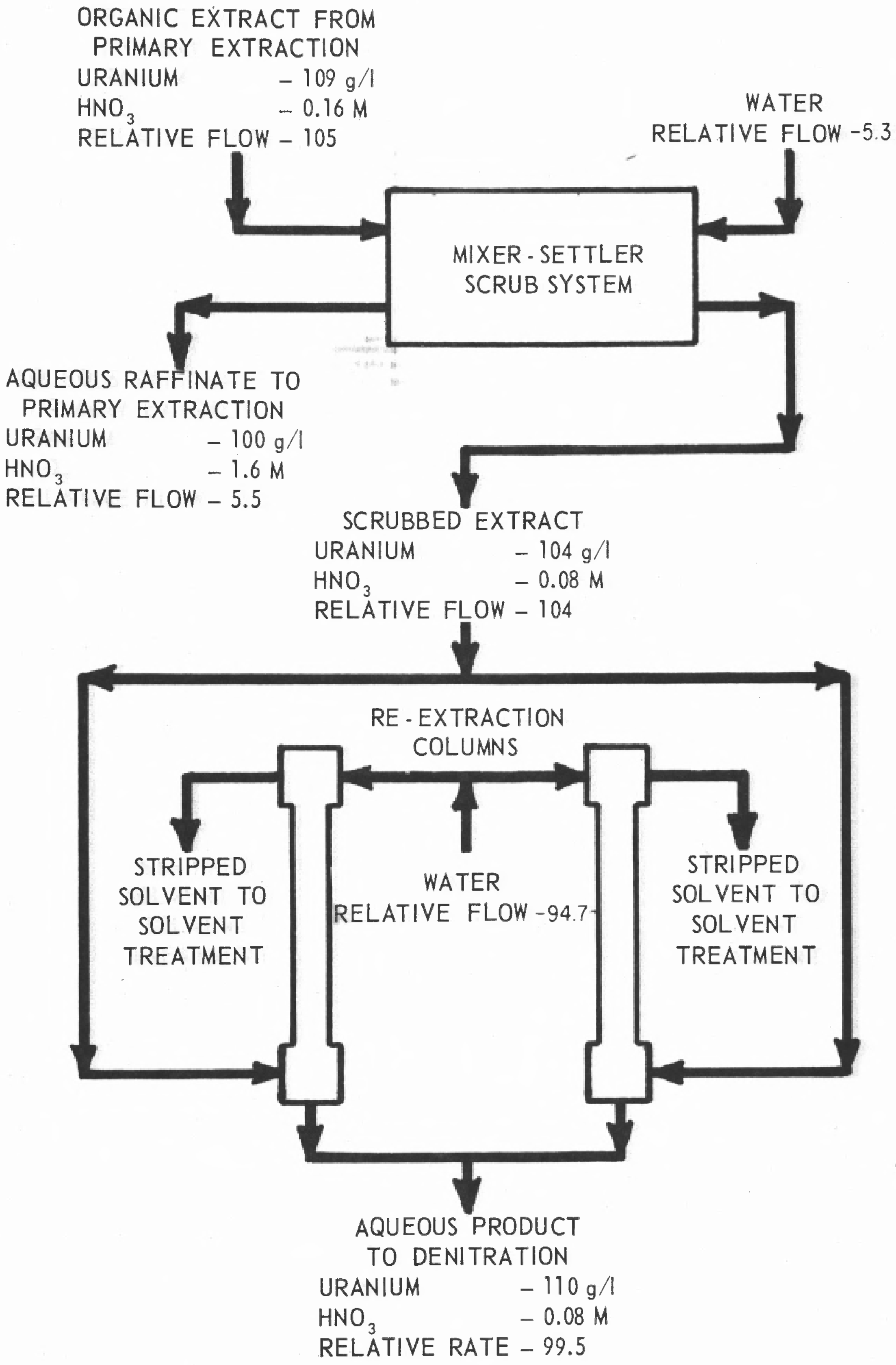


FIGURE 7 Scrub and Re-extraction Operating Conditions

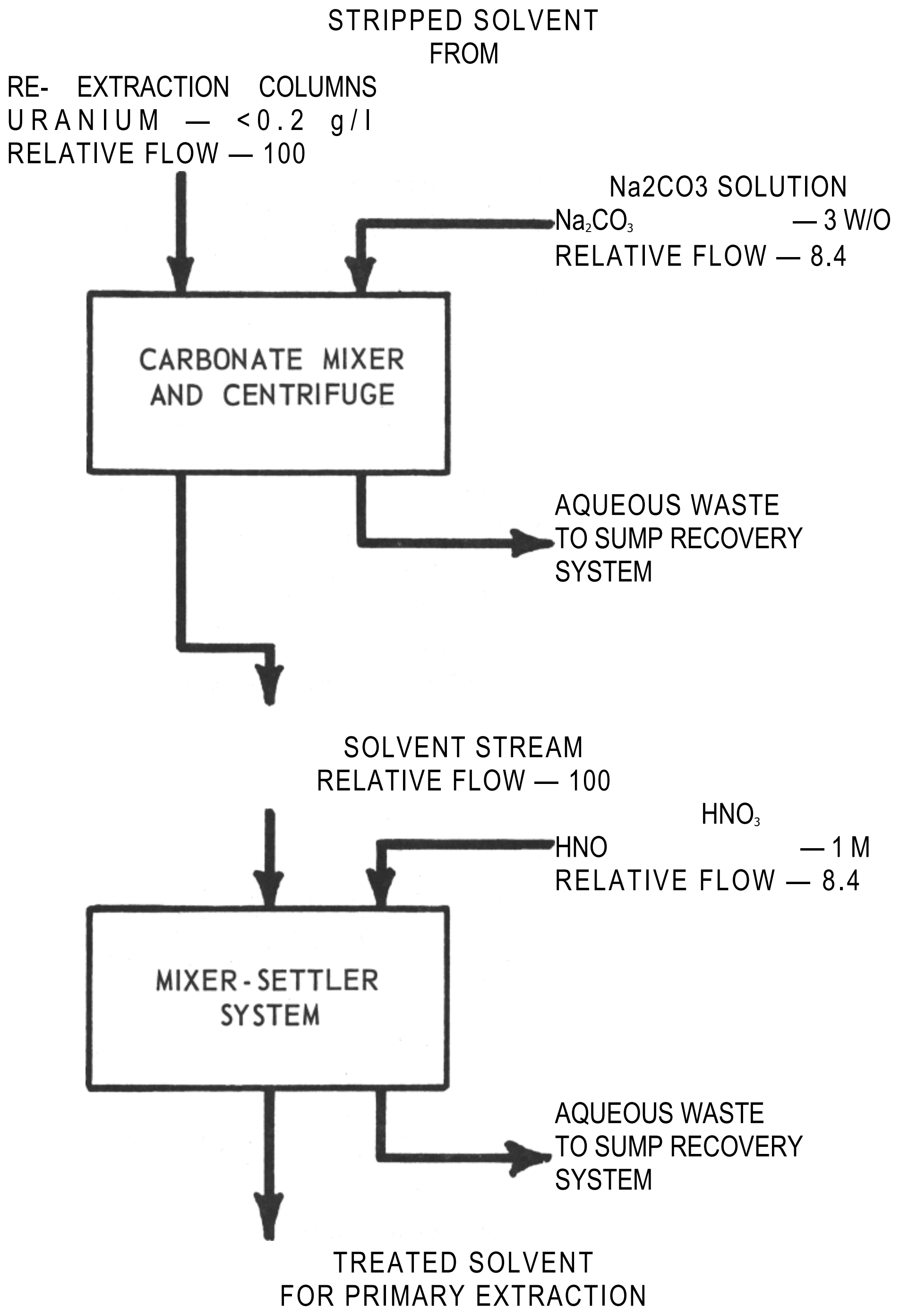


FIGURE 8 Solvent Treatment (Carbonate) Operating Conditions

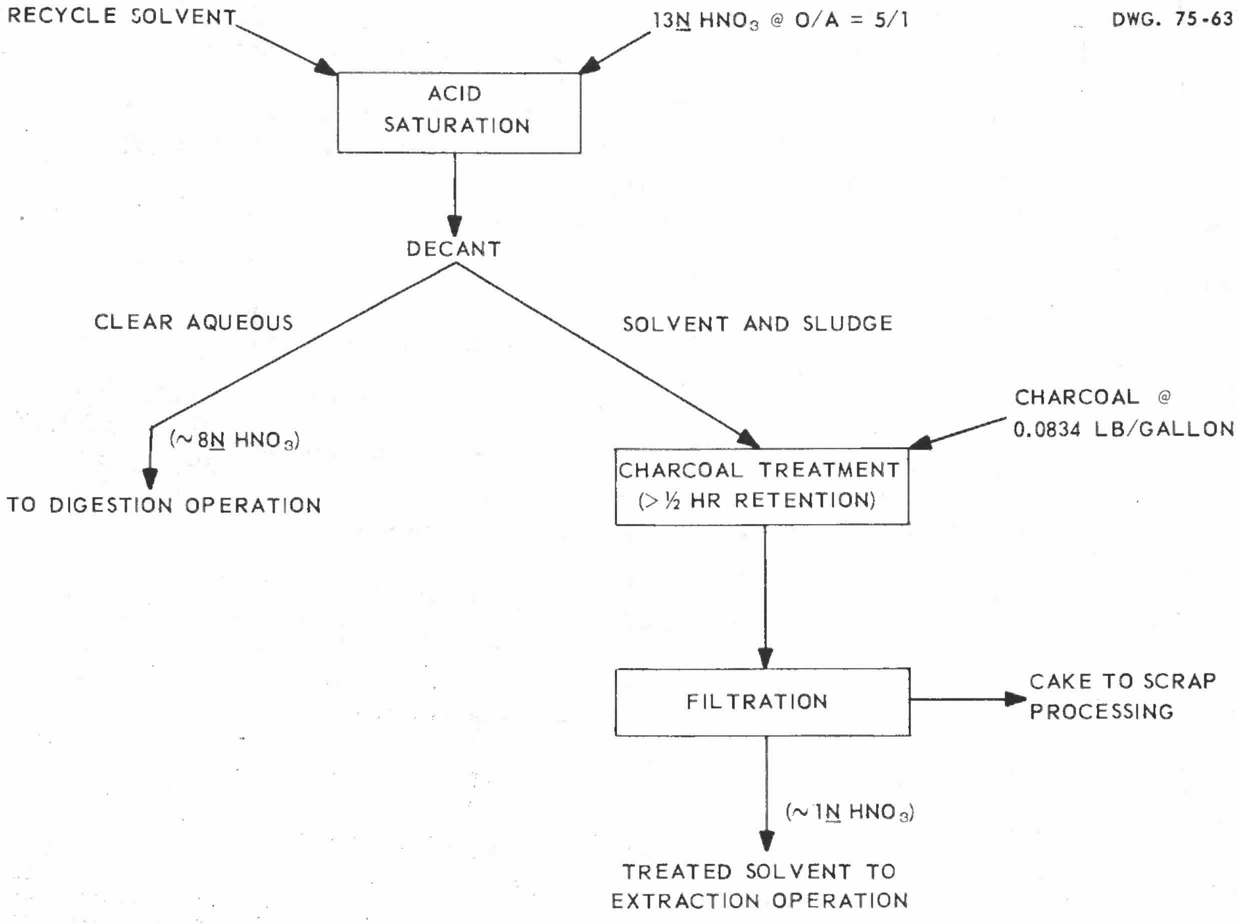


FIGURE 9 Acid-Charcoal Solvent Treatment

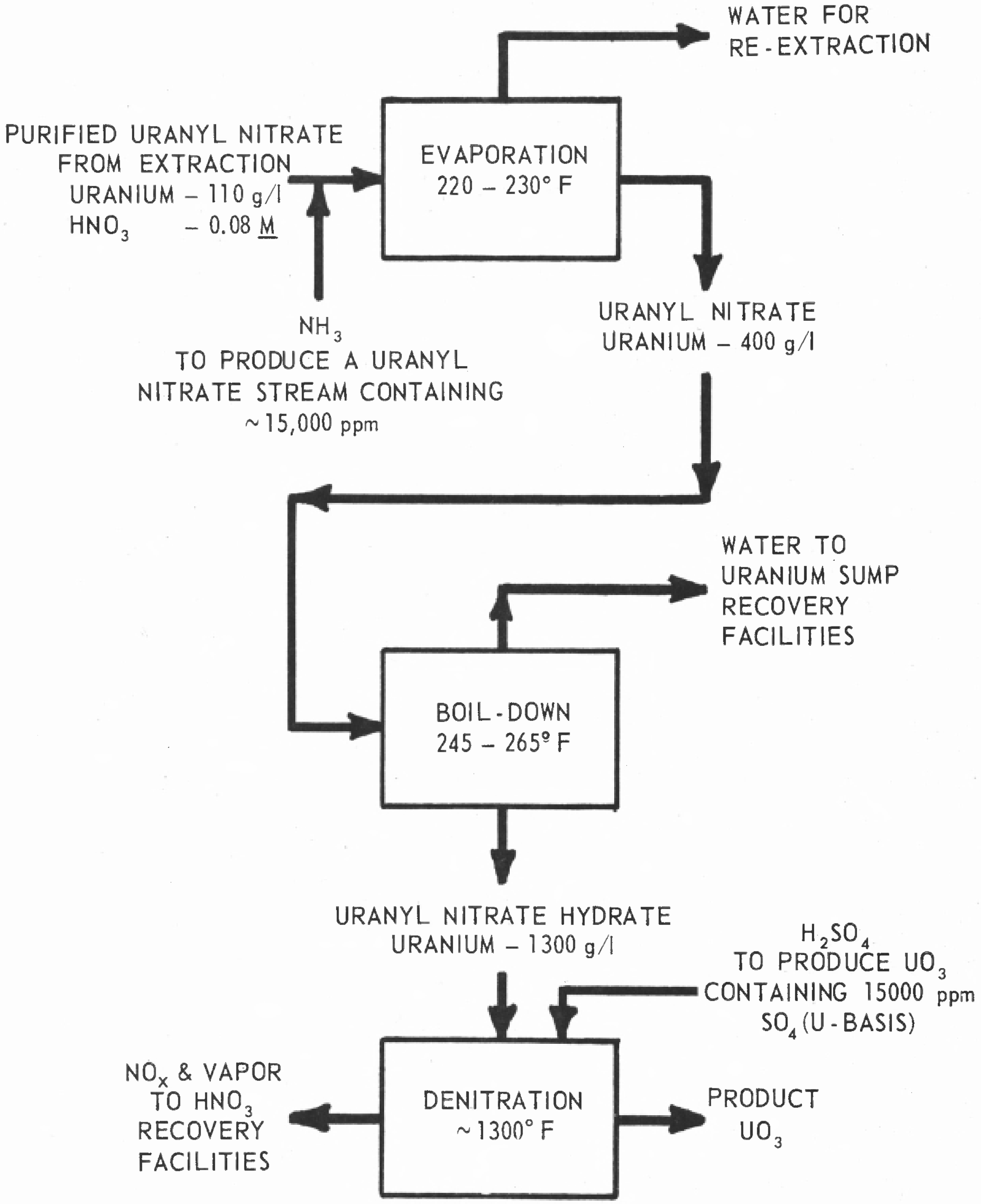


FIGURE 10 Operating Conditions for Denitration

TABLE 1
SPECIFICATIONS FOR URANIUM CONCENTRATE PURCHASE CONTRACTS

U:	63.6 percent minimum
$H_2$0:	Intent to be free-flowing*
Organic:	0.1 percent maximum; intent to keep out surfactants*
Insoluble U3 08 :	0.1 percent maximum
V:	0.73 percent
As:	2.0 percent maximum
PO4:	2.0 percent maximum
Ca:	1.5 percent maximum
SO_4:	10.0 percent maximum
percent Ca X percent SO_4:	8.5 percent maximum
CO_3:	1 percent maximum
B:	0.2 percent maximum
Cl:	0.2 percent maximum
F:	0.1 percent maximum
Mo:	0.2 percent maximum
Zr:	2.0 percent maximum
Th:	2.0 percent maximum
Rare Earths:	150 ppm each for Gd, Dy, Eu, and Sm
**Exotics:	Intent to keep out excessive amounts

*Intention statements that vendors will undertake to produce material suitable for refinery use; AEC will test as required (examples given).

**Includes Ag, Cd, Co, Hf, Hg, Ru, Sb, Ta, Ti, W, etc. (impurities that would be objectionable in refinery products, but which normally cause no trouble in meeting product specifications).

TABLE 2
SUMMARY OF WESTERN USA RECEIPTS FROM ALL MILLS AT GRAND JUNCTION FOR TM, PERIOD OF JULY THROUGH SEPTEMBER,1968

Compound or Element	No. of Lots Assayed	Average of All Lots Assayed (%)
U	100	74.02
✓	100	0.13
PO_4	26	0.18
Cl, Br, I	47	0.02
F	13	0.01
Mo	100	0.08
SO_4	46	1.56
Fe	28	0.46
As	26	0.06
CO_3	43	0.22
Ca	31	0.23
B	13	<0.005
H2O	100	1.18
Insol. U308	25	0.01
Na	28	2.83
Th	12	<0.10
Zr	12	<0.10
K	28	0.16

TABLE 3
TYPICAL REFINERY PURIFICATION RESULTS FOR ORE CONCENTRATES

Compound Or Element	Average Concentrate Feed Material Analysis	Typical UO3 Results for Campaign	Target Purity Levels (Maximum)
U	69.9 percent	82.0 percent	80.7 percent
Al		<4 ppm	100 ppm
As	0.2 percent		-
B	<0.005 percent	<0.15 ppm	0.25 ppm
Be		<1 ppm	10 ppm
Bi		<1 ppm	
Ca	0.35 percent	<10 ppm	15 ppm
Cd		<0.20 ppm	0.25 ppm
Cr		11 ppm	20 ppm
Cu		<1 ppm	50 ppm
Dy	0.001 percent	<0.25 ppm	0.25 ppm
Eu	<0.001 percent	<0.25 ppm	0.25 ppm
F	<0.01 percent	<100 ppm	250 ppm
Fe	0.17 percent	35 ppm	50 ppm
Gd	<0.001 percent	<0.25 ppm	0.25 ppm
Mg		<4 ppm	25 ppm
Mn		<4 ppm	5.0 ppm
Mo	400 ppm	<1 ppm	100 ppm
Na		<1 ppm	15 ppm
Ni		3 ppm	15 ppm
P	0.08 percent	40 ppm	150 ppm
Si		<5 ppm	20 ppm
Sm	<0.001 percent		0.25 ppm
Sn		<1 ppm	100 ppm
Th	<0.01 percent	-	50 ppm
V	1820 ppm	<1 ppm	15 ppm
Zn		<10 ppm	20 ppm
Zr	<0.30 percent	<20 ppm	65 ppm
PO_4	0.24 percent	See P Above	See P Above
SO_4	2.57 percent	1350 ppm	1300-1800 ppm
CO_3	0.4 percent		

Note: percent - Sample Basis
ppm - Uranium Basis

PRODUCTION OF URANIUM TETRAFLUORIDE AND URANIUM METAL

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ABSTRACT

The main sources of feed materials are given for the production of uranium tetrafluoride and uranium metal at the National Lead Company of Ohio. The historical background of uranium tetrafluoride and uranium metal production facilities is presented together with the primary manufacturing techniques currently in use.

INTRODUCTION

It has been some years since the production technology of uranium tetrafluoride and uranium metal was updated in the literature. Although the book, *Uranium Production Technology,'* (published in 1959) is generally regarded as the basic source of information on feed materials and uranium metal technology, we believe it is now timely to report on current practices at the National Lead Company of Ohio.

Much early work on the technology of uranium production was performed by Spedding, Wilhelm,[2] and co-workers at Ames Laboratory, Iowa State University. Wilhelm's report in the *Journal of Chemical Education*[3] on these wartime activities is both informative and entertaining. Later, when the production of uranium was shifted to industry, a number of companies shared in the development of production technology. Among the more important contributors were Mallinckrodt Chemical Works, St. Louis, Mo., Union Carbide Corporation, Oak Ridge, Tenn., and Paducah, Ky., E. I. duPont, Chambers Works, Del., Electro Metallurgical Company, Niagara Falls, N. Y., Harshaw Chemical Works, Cleveland, Ohio, and the National Lead Company of Ohio.

At present, two large-scale production facilities remain in the AEC complex for uranium tetrafluoride and uranium metal production: the Feed Materials Production Center (FMPC) at Cincinnati (Fernald), Ohio, operated by National Lead Company of Ohio, and the gaseous diffusion plant at Paducah, Kentucky, operated by Union Carbide Corporation. The primary emphasis at the FMPC is on the production of uranium metal fuel core products, while the Paducah facility primarily converts UF_4 to UF_6 for gaseous diffusion (isotope'separation).

URANIUM TETRAFLUORIDE PRODUCTION

Uranium tetrafluoride, or "green salt," is the key intermediate compound in the production of uranium metal. Uranium tetrafluoride is also an intermediate in the production of UF_6, the compound employed in the gaseous diffusion operations, as mentioned above, for separating ^{2}"U from ^{238}U. This activity is becoming increasingly significant in supplying fuel for the commercial nuclear power industry.

The starting material for the production of UF_4 is UO_3, which is known as "orange oxide." This oxide is the product of the thermal denitration of purified and concentrated uranyl nitrate. The physical and chemical properties of the orange oxide determine, to a large extent, the processing characteristics of the material as it goes through the subsequent production operations. The main chemical reactions involved are

$$UO_3 + H2 \rightarrow UO2 + H_2O$$

and

$$UO_2 + 4HF \text{ —} UF_4 + 2H_2O.$$

Fig. 1 shows the production flow diagram.

The orange oxide used to make UF_4 comes from several sources and contains various percentages of ^{235}U ranging from less than 0.2% ^{235}U through the natural 0.7 percent to as high as 2 percent ^{235}U. We have not consumed any ore concentrates from the AEC inventory for more than one year. The current primary sources of orange oxide are as follows:

1. From the FMPC 'Refinery and orange oxide facility (indirect gas-fired stirred-pot denitration). The refinery feed consists of residues from various uranium metal operations, residues and surplus materials from various off-site uranium programs, uranyl nitrate from Nuclear Fuel Services, West Valley, N. Y., as separated from irradiated AEC and commercial nuclear reactor fuels.

2. Savannah River, South Carolina (E. I. duPont), from irradiated fuel reprocessing (electrically heated stirred-pot denitration).
3. Hanford, Washington (Atlantic Richfield Hanford Company), from irradiated fuel reprocessing (electrically heated stirred-trough denitration).

As will be discussed later, each of these orange oxide feed materials has its own peculiarities which require special attention.

Table 1 lists the specifications for UO_3 from natural uranium. In the specifications, the metallic impurities are essentially set by the tolerance in the uranium metal produced from the UO_3. Sodium is an exception, as this impurity has a detrimental effect[4] on the reaction of the HF and UO_2. Sodium forms relatively low-melting mixed salts with the UF_4 which restrict the reaction of HF and the unconverted UO_2. Quantities above 100 ppm can lead to more serious problems in the reactor tubes by forming plastic masses which cause high feed screw torques or plugging.

Orange oxide from our refinery and, generally, that from Savannah River is processed to UF_4 in a straightforward manner. A hopper of orange oxide containing about 5 tons is placed on a weightscale feed system and is fed through a seal hopper into the first stage of a two-stage fluidized bed reactor (operated at 1,100° ± 50°F) with dissociated ammonia ($N_2 + 3H_2$) as the fluidizing and reducing gas. The UO_3 is reduced to UO_2 or "brown oxide"; the brown oxide from the fluid bed unit is conveyed through a ribbon-screw horizontal-tube reduction reactor (that had originally been used for the UO_3-to-UO_2 reduction) and discharged into another seal hopper which feeds a series of three hydrofluorination ribbon-screw reactors. The UO_2 is gradually converted to UF_4 as it is mixed and moved forward and downward through this series of reactor tubes; anhydrous HF is metered into the bottom reactor tube (solids discharge end) and flows countercurrent to the solids flow.

The Hanford orange oxide requires a more vigorous treatment to produce top-quality UF_4. This oxide is reduced to UO_2 in a fluid bed reactor, is reoxidized to U_30_8 ("black oxide"), and then is fed as black oxide to the standard bank of reactors for reduction to UO_2 and hydrofluorination to UF4.[5]

Several significant improvements during the last 15 years have led to lowering overall production costs. The first of these was the improved reaction performance realized when about 1,500 ppm (uranium basis) sulfate was added as sulfuric acid to the denitration pot charge.[6] Another involved the successful development of the fluidized bed reduction reactor' (mentioned above) in which the UO_3 is reduced to UO_2. It was realized earlier that the exothermic reduction reaction had to be done carefully so that thermal damage was not done to the UO_2 (or intermediate U_30_8) since this would lead to problems in getting high conversion levels in the UF_4 step. The 'fluid bed reactor gave the desirable, nearly uniform, temperature control for practically each oxide particle during conversion and yielded a UO2 product which could be hydrofluorinated at several times the feed rate previously employed. These improvements' permitted the simple condensation of the hydrofluorination off-gas as about 30 percent aqueous HF which is returned to the vendor for credit.

The reduction-oxidation-reduction sequence mentioned above for the Hanford orange oxide was a development that permits the processing of this material to high levels of conversion to UF_4 at acceptable throughput rates. This orange oxide is produced as spherical particles, and grinding to our required particle size distribution does not sufficiently open up the particle surfaces for acceptable UF_4 conversion levels. The ROR treatment stresses, strains, and opens the particles so that good hydrofluorination results are obtained.

Another worthwhile improvement in reducing maintenance and keeping the hydrofluorination operation on stream is the successful use of teflon-lined pipe to carry the reactor off-gases (30 percent HF, 70 percent H_2O) to the Karbate condenser system.

Other developments in the hydrofluorination processing which are reported, but which we do not use, include (1) recovery of the dilute HF from the off-gas with recycle to the hydrofluorination system[8] and (2) fluid bed reactors for the hydrofluorination step.[9] Both of these approaches have their merit's and can be of interest for particular applications. The conversion of UO_2 to UF_4 is an exothermic and highly reversible reaction, so the mode of operation with respect to temperature and $HF\text{-}H_20$ concentration must receive close attention. Our standard reference data in this area was established by our co-worker, Briggs.[10,11]

Green salt must, in addition to having an acceptably low metallic impurities content, have a high UF_4 assay to process properly in subsequent uranium metal operations (see table 2 for UF_4 specifications). Ordinarily, only small amounts of UO_2 and UO_2F_2 (<2 percent) are permissible in the green salt. The UO_2 derives from (1) incomplete conversion in the hydrofluorination operation, (2) thermal damage to the oxide in the reduction of UO_3, (3) an imbalance in the UO_2-HF feed ratio, or (4) an improper temperature/$HF\text{-}H_20$ profile in the hydrofluorination reactors. The UO_2F_2 derives from (1) an inadequate conversion in the oxide reduction step or (2) air inleakage during hydrofluorination. The significance of UO_2 and UO_2F_2 in UF_4 during uranium metal production operations will be discussed below.

Of historical interest was the production of UF_4 by the National Lead Company of Ohio using an aqueous process (WINLO) with uranium residues as the feed;'[2] this process was discontinued when techniques were developed for blending these residues into the main refinery extraction feed system. Another process noted in passing was the moving bed reactor for UF_4 production.'[3]

URANIUM METAL PRODUCTION

The production of uranium metal continues by the time-honored process developed by the Iowa State group:

$$UF_4 + 2Mg \quad U + 2MgF_2.$$

By proper blending and preheating of the ingredients, temperatures are attained by this exothermic reaction such that molten uranium and molten magnesium fluoride slag are present at the end of the short reaction period. Upon cooling, the uranium regulus (or derby, as we call it) is readily separated from the slag mass.

The uranium metal production flow diagram is shown in fig. 2. The reaction is performed inside a Cor-ten (high strength, low alloy steel) furnace pot containing a liner of magnesium fluoride slag. This insulating liner is tamped in place around a hollow mandrel on a pneumatically-operated jolter. After the mandrel is withdrawn, blended UF_4 and magnesium metal powders are charged into the lined furnace pot using a special filling machine. The nearly filled furnace pot is topped with a layer of magnesium fluoride (same material as side liner), then closed by bolting on a steel lid. The charge assembly is then placed in an electrically heated furnace operating at about 1,300°F (a thermocouple in contact with the furnace pot mid-wall is used, and the actual temperature used varies according to the nature of the UF_4 being processed). The reaction occurs spontaneously after a heating time of about 31/2 hours. The furnace pot is then removed from the furnace, air-cooled for a time, then water-cooled to room temperature. The furnace pot is then upended and jolted to discharge the contents.

The uranium regulus, or derby, is cleaned mechanically, then remelted in an induction-heated vacuum furnace with reject metal from other fabrication operations, and cast into cylindrical ingot molds for subsequent rolling or extrusion into fuel core blanks. These blanks are then precision-machined to final size.

The magnesium fluoride slag and liner are processed through a crushing, screening ball-milling circuit after which part of the material is reserved for future liner material. The rest is treated with nitric acid for recovery of the contained uranium. (For slag containing less than 0.2 percent ^{235}U, economics favor disposal rather than recovery). Generally, but not always, the slag and slag liner materials are kept segregated according to the isotopic level being processed.

The isotopic levels of UF_4 currently being processed include:

1. "Near-normal" produced by combining materials which are slightly above and below natural ^{235}U isotopic percentages so that the product approximates the ^{235}U ratio of natural uranium.
2. Slightly enriched ^{235}U materials produced from irradiated fuel reprocessing operations at the nuclear reactor operations, blended with other enriched materials to the desired isotopic level.
3. Depleted UF_4 (<0.2 percent ^{235}U) obtained from the AEC inventory associated with the gaseous diffusion operations.

The various' UF_4 sources are noted because some changes in operating technique are required to obtain optimum production results with each type. The depleted UF_4, obtained by hydrogen reduction of UF_6, has different characteristics than the UF_4 obtained by reduction and hydrofluorination of orange oxide.

Magnesium quality is another important variable in the production of uranium metal. From the early 1950's through 1964, our magnesium was obtained from an AEC contractor, Nelco Metals, Inc., Canaan, Conn., and employed the ferrosilicon process. The ingot magnesium was ground to our particle size requirements by Metals Selling Corp., Putnam, Conn. or Reade Manufacturing Co., Lakehurst, N. J. At the suggestion of the AEC, we began evaluation of Nelco cut-crown magnesium'[4] in 1964. With the cut-crown magnesium, the magnesium condensate masses from the retort operation are chopped up to a nominal 6-mesh size without going through the melting and ingot casting steps. Savings in magnesium costs by use of the cut-crown material were significant, but the higher nitrogen and oxygen content had a generally detrimental effect on the uranium metal product. In 1965, we began to review additional sources of magnesium and found that Dow Chemical Company manufactured electrolytic process magnesium which looked promising.' A difficult element to control in the electrolytic magnesium process is iron (our upper specification limit at the time was 75 ppm); Dow had produced limited quantities of low-iron magnesium by a patented process involving bubbling of titanium tetrachloride into the molten magnesium prior to casting. A significant cost was incurred in the iron removal step, and, for reasons which have never been fully understood, the magnesium had to be used in our process within narrow limits around the stoichiometric requirement, or damaging pressures were generated during the reduction reaction phase. Specifically, we found that Dow could supply a grade of magnesium containing 250 to 350 ppm iron (grade 6), and this would be satisfactory for our use" provided the range of iron values could be supplied within the 250 to 350 ppm limits; by this time, the use of controlled iron additions to the finished uranium product was an established procedure for metallurgical considerations. This Dow magnesium was phased into production use while the availability of cut-crown magnesium ceased with termination of magnesium metal operations at the Canaan plant. Our current magnesium specifications are given in table 3.

Beginning in 1966, magnesium from the national stockpile became available for our use. This material was stockpiled in the early 1950's (all ferrosilicon process, low iron content; many more tons electrolytic source, too high in impurities), and our consumption from this source has ranged from Dominion, Somerville, N. J., to Pacific Northwest and Kaiser, Hastings, Nebr., to, currently, Pacific Northwest, Sharonville, Ohio. Due to the increased requirements for magnesium metal by other consumers, Dow has withdrawn as a supplier for the uranium industry. Alabama Metallurgical Corp., Selma, Ala. has also supplied part of our magnesium requirements in recent years but has recently ceased magnesium production (the last facility in the U. S. using ferrosilicon process). We are hopeful that the magnesium of Pacific Northwest manufacture from the Sharonville Depot will continue to be made available for our use through the coming years.

The uranium tetrafluoride-magnesium reaction has been carried out on a production basis in furnace pots of widely varying sizes. These have ranged in capacity from the equivalent of only a few pounds of uranium (used primarily for highly enriched material) up to the giant "dingot" charge of 3,300 pounds of uranium developed by Mallinckrodt.[17] Our standard furnace pot is about 16 inches in diameter and produces about 350 pounds of uranium per charge. A 20-inch furnace pot was successfully developed" here. This pushed the existing reduction equipment to its limit and produced 50 percent more metal per charge. A shortage of capital funds militated against conversion to this larger reduction unit.

A number of other techniques have been investigated for the production of uranium metal. All have been discontinued short of completely successful demonstration. These include (1) an electrolytic process by Mallinckrodt," (2) a pressurized, semi-continuous reduction process by the National Lead Company of Ohio[2°] using the standard UF_4 magnesium reactants in powder form, and (3) a process using large briquetted charges[21] in a standard furnace pot. Here the main problem was the cost of the presses needed for briquette forming.

As was mentioned in the uranium tetrafluoride discussion above, a high-purity UF_4 containing only small percentages of UO_2 and/or UO_2F_2 is required for optimum uranium metal production. The UO_2, as well as any oxides in the magnesium, is incompletely reduced to metal in the process, and we believe that these oxides generally function as solid emulsifying agents for the molten metal and slag phases (low solubility in both phases) and interfere with a clean separation of the slag and metal at the end of the reaction. We also know that metal which is contaminated with oxide inclusions carries the inclusions through the subsequent remelt and fabrication steps. This results in a high reject rate in the machined uranium fuel cores (nitrogen in the magnesium metal can produce similar effects).

The UO_2F_2 can also serve as an oxide source in the metal reduction step, but its most serious effect is to increase the firing time; that is the time the reduction charge remains in the furnace until spontaneous initiation of the reaction takes place. It is usual practice to vary the furnace operating temperature in order to realize a target firing time which results in high metal yields and good_ slag-metal separation. The UO_2F_2 content of the UF_4 also has an effect on the pressure developed during the reaction phase, but the reasons for this are not completely understood. Theoretically, the reaction of UO_2F_2 and magnesium releases more heat than the primary UF_4-Mg reaction. This could, in turn, result in higher pressure from the excess magnesium in the charge. We also believe that the longer firing times associated with increasing UO_2F_2 levels would serve in a similar manner due to the higher sensible heat at initiation of the reaction phase. The higher pressures may also be the result of UO_2F_2 forming gaseous fluorine compounds (e.g., OF_2).

The green salt produced from the reduction of uranium hexafluoride is essentially pure UF_4 , but it requires attention in metal operations because of other peculiarities. The relative absence of UO_2F_2 tends to result in premature initiation of the reaction; hence furnace operating temperatures must be lowered. The relative absence of magnesium filming agents such as UO_2F_2 also appears to encourage partial reduction of the UF_4 to UF_3 as the preheating continues so that the rate-limiting step, UF_3 to uranium metal, lacks the driving force necessary for high metal yields. This high-purity UF_4 also tends to interact with the magnesium fluoride liner to a greater extent than the other UF_4 types, resulting in a slightly oversize metal regulus and lower yields due to the UF_4 combining with the liner material. To prevent the latter, we have implemented a technique borrowed from Union Carbide at Paducah which involves the uniform spraying of a small quantity of water (0.01 percent, U basis) onto the sidewall liner before placing the charge into the lined furnace pot. We have also found that this UF_4 is more sensitive to magnesium excesses than other types and that a relatively uniform application of heat to the furnace pot surface is desirable.22

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Figures and tables follow

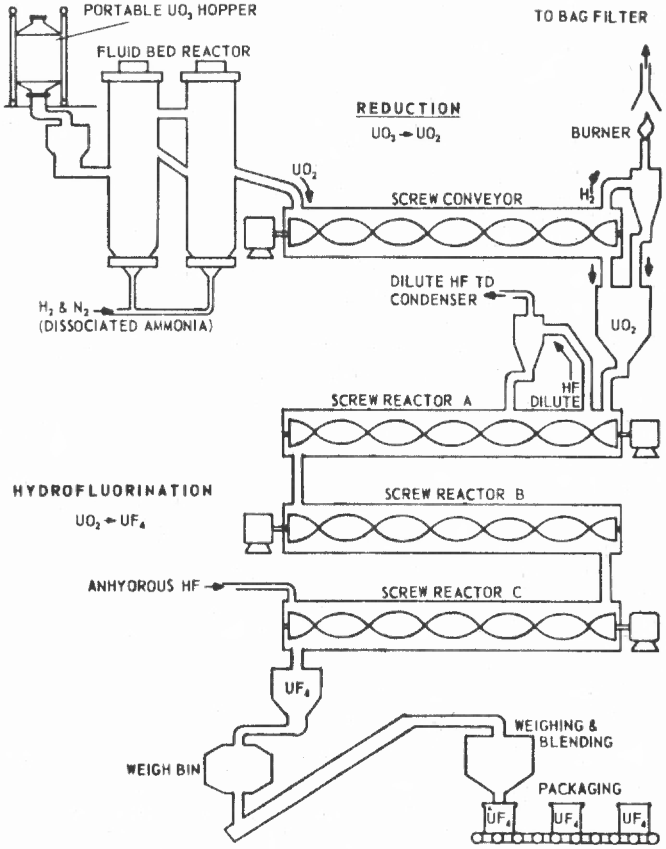

Figure 1. Uranium-Tetrafluoride Production Flowsheet

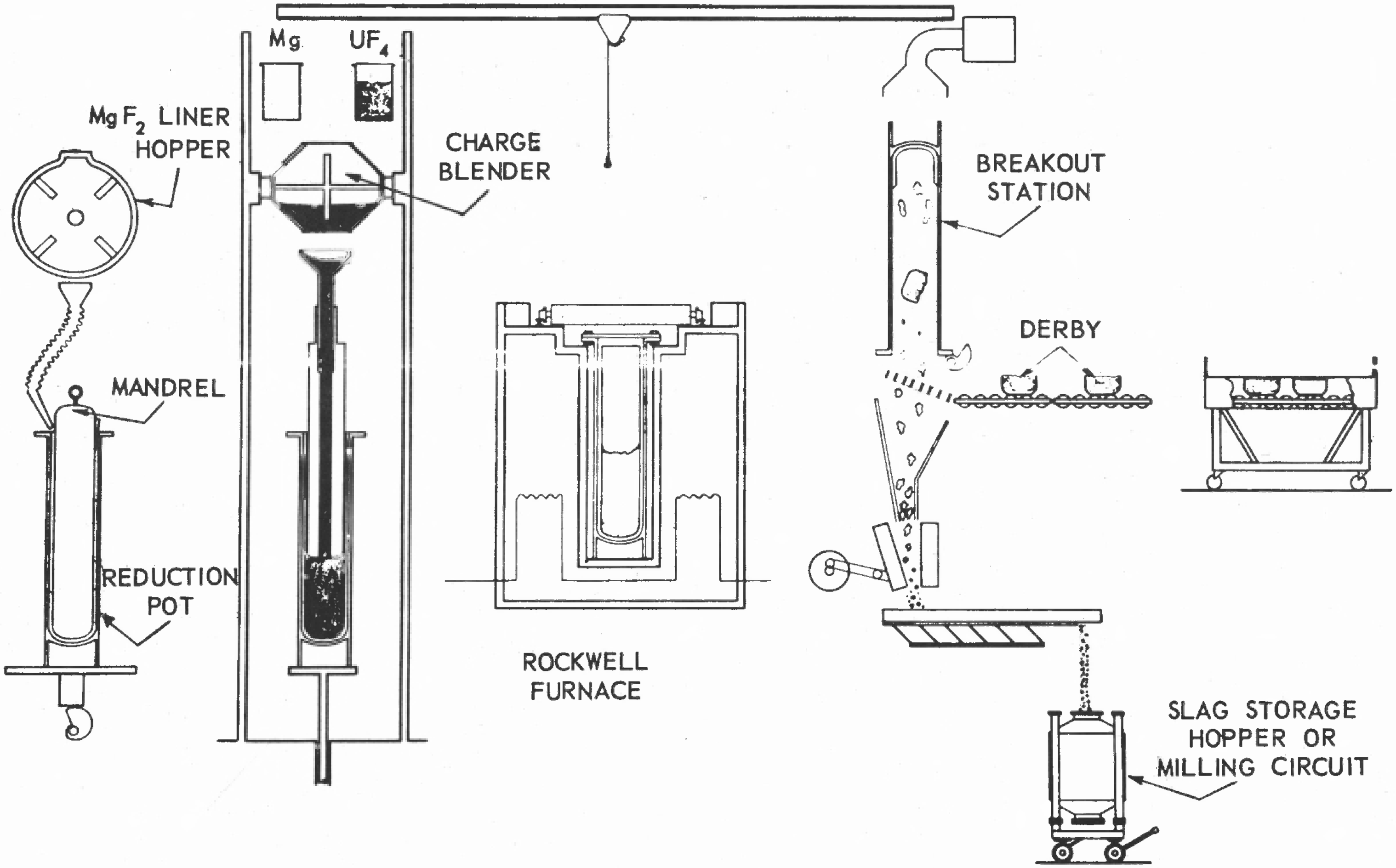

Figure 2. Uranium Metal Production Flowsheet

TABLE 1
ORANGE OXIDE (UO_3) SPECIFICATIONS FOR THE HYDROFLUORINATION PROCESS

Chemical

UO_3 assay	97.0 percent minimum
NO3	1.0 percent maximum
H20	1.6 percent maximum

Impurities	ppm (U basis) max
Chromium	20
Iron	50
Nickel	15
Sodium	25
Thorium	750
Sulfate (SO4)	1,300 minimum, 1,800 maximum

Physical

U. S. Sieve No.	Minimum, percent	Maximum, percent
+40		2
-80	85	
-325	50	70

Tap Density	3.8 g/cm³ minimum

TABLE 2
GREEN SALT (UF_4) SPECIFICATION FOR URANIUM METAL PRODUCTION

Chemical*

UF_4 assay	96.2 percent minimum
UO2	2.0 percent maximum
UO2 F2	1.8 percent maximum
H_2O	0.05 percent maximum

Impurities	ppm (U basis) maximum
Chromium	40
Copper	80
Iron	75
Nickel	80

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* The physical characteristics of UF_4 are essentially fixed by the parent UO_3 and are not specified.

TABLE 3

MAGNESIUM METAL SPECIFICATIONS FOR USE IN URANIUM METAL PRODUCTION

Chemical	
Magnesium	99.8 percent minimum
Impurities	ppm, maximum
Aluminum	300
Boron	0.3
Cadmium	1.0
Chromium	50
Copper	200
Iron	75 (or 250 minimum, 350 ppm maximum)
Manganese	75
Nitrogen	200
Nickel	50
Silica	250
Zinc	300
Zirconium	100
Others, each	100*
Physical	
U. S. Sieve No.	Percent
+10	2 (maximum)
-10 +20	50 to 66
-20 +30	26 to 40
-30 +40	3 to 10
-40 +50	1 to 3
-50	2.5 (maximum)
-120	0.2 (maximum)

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* Except oxygen and calcium which shall be included in the total impurity content maximum of 2000 ppm (0.2 percent) in order to maintain the 99.8 percent minimum magnesium content.

MICROBIOLOGICAL LEACHING OF URANIUM

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INTRODUCTION

The conventional procedure for recovering uranium is either an acid or carbonate chemical leach of the finely-ground ore. Soon after the uranium mines in the Elliot Lake area of Ontario were developed, the operators began to notice that the mine waters became acid and contained significant levels of the soluble uranium (1, 2, 17). Similar observations were made in Portugal (3) and in South Africa (4). More recently, significant quantities of uranium have been observed in the leach water from copper waste dumps (5, 16). In every case the iron- and sulfide-oxidizing bacterium, *Thiobacillus ferrooxidans,* has been found in the mine waters.

Uranium occurs in a number of mineralized forms but in the Elliot Lake area it is most frequently present as uraninite and brannerite (7). These minerals are a mixture of tetra- and hexa-valent uranium, with the latter being soluble in sulfuric acid. Since extraction data suggests that the non-soluble, tetra-valent form was being solubilized, it must have oxidized to the soluble form.

ROLE OF BACTERIA

Bacteria could play two roles in this oxidation: direct oxidation of $U^{'4}$ to $U^{'6}$, or the intermediate role of replenishing supplies of ferric iron which is known to perform the oxidation step. To the best of our knowledge there isno evidence for direct microbiological oxidation of uranium, especially by T *ferrooxidans.* Therefore, although Zajic (8) states that the amount of energy available is adequate for autotrophic growth, we will talk only about the indirect role of *T. ferrooxidans.*

The chemical oxidation and solubilization of uranium from Elliot Lake ores is shown in equations 1 and 2.

$$UO_{2_2} + Fe_{2_2}(SO_4)_3 + 2H_2S0_4 \rightarrow_4$$
$$UO_2\ (SO_4)_3^{4-} + 2FeSO_4 + 4H^{+}{}_{+} \quad (1)$$

$$UO_3 + 3H_{,2}\,SO_4 \longrightarrow UO_2\,(SO_4)_3^{4-} + H_2O + 4H^{+}{}_{+} \quad (2)$$

The ferrous iron produced can be oxidized back to the ferric form by T *ferrooxidans* according to equation (3)

$$2FeSO_4 + H_2\,SO_4 + 1/2\ 0_2 \rightarrow Fe_2\,(SO_4)_3 + H_2O \quad (3)$$

Since ferric sulfate has limited solubility, it hydrolizes and precipitates either as ferric hydroxide according to equation (4)

$$Fe_2(SO_4)_3 + 6H_20 \longrightarrow 2Fe(OH)_3 + 3H_2SO_4 \quad (4)$$

or more frequently, we believe, as a basic ferric sulfate or jarosite-type mineral, according to equation (5)

$$3Fe_2\,(S0_4)_3 + 12H_2\,0 \longrightarrow$$
$$2HFe_3(SO_4)_2(OH)_6 + 5H_2SO_4 \quad (5)$$

Both of these equations remove iron from solution and produce free sulfuric acid.

In addition to its ability to oxidize ferrous iron, *T. ferrooxidans* can oxidize insoluble sulfide minerals such as pyrite, pyrrhotite, chalcopyrite, sphalerite-, marmatite, and others. It has been shown that the bacterium attacks the sulfide and the ferrous iron portion of such minerals directly (9), producing, using pyrite as an example, both ferric iron and sulfuric acid, according to equation (6).

$$2FeS_2 + 7.5O_{2_2} + H_20\ \underline{\text{ bacteria }}\ \ Fe_2(SO_4)_3 + H_2SO_4 \quad (6)$$

In actual fact, the reactions involved are a combination of equations (5) and (6), because some iron does remain in solution, while the remainder precipitates as a basic ferric sulfate.

Equation (7) shows the overall reaction for the bacterial pyrite oxidation

$$2FeS_2 + 7.50_2 + 5H_20 \rightarrow$$
$$2/3\ HFe_3\,(SO_4)_2\,(OH)_6 + 2\text{-}2/3H_2SO_4 \quad (7)$$

The amount of pyrite is far greater than the amount of uranium solubilized so that acid is produced in excess of that required by equation (8), which is a combination of equations (1), (2) and (3).

$$UO_3 + UO_2 + 6H_2\,SO_4 + 1/2\ O2$$
$$2UO_2\ (SO_4)_3^{4-}{}_4 + 2H_20 + 8H^{+} \quad (8)$$

The role of bacteria in the microbiological leaching of uranium appears to be confined to the regeneration of the chemical oxidant, ferric iron, and the production of the solvent, sulfuric acid. There may be an additional indirect effect in that oxidation and removal of the associated sulfides may expose additional uranium to the chemical oxidant and solvent.

ENHANCEMENT OF BACTERIAL ACTIVITY

In order to enhance the microbiologically-associated solubilization of uranium, it is necessary to promote the microbiological oxidation of ferrous iron and, if present, pyrite. Since the energy released during these oxidative steps can be used for growth by the bacterium, and growth is the sole reason for the occurrence of the bacterial oxidation, the leaching environment should be optimized to promote rapid growth of the bacteria.

The important factors in the microbiological oxidation of sulfide minerals are adequate numbers of the leaching bacterium, T *ferrooxidans;* adequate supplies of moisture; the correct pH; an available energy source; an adequate supply of oxygen and carbon dioxide; an adequate supply of essential nutrients, and the absence of any inhibitors. We have been working on the optimization of these requirements for a number of years and I would now like to talk about this work in some detail.

Thiobacillus ferrooxidans has emerged as the correct name for the only species of bacteria capable of oxidizing ferrous iron and insoluble sulfide minerals (10,11). It is a chemoautotrophic bacterium, which means that it obtains its energy from the oxidation of inorganic compounds and utilizes carbon dioxide as its sole carbon source. It is a soil micro-organism which invariably can be found wherever acidic conditions occur in nature in association with either ferrous iron, sulfur, or mineral sulfides. As is typical for this type of bacterium, it has a relatively slow generation time. Values of approximately 6.5 hours have been reported from our laboratory, as the time for one cell to divide into two, using ferrous iron as an energy source (12). On chalcopyrite it required 14-17 hours. In the natural environment however the time is undoubtedly much longer. Bacterial growth is exponential and thus, once a moderate population has been established, the increase in actual numbers will be quite rapid if conditions are favourable. If a moderate population is not initially present, it can be introduced by inoculation, using bacteria especially grown for the purpose, or material from an area of high population. In this regard, sediments are usually better than clear water because T *ferrooxidans* has a marked preference for attaching itself to solid surfaces (12).

Bacteria require a moist environment. It can be as little as a film of moisture on a particle surface, through to complete submersion. This moisture acts as a vehicle for transferring the nutrients, oxygen and carbon dioxide, required by the organism, as well as for removing the products of its activity. It also permits this motile organism to move to other surface areas. We are currently attempting to establish the minimum moisture level that will support the activities of *T. ferrooxidans.*

The aqueous environment also permits the establishment of the pH levels required by T *ferrooxidans.* It has been shown that our strain will only oxidize ferrous iron over the pH range of 1.4 to about 3.5, with an otpimum at pH 2.5 (12). Oxidation of sulfide minerals occurs over the range 1.2 to 3.5, with an optimum between 1.8 and 3.5.

Other workers have found that their microbiologically assisted uranium leaches occurred over the pH range 2 to 2.5 (1,13,14), although on occasion the pH dropped to as low as 1.3.

Once the bacteria have been introduced into an aqueous environment of the correct pH, they will begin to oxidize the substrate available in order to obtain the necessary energy for growth. In natural situations the environment may be extremely small initially, say, the surface of a pyrite crystal surrounded by host rock associated with calcite. The bacteria will attack the pyrite, producing acid which neutralizes the surrounding calcite and thus acidifies and expands the environment. Eventually the acidified zone will reach the next particle of pyrite and the process will intensify. If the bacteria run out of substrate or some other essential nutrient before the acidified zone expands, the whole system comes to a halt. Where economically feasible, man helps the bacteria become established by adding sulfuric acid to insure the maintenance of the acidic zone.

In order to oxidize the available substrate, the bacterium must be capable of completing the oxidation reactions and utilizing the energy obtained. Completion of the oxidative process requires oxygen as the ultimate electron acceptor. Once the electron has been extracted from the ferrous iron or sulfide, it, and a substantial part of the reaction energy, is sequentially passed down an enzyme chain until it finally is used to reduce oxygen. At each step in the chain, energy is progressively removed and, stored. This energy removal by the bacteria is responsible for the fast bacterial oxidation rates compared to chemical oxidation rates. Thus the availability of oxygen to act as the electron acceptor can be a limiting factor. On this basis, a thin film of moisture which permits rapid oxygen transfer is far preferable to a submerged situation, since oxygen transfer into this water is limited by the air-water surface area.

Once the energy has been removed by the bacteria it must be utilized for growth or again the reaction stops due to saturation of energy stores. The major use for energy is "fixing" carbon dioxide into cellular material. Since the bacteria can use only dissolved carbon dioxide, and not carbonate or bicarbonate ions, the supply must be continually replenished from the air or through the chemical reaction between Sulfuric acid and limestone. In addition, cellular material is made up of many other components such as hydrogen, nitrogen, phosphorus, calcium, magnesium, etc. In our laboratory studies we have only been able to demonstrate a requirement for a nitrogen and a phosphorous source. Everything else seems to be supplied, in the trace amounts required, by the host rock.

Nitrogen cannot be supplied as the gas, or as nitrite or nitrate (15). The most practical source is the ammonium ion. Since there is very little ammonium ion naturally present in the ore, we feel that it frequently is a limiting factor and should be added as ammonium sulfate. A lack of ammonia nitrogen limits the total bacterial populations which can develop and thus ultimately will limit the extraction attainable.

Phosphorus is required as phosphate, and in many cases there are sufficient supplies available naturally. In living matter, the primary function of phosphate is transferring and storing energy. Its availability controls the rate of oxidative reactions and thus controls the rate of extraction if there is no other limiting factor.

Now that we have provided the bacteria with an aqueous environment at the correct pH, and with adequate supplies of substrate, oxygen, carbon dioxide and nutrients, it should oxidize ferrous iron or pyrite rapidly. However, in actual practice there may be a problem of end-product toxicity, depending on the source of the bacteria. Goren (21) found that freshly isolated organisms are not tolerant to uranium and we have found that our strain of *T. ferrooxidans* was inhibited (16). We know that cations such as hydrogen, copper, zinc, nickel, etc. do not bother this organism. We have had the organism growing in copper and zinc concentrations as high as 56 and 120 g/1 respectively. However, high concentrations of anions, with the exception of sulfate, generally appear to be inhibitory. When uranium dissolves in sulfuric acid, the uranyl sulfate ion formed is negatively charged and thus can be inhibitory. The bacterium can be adapted to this ion (16,21) and we have observed strains active in uranium mines at concentrations in excess of 12 g/1 U_30_8. The levels a particular strain of bacteria can tolerate may influence the frequency with which a bacterial leaching operation should use a wash-down in order to remove solubilized uranium.

COMMERCIAL PRACTICE

Our laboratory studies into the requirements of the leaching bacteria have suggested that the leaching area should contain an energy source, it should be kept damp but not flooded, it should be within the pH range 2 to 3, there should be adequate ventilation to supply the required oxygen and carbon dioxide and there should be a supply of ammonium sulfate and phosphate available to the bacteria. Ideally, the temperature should be around 35˚C but bacterial activity will continue, although at a depressed rate, down to at least 3˚C. The area should be washed at a time when either all the available ammonium ion has been used up or the concentration of soluble uranium becomes inhibitory.

The techniques used for the commercial leaching by microbiological action in the uranium mines at Elliot Lake have been published (7,17,18,19), and the desirability of a cyclic washing process and of an acidic pH value are well documented.

Increased production on a commercial scale is the ultimate aim of our microbiological leaching research program and early in 1967 we had an opportunity to apply our laboratory results to such a commercial operation. Rio Algom Mines Ltd., one of our program sponsors, asked us to study the leaching operation at their Nordic Mine in Ontario. This underground uranium mine follows leaching procedures as outlined for the Milliken Mine (18). Company records showed a peak in production during August and September, a low value usually occurring in February, and then relatively stable production at approximately 50 percent of the peak level for the remainder of the year. In addition the greatest output from an individual stope usually occurred during the first washing, then it dropped sharply and did not show any signs of increasing until after three or four washing cycles. When production did increase it never approached the output obtained during the first washing.

During our initial visit to the mine in February it was evident that the stopes were excessively dry, muck moisture content being as low as 0.2 percent. When we revisited the mine in August, it was damp, with condensate evident on the back and walls. Laboratory studies carried out on the mine water after the initial visit indicated that it was nutritionally inadequate for microbiological leaching.

On the basis of these observations a series of 14 experimental stopes were prepared and subjected to different environmental leaching conditions. Some were kept damp by monthly spraying, some were sprayed continuously, and others were treated by the company's normal leaching practice of applying water every three months as part of the washing cycle. In addition, both wet and dry stopes were treated with various combinations of ammonium sulfate, potassium phosphate and ferrous sulfate. The ferrous sulfate was included because of the chemical role ferric iron plays in the oxidation of tr^4 to U". All the stopes, with the exception of the continuous-spray stopes, were washed manually with high-pressure hoses in the normal manner every three months (18). Nutrients were added after washing when required, either by broadcasting dry salts or by spraying a concentrated solution.

Since the stopes varied in size, quantity of muck and uranium grade, the results of our tests have been expressed in terms of lbs of U_30_8 extracted per manhour washing.

Presented in fig. rare the results from the stopes which were kept wet between the washing periods. It can be seen that the four stopes that received nutritional supplementation showed a relatively constant cumulative extraction rate. Stope 1015W, which did not receive any nutrients and was washed for the first time in July rather than in April, showed the decline in cumulative production typical of the leaching process the company was using at that time. The two stopes which were sprayed continuously and did not receive nutritional supplementation gave extraction curves identical to stope 1015W.

The curves show that the stope which had only ammonium sulfate added performed equally as well as those stopes that had ammonium sulfate plus phosphate and ferrous sulfate added. Stope 1112W, which had 25 lbs of ferrous sulfate added, performed very well. This iron, once in solution, is oxidized rather easily by the bacteria and the resultant ferric iron is thus available in large quantities for the uranium oxidation.

Fig. 2 presents the results from the stopes which were kept dry, between washings, as was normal practice. It is quite noticeable that the cumulative production from the stopes generally tended to decline. Stopes 1114E and 1115E each had 40 lbs of Medium 9K salts spread in powder form over the muck. Stope 1115W had the same amount of salts added but they were dissolved in H_2O and applied by spraying. No difference can be noted however between the shape of the three curves.

The results from the experimental stopes indicate that the addition of both ferrous sulfate and ammonium sulfate was no more beneficial than the addition of either one alone.

In summary, the experimental results showed that initial production rates were maintained or exceeded in those stopes that were kept damp and had nutrients added. When no nutrients were added, production rates declined in a manner similar to the results obtained in the control and non-experimental stopes. Production declined in all the stopes which were not kept damp between washing, regardless of whether or not nutrients were added.

During the time of this experiment, production in January and February increased by approximately 30 percent which is quite significant when it is considered that only 4 experimental stopes out of approximately 50 under leach were operating under optimal conditions. Thus a technique for increasing overall production was verified.

The marked cycling in production could be explained, at least in part, by the mine being damp in the summer months due to the moisture-laden, outside air cooling in the mine and losing moisture. This resulted in a leaching environment more favourable to microbiological action which showed up in the fall washings as increased production. In the winter the cold, dry outside air was warmed in the mine and picked up moisture, thus removing moisture from the leaching stopes and inhibiting bacterial action.

Humidifiers have now been installed to alleviate this problem. The company has recently informed us that better regulation of air flow and humidity, plus improvements in nutrient addition and leaching techniques, have pretty well eliminated the cyclic situation. In addition, production has now increased by about 50 percent.

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Figures follow

Figure 1
CUMULATIVE U_3O_8 EXTRACTION IN WET STOPES

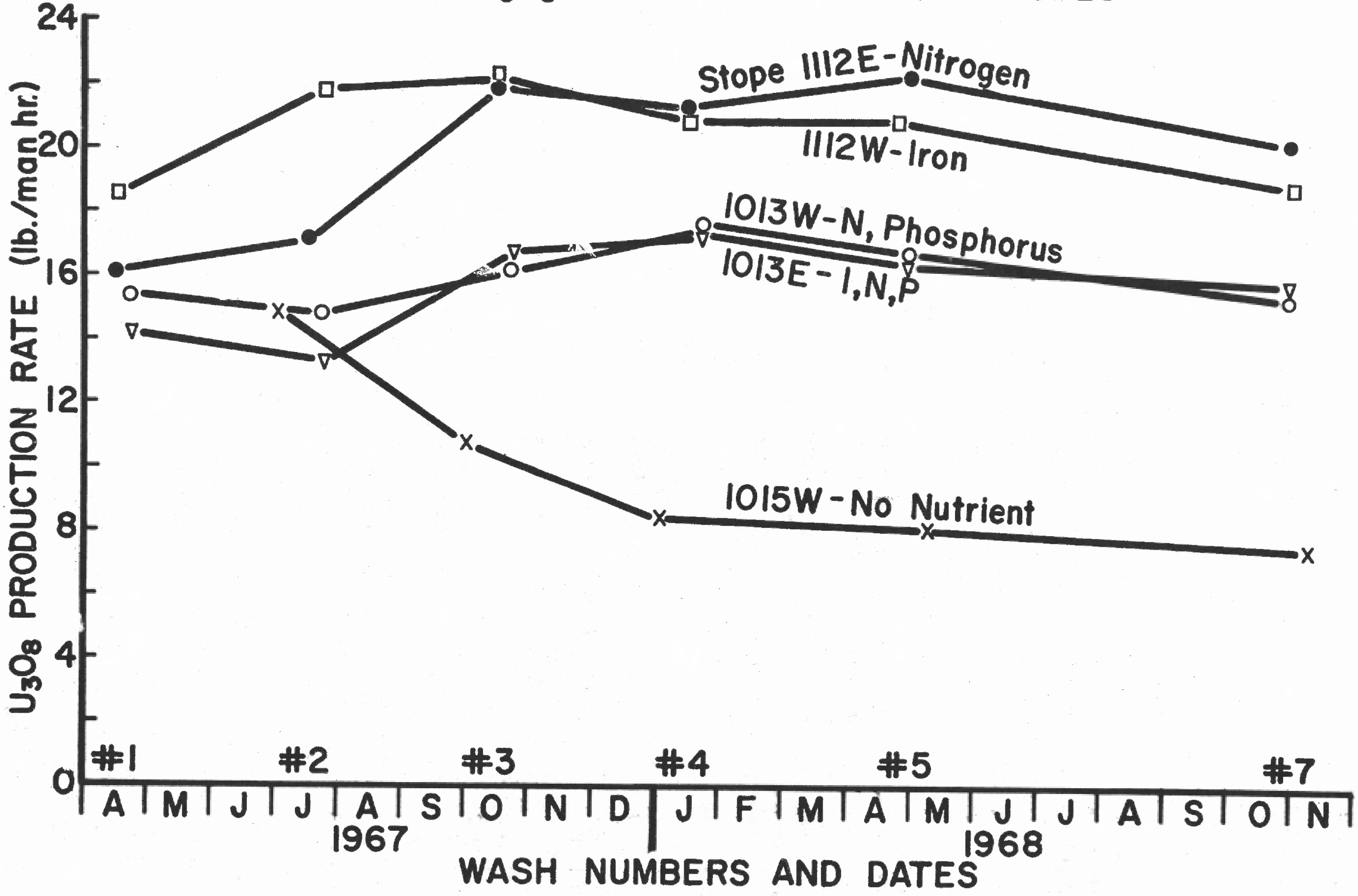

Figure 2
CUMULATIVE U_3O_8 EXTRACTION IN DRY STOPES