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Well Construction Information for In Situ Uranium Leaching

By Daryl R. Tweeton and Kevin Connor



UNITED STATES DEPARTMENT OF THE INTERIOR Cecil D. Andrus, Secretary BUREAU OF MINES

UNIVERSITY OF UVAH RESEARCH INSTITUTE EARTH SCIENCE LAB.

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering the wisest use of our land and water resources, protecting our fish and wildlife, preserving the environmental and cultural values of our national parks and historical places, and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to assure that their development is in the best interests of all our people. The Department also has a major responsibility for American Indian reservation communities and for people who live in Island Territories under U.S. administration.

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WELL CONSTRUCTION INFORMATION FOR IN SITU URANIUM LEACHING

by

Daryl R. Tweeton¹ and Kevin Connor²

ABSTRACT

This Bureau of Mines publication describes present practices of making injection wells for in situ uranium leaching. Casings, screens, drilling fluids, coring, logging, cementing, and developing are discussed with the objective of aiding those who are starting an in situ leaching operation. Improper choices of materials or techniques can result in wells that are either useless or wells that have an undesirably high resistance to injection. Important factors include careful selection of screen slot size, use of logs for choosing the cementing basket depth, proper cementing techniques, and careful choice, use, and flushing of drilling fluids. The information was obtained through observation of well construction and through discussion with in situ leaching companies, drillers, and suppliers.

INTRODUCTION

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In situ leaching consists of injecting chemicals (lixiviant) into an ore body, dissolving the desired mineral, and pumping the lixiviant and dissolved minerals out of the ore body. Usually separate wells are used for injecting and recovering the lixiviant. In situ leaching has the following advantages over conventional mining: smaller capital cost for small or deep deposits, shorter lead time before production, minimum surface pollution, lower labor costs, and improved safety for workers. It thus can make feasible the recovery of uranium from deposits that are too small or too low-grade to profitably recover by conventional mining.

Despite the potential benefits, in situ leaching contributes only a small fraction of our national uranium production. Therefore, the Federal Bureau of Mines is conducting research to improve technology with the anticipation that in situ leaching will contribute more to the Nation's uranium production and reserves.

Research physicist. Mining engineer. Both authors are with the Twin Cities Mining Research Center, Bureau of Mines, Twin Cities, Minn. Research at the Twin Cities (Minn.) Mining Research Center began in 1975 in cooperation with a private company at an experimental test site in Wyoming. The study demonstrated the importance of properly constructing injection wells. The first set of wells had a high resistance to injection despite several attempts at acid flushing. So little lixiviant could be circulated that the leaching test was not a reliable basis for planning commercial operation; therefore, the test was repeated the following year with better wells. Discussion with other leaching companies showed that well clogging was a common problem, and that the degree of clogging was strongly influenced by well con struction techniques. Without good injection wells, not enough lixiviant contacts the ore to provide good uranium recovery.

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FIGURE

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There is little public literature on injection wells for in situ uranium leaching. However, some literature on other types of wells was found to be useful. Reference $(\underline{7})^3$ discusses planning and constructing water wells, ground water movement and chemical characteristics, testing wells, screen selection, drilling and developing wells, and pumps. However, techniques that are suitable for water production wells are not necessarily suitable for injection wells. Lixiviants are far more corrosive than ordinary water. Also wells usually have more fluid resistance to injection than to recovery.

Brown and Silvey (2) described some of the causes and cures for clogging in certain recharge wells. They concluded that clogging was largely caused by dispersion of interstitial clay, and that suitable clay stabilizers such as calcium chloride could minimize clogging during injection. White, Baptist, and Land (9) also concluded that clay dispersion, not clay swelling, was the dominant factor in reducing the water permeability of certain cores.

The lack of public literature on wells for leaching makes it difficult for companies that are just beginning in situ uranium leaching to avoid repeating mistakes made by others, so the Bureau prepared this circular describing current practices. A future report will describe investigations into improved methods. An overview of Bureau research on this and related topics is given by Olson, Larson, and Tweeton (4).

ACKNOWLEDGMENTS

Much of the information relating specifically to in situ leaching wells was obtained in discussions with Intercontinental Energy Corp. (IEC), Denver, Colo., and Tep-Cor, Inc., Alice, Tex., as a result of a cooperative agreement between IEC and the Bureau of Mines.

WELL DESIGN

Important considerations in the design of the well include the type and diameter of the casing and the type and slot size of the screen.

³Underlined numbers in parentheses refer to items in the list of references the end of this report.

Casing

Although some companies use 5- or 6-inch-diameter casing to allow a 11s. arger pump to be installed, the most common casing diameter is 4 inches, hich allows 4-inch screens to be used and provides adequate screen area for fuid flow. This diameter allows small submergible pumps to be used. The ption of installing a pump in an injection well is useful during well develtoment and during postleach restoration of the water quality, even though the mp is not left in the well during leaching. This option also permits later nonversion of an injection well to a recovery well. **ο**π -

The most common casing material is polyvinyl chloride (PVC) plastic which as replaced stainless steel because PVC is much cheaper. A disadvantage of ,um installing PVC during Wyoming winters is that the glue does not set properly then colder than 4°C (40°F).

An alternative which makes glue unnecessary is Yelomine⁴ PVC pipe manu-:hat actured by Certain-Teed Products Corp., St. Louis, Mo. It uses a patented connector in which a nylon strap is slipped around the joint in a special 1so, moove to hold the coupling secure. An O-ring inside the coupling prevents Yelomine is slightly more expensive than standard PVC, but it is eaking. laimed to be stronger. Wells deeper than 500 feet are sometimes cased with Ing iberglass which is stronger than PVC. l by





FIGURE 1. - Tapered screen slots minimize plugging from

sand grains.

Screens

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Just as for casings, plastic screens have replaced stainless steel because of its cheaper cost. There are several manufacturers of plastic well screen each claiming advantages. All of the screens have tapered slots with the narrowest part of the slot to the outside which minimizes plugging with sand grains (fig. 1). A grain small enough to enter the

⁴Reference to specific equipment (or trade names or manufacturers) is made for identification. only and does not imply endorsement by the Bureau of Mines.

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narrowest part of the slot is unlikely to be trapped in the wider parts of the slot. If the slot is not tapered, grains are more likely to be trapped part way through. The type of screen having the greatest open area is wound over thin plastic ribs, and it is sold by Johnson Div., Universal Oil Products, St. Paul, Minn. A different design, which gives less open area but more strength, is wound over a plastic pipe containing closely spaced holes and it is available from Well Supply, Inc., and Wesco, Inc., both of Houston, Tex.

The slot size should be chosen carefully to allow optimum well develop: ment. Too small an opening will not allow enough of the fine material from near the well to be flushed through the screen and pumped out. Too large an opening will allow material from the formation to continue to flow through the screen. A common recommendation is to choose a slot size that allows 60 wt-pct of the material to pass through. This slot size is usually from 0.008 to 0.025 inch (0.20 to 0.63 mm). Thus, cores must be taken for grain-size analysis (7, p. 179) before selecting the slot size.

An alternative to conventional screens is to case and cement the well to the bottom of the deposit, then use a water-jet device developed by the Bureau of Mines to perforate the casing and cement. This method has the advantage that the perforation pattern can be tailored exactly to the deposit. The perforator, described in a Bureau publication by G. A. Savanick (5), uses a 10,000-psi water jet to make small holes through the casing and cement that are small enough to provide sand control.

Another alternative is to case and cement to the bottom of the deposit, then remove the casing and cement by underreaming at the desired depths. If the formation is sufficiently consolidated, no screen is necessary. If the formation is poorly consolidated, a telescoping screen of smaller diameter, than the casing is slid into position after underreaming.

DRILLING

Of the several methods of drilling, the most common is hydraulic rotary drilling where the drilling fluid is liquid. Foam and air drilling have also been used successfully.

Foam and air drilling are similar in many ways to hydraulic rotary drilling, except the drilling fluid that carries the cuttings up is foam or air instead of liquid. Since hydraulic rotary drilling is much more common, this circular will emphasize drilling with liquids.

Hydraulic Rotary Drilling

Hydraulic rotary drilling is well-known and described in reference (7, p. 47). The choice, use, and flushing of drilling fluid is very important. Any drilling fluid that is not removed during development will be forced into the formation during injection and hence it will contribute to clogging. Drilling fluids made from bentonite are especially prone to cause clogging because bentonite is hard to remove and swells.

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Drilling fluids made from guar gum are less likely to cause clogging than bentonite, and they are often used in drilling injection wells. Examples of such fluids are Revert (8), sold by Johnson Div. of Universal Oil Products and Loloss (3), sold by Baroid Services Div., NL Industries, Inc. The advantage claimed is that guar gum drilling fluids can be broken down to a fluid having the viscosity of water by enzymes or chemicals after drilling is completed. However, there are conditions where guar gum fluids will gel and resist break-The literature describing Revert states that a combination of cering down. tain chemical constituents in the water such as boron, copper, aluminum, and calcium, coupled with a pH over 8, can cause gelling. The same literature suggests methods for treating the water to avoid gelling. The amount of the chemical constituents that can be present at a given pH before gelling occurs has not been published. When using the fluids it is important to follow all the manufacturer's directions including the warnings of the effects of trace chemical constituents and improper pH. This seemingly obvious advice is stated because the Bureau has encountered several instances of clogging where failure to pretest the water and insure its suitability may have been a contributing factor. In hot weather it may be advisable to preserve guar gum drilling fluids with formaldehyde to prevent them from breaking down before the drilling is completed.

Newer fluids are being recommended by some manufacturers. For example, aroid now recommends Drispac or Quik-trol rather than Loloss for drilling injection wells. Drispac is a polyanionic cellulose polymer (3) which has been used successfully for drilling injection wells. Quik-trol is an organic polymer (3). Baroid indicates that these two drilling fluids are more effective than guar gum fluids at encapsulating clays and hence preventing the buildup of a fine clay suspension on the borehole wall.

Baroid stresses the need to control the solids content of the fluid by removing clay particles during drilling. Equipment is available for this purose, and some of it is small enough to be used during injection well drilling. The buildup of solids was a problem at the IEC site which was attributed to the portable mud pits being too small to allow adequate settling of the susended particles. It would have been preferable to use larger pits, but this is prevented by extremely wet conditions.

Drilling wells straight and vertical is important for several reasons. A tooked hole makes it difficult to lower the casing especially with a cementby basket. Casings have broken when excessive force was used. A crooked ble also makes it difficult to lower a submergible pump down the casing if the pump is long and its diameter is only slightly smaller than the casing. If the holes are not vertical, the well pattern at the ore depth will differ fom the surface pattern. This may lead to poor distribution of the lixiviant.

Using as small a downward thrust (pulldown) as practicable at the top of the drill string will help insure a straight hole. Applying part of the nectosary force downhole with two drill collars worked well for Tep-Cor at the the the drill string tends to the the drill go crooked, but weight applied near the bottom of the string telps the drill go straight and vertical. Most companies do not try to drill

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FIGURE 2. - Tailpipe with sediments accumulation.

the full-diameter hole in one pass. Drilling a pilot hole a little more than half the final diameter requires less downward thrust and yields a straighter hole. However, one company has found that using more drill collars and a high bit rpm allows straight holes up to 6-3/4-inch diameter to be drilled in one pass. The Bureau's experience suggests that, in an ordinary formation, a careful driller can avoid being more than about 6 feet out-of-vertical at a depth of 250 feet when using a pilot hole.

The final diameter must be large enough to accommodate the casing with its couplings and cementing basket if used. This is considerably larger than the nominal inside diameter (ID) casing size. For example, a 4-inch ID casing requires a borehole diameter of at least 6-3/4 inches. Tep-Cor preferred 7-3/8-inch-diameter boreholes to facilitate installing the casing. The outside diameter (OD) of the couplings is about 5 inches. There must be room for the cement to flow up the annulus between the casing and the formation to allow a good seal. Trans

The hole must be drilled deeper than the screen bottom to allow for some material sloughing to the bottom of the hole and for a tailpipe to extend below the screen. The tailpipe is a piece of casing, usually 5 to 10 feet long, attached to the bottom of the screen and capped at the bottom end. This allows material to settle in the tailpipe without blocking the screen as shown in figure 2. Placing about a foot of plaster of paris in the cap helps prevent drilling through it.

Foam and Air Drilling

Foam or air drilling offers the promise of minimizing the lowpermeability skin on the borehole wall. However, it provides less support for the borehole wall and hence increases the risk of collapse.

Air drilling was used successfully in a Wyoming operation. The welled were drilled to a competent layer above the uranium-bearing zone using a guar gum based drilling fluid. A 6-inch-diameter casing was installed and cemented. Then a hole for a 4-inch-diameter screen was drilled through the uranium bearing zone using compressed air as the drilling fluid. The hole was full of . water, a 4-inch-d . The scre . space be

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The is and he moducts moducts. ater, and the air and water made a froth that carried up the cuttings. A inch-diameter screen was slid down the 6-inch casing to the desired depth. the screen was capped at the bottom and had a packer at the top to seal the mace between the screen and casing.

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This method produced wells having a low resistance to injection. Those the try this method should keep in mind that a poorly consolidated formation ay collapse before the screen can be installed. Various manufacturers offer foam drilling fluids that provide better wall support than air and water.

CORING

Coring poorly consolidated deposits is difficult. Part of the core may e washed out of the barrel during drilling. Also, the core may stick in the Marrel so hard that forcing it out breaks it up. Double-tube core barrels (1, p. 181) prevent the drilling fluid from flowing over the core in the bartel and hence help keep the core from washing out. Split-tube core barrels have an inner tube that is in two parts allowing the core to be lifted out when the tube is open and thus eliminating the need to force the core out the the end of the barrel.

Excellent core recovery was obtained by Tep-Cor Drilling Co. at the IEC site with a simple solid-core barrel. The drifling fluid was Revert at a Marsh viscosity (7, p. 222; 3) of 50 sec. This is slightly thicker than the 40-sec Marsh viscosity used during drilling, but it is near the viscosity tange recommended for Revert (8, p. 4). Core drilling was done slowly to woid forcing the core tightly into the barrel. Coring 10 feet took 1 to 2 Sours. Essentially no pulldown force was applied, so the force on the NX-size bit was from the weight of two drill collars, each weighing 300 to 400 pounds, and 250 feet of drill string. To minimize core washout, the mud pump was Nowed until it was just adequate to bring up the cuttings. Most of the 10bot core sections could be pushed out of the barrel with a rod. If more force was needed, the mud pump was connected to the barrel and the core was Numped out. This step had to be done carefully because once the core started to move, it moved easily. If excessive pressure was used, the core could be ejected so rapidly that it went over the core table and fell on the ground.

For those who are new to coring, Acker (1) is a useful reference. Most Wpes of coring and related drilling are discussed, and previous experience is t assumed.

LOGG ING

Well logging is performed on the uncased hole. Three logs aid in decid-^{In}g the exact depth to set the screen and cementing basket. These logs are Atural gamma, resistivity or resistance, and caliper.

nted. The natural gamma log helps in deciding where the highest uranium grade ¹⁶ and hence where to set the screen as shown in figure 3. Uranium decay Products emit gamma rays and, if the uranium has not moved away from its decay Noducts, the areas of highest natural gamma rays correspond to the areas of



FIGURE 3. - Gamma lag-well profile comparison.

highest uranium content. The gamma log is referred to as a "natural" log to distinguish it from induced gamma logs, where a radioactive source is in the probe and gamma rays from the artificially produced nuclides are measured.

A resistance or a resistivity log is used in deciding where to set the cementing basket, which must be set in a competent zone of shale or other vell consolidated material to prevent seepage into the screened zone. A resistivity log measures the resistivity of the formation between the ends of the probe. A resistance log, which is more common, measures the resistance from point on the surface to the downhole probe. These logs can help indicate the proper place for the basket because the resistivity of fine-grained material such as shale and clay is lower than that of coarser grained material such as sand.

The caliper log indicates the diameter of the hole, and it also indicated if sloughing has occurred. The caliper has spring loaded fingers that are extended once the tool has been lowered to the bottom of the hole (fig. 4). The caliper is then brought up the hole constantly measuring the hole diameter. The cementing basket must not be placed in a zone that has sloughed.



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INSTALLING CASING AND SCREEN

After logging is completed, the casing and The screen are installed. first step is to measure and cut the casing so that the screen and cementing basket will be at the chosen depths. The tailpipe is then capped and attached to the bottom of the screen. Small holes should be drilled in the casing just below the cementing basket plug to allow air to escape as the assembly is lowered

FIGURE 5. - Casing operation using PVC pipe.



FIGURE 6. - Centralizer.

should be installed as soon as possible after drilling and logging are completed. If installation is delayed, the risk of clay swelling and sloughing are increased. In one instance, a caliper log showed that clay swelling reduced the diameter of a 6-3/4-inch hole at one point to 5-1/2 inches. Instead of reaming out that point, the driller forced the casing down the hole. The cementing basket stuck at the narrow point, and so much thrust was applied to force the casing down that it broke below ground. The casing could not be retrieved, and the well was lost (fig. 7).

into the water, "Weep holes" of 1-inch diameter are drilled above the plug.

The hoist on the drill rig holds the screen and casing as they are lowered into the hole and connected as shown in figure 5. If glued casing connections are used, screws are also put through the couplings for extra strength.

A centralizer (fig. 6) is slipped over one or more of the casing sections to keep the casing centered in the hole permitting the cement to seal all sides. The centralizers as purchased have six staves (sidebars). At the IEC site, alternate staves were removed, because the staves were quite stiff and a large amount of force was required to push them down the hole with all six staves attached.

One should be careful not to overshoot the depth when lowering the casing. The basket may be ruined if the casing is pulled up more than the distance, about 2 feet, that the basket can slide on its section of casing.

The casing and screen

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results in a loss or dilution of leaching solution and possible escape of pollutants. Portland type I cement is often used, with about 6 or 7 gallons of Water per 94-pound sack of cement. Some companies have used up to 14 gallons of water per sack. However, cement tends not to stay in suspension with more than 10 gallons of water per sack. Also, shrinkage increases as water content increases. To reduce shrinkage and help insure a good seal, 1 to 4 pounds of juld bentonite per sack of cement can be added.

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FIGURE 9. - Control of fluid injection direction through cementation.

The method of placing the wet cement slurry is important. If it were is merely poured along side the casing, adequate sealing would be unlikely. The cement would bridge the gap above spots where the casing was close to the formation.

The Texas Water Quality Board requires the casing method of cementing (7, p. 242). In the variation of this method used for in situ leaching wells, a cementing basket (fig. 10) is attached to the casing above the screen before the casing is lowered into the well. The basket comes on a short section of casing that contains plaster of paris and a plywood plug. The cementing basket is attached so that it will be at a shale or other competent layer above the ore. Holes of about 1-inch diameter called weep holes are drilled either in the casing attached to the basket or near the bottom of the next higher casing (fig. 11).

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After the casing has been lowered into position, the wet cement slurry is Aunped down the inside of the casing and flows out the weep holes above the Aunped down the inside of the casing and flows out the weep holes above the Aunor the screen, and it forces the cement to flow up the annulus between the Austring and the borehole wall as shown in figure 12. After a volume of cement Aufficient to fill the annulus has been injected, water is pumped into the Austring to force or "chase" most of the cement out of the casing, through the Auge holes and up into the annulus. Volumes are chosen so that some cement is



FIGURE 12. - Cementing operation.

left in the casing as shown in figure 13. After the cement has set, the excessive cement and the plug in the cementing basket section are drilled out. The well is then ready for development.

Incomplete sealing may result if much sloughing occurs above the **cement**. ing basket. Ordinarily, a small amount of sloughing at one point will not seriously impair the sealing, since the cement will isolate this spot. However, if substantial sloughing occurs, the seal may be poor over enough distance that some aquifer mixing may be possible. For this reason, it is desirable to minimize the time between lowering the casing and cementing. Letting the casing stand overnight in the hole without being cemented should be avoided whenever possible.





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If the cementing basket is not making good contact with a competent shale or other layer, the cement may be able to pass the basket and cover the screen. This can happen if there is sloughing at the basket, as in figure 14, or if the fingers of the basket are bent in during the setting of the casing and do not spring out again. There are cementing baskets with fingers that will not spring back after being pressed against the casing; these should be avoided.

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An alternative to the casing method of cementing is to force the cement through a small pipe outside of the casing (7, p. 240), if there is sufficient space between the casing and the borehole wall. How-

ever, most companies appear to favor the casing method.

DEVELOPING

Well developing is defined as "those steps in completing a water well that aim to remove the finer material from the aquifer, thereby cleaning out, opening up, or enlarging passages in the formation so that water can enter the well more freely" (7, p. 295). Proper well development is essential for both injection and recovery wells, but it may be impossible if the wrong drilling fluid is used, if the drilling fluid is used incorrectly, or if the screen slot size is incorrect.

Wells can be developed either by gravel packing or by natural develop ment. Natural as used here only denotes the absence of gravel packing; it does not mean avoiding forcing water into and out of the formation. Gravel packing consists of placing graded material around the well bore in an annular space drilled or reamed for this purpose. Gravel packing has two disadvantages: It is more expensive than natural development and it makes removal of the fine material more difficult because it must move through the gravel pack Gravel packing is seldom used in in situ uranium leaching wells; it may be beneficial in extremely fine sand deposits, but it is usually unnecessary.

The first step in development is a gentle washing of the screens with simple jetting tool attached to the lower end of the drill string. This

-pressure operation should not be confused with high-pressure jet developnt. A thorough washing of a 10-foot-long, 4-inch-diameter screen will take to 2 hours.

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The next step is pumping to remove the drilling fluid and fine particles in the borehole wall. Only after pumping brings up clear water should more gorous development such as jetting, airlifting, or surging be attempted. gorous development before pumping may force drilling fluid into the formaion and make proper development impossible.

ing Developing with a high-pressure (200 to 300 psi) jet (7, p. 307) or airifting after pumping can provide more vigorous water movement and break up 'e are $\hat{\mathbf{m}}$ d grain bridges (7, p. 299) that may have formed on the screen. Jetting is ffective, but must be used carefully to avoid breaking the screen if screens pring th inner ribs are used. A rotating jetting device can catch on a rib and reak it. Either a jetting device with no projections should be used, or the tting device should not be rotated while jetting. Breakage would be less kely with a screen wrapped on a perforated pipe, but this type of screen les not allow the jetting action to be so effective. The force of the water the t itself does not break the screen. A Bureau of Mines laboratory test ting bowed that even the ribbed-type screen did not break with a water-jet presmre of 675 psi. utside

:40), Airlifting consists of injecting air fast enough into the bottom of the Il through a small pipe so water is lifted out of the well. The resulting ing and Toulence in the well bottom breaks up the sand bridges. 7W -

Mechanical surging (7, p. 299) consists of operating a plunger up and 🕅 in the casing. The resulting in-and-out flow is very effective at ^{ea}king sand bridges; however, surging is seldom needed. If it is used, it buld be used with care. In large amounts of clay, the clay can stick to the reen and clog it. The screen can be broken if surging is done too vigorg out, ter the sly, especially if it is partially clogged.

The use of chemicals can aid in development; for example, a small amount flocculating agent appears to help remove guar gum based drilling fluids fom the borehole wall and to help drop clay in the mud pit. IEC obtained od results adding 2 oz of Cyfloc-326, a flocculating agent available from CO Services Div., Halliburton Co., to the circulating fluid during develop f^{at} of 7-3/8-inch-diameter, 250-foot-deep wells that had been drilled with Wert. Flushing with a combination of hydrofluoric and hydrochloric acid has en used successfully in oil wells (6), and it has been suggested for improvannu¹⁸¹ 8 injection wells for in situ leaching. The combination may be more effecoval ^{of} We than the presently used hydrochloric acid flushing.

	SUMMARY	
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4. The method and th	oroughness of development.	بن بر المراجع المراجع محمد
Neglecting any of these far ance to serve their intended	ctors can lead to wells with a ed purpose.	too much fluid resist.

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Well Construction Information for In Situ Uranium Leaching

Information Circular 8769

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Well Construction Information for In Situ Uranium Leaching

By Daryl R. Tweeton and Kevin Connor



UNITED STATES DEPARTMENT OF THE INTERIOR Cecil D. Andrus, Secretary BUREAU OF MINES As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering the wisest use of our land and water resources, protecting our fish and wildlife, preserving the environmental and cultural values of our national parks and historical places, and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to assure that their development is, in the best interests of all our people. The Department also has a major responsibility for American Indian reservation communities and for people who live in Island Territories under U.S. administration.

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WELL CONSTRUCTION INFORMATION FOR IN SITU URANIUM LEACHING

by.

Daryl R. Tweeton ¹ and Kevin Connor²

ABSTRACT

This Bureau of Mines publication describes present practices of making injection wells for in situ uranium leaching. Casings, screens, drilling fluids, coring, logging, cementing, and developing are discussed with the objective of aiding those who are starting an in situ leaching operation. Improper choices of materials or techniques can result in wells that are either useless or wells that have an undesirably high resistance to injection. Important factors include careful selection of screen slot size, use of logs for choosing the cementing basket depth, proper cementing techniques, and careful choice, use, and flushing of drilling fluids. The information was obtained through observation of well construction and through discussion with in situ leaching companies, drillers, and suppliers.

INTRODUCTION

In situ leaching consists of injecting chemicals (lixiviant) into an ore body, dissolving the desired mineral, and pumping the lixiviant and dissolved minerals out of the ore body. Usually separate wells are used for injecting and recovering the lixiviant. In situ leaching has the following advantages over conventional mining: smaller capital cost for small or deep deposits, shorter lead time before production, minimum surface pollution, lower labor costs, and improved safety for workers. It thus can make feasible the recovery of uranium from deposits that are too small or too low-grade to profitably recover by conventional mining.

Despite the potential benefits, in situ leaching contributes only a small fraction of our national uranium production. Therefore, the Federal Bureau of Mines is conducting research to improve technology with the anticipation that in situ leaching will contribute more to the Nation's uranium production and reserves.

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Both authors are with the Twin Cities Mining Research Center, Bureau of Mines, Twin Cities, Minn. Research at the Twin Cities (Minn.) Mining Research Center began in 1975, in cooperation with a private company at an experimental test site in Wyoming. The study demonstrated the importance of properly constructing injection wells. The first set of wells had a high resistance to injection despite several attempts at acid flushing. So little lixiviant could be circulated that the leaching test was not a reliable basis for planning commercial operation; therefore, the test was repeated the following year with better wells. Discussion with other leaching companies showed that well clogging was a common problem, and that the degree of clogging was strongly influenced by well construction techniques. Without good injection wells, not enough lixiviant contacts the ore to provide good uranium recovery.

There is little public literature on injection wells for in situ uranium leaching. However, some literature on other types of wells was found to be useful. Reference $(7)^3$ discusses planning and constructing water wells, ground water movement and chemical characteristics, testing wells, screen selection, drilling and developing wells, and pumps. However, techniques that are suitable for water production wells are not necessarily suitable for injection wells. Lixiviants are far more corrosive than ordinary water. Also, wells usually have more fluid resistance to injection than to recovery.

Brown and Silvey (2) described some of the causes and cures for clogging in certain recharge wells. They concluded that clogging was largely caused by dispersion of interstitial clay, and that suitable clay stabilizers such as calcium chloride could minimize clogging during injection. White, Baptist, and Land (9) also concluded that clay dispersion, not clay swelling, was the dominant factor in reducing the water permeability of certain cores.

The lack of public literature on wells for leaching makes it difficult for companies that are just beginning in situ uranium leaching to avoid repeating mistakes made by others, so the Bureau prepared this circular describing current practices. A future report will describe investigations into improved methods. An overview of Bureau research on this and related topics is given by Olson, Larson, and Tweeton (4).

ACKNOWLEDGMENTS

Much of the information relating specifically to in situ leaching wells was obtained in discussions with Intercontinental Energy Corp. (IEC), Denver, Colo., and Tep-Cor, Inc., Alice, Tex., as a result of a cooperative agreement between IEC and the Bureau of Mines.

WELL DESIGN

Important considerations in the design of the well include the type and diameter of the casing and the type and slot size of the screen.

³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

Casing

Although some companies use 5- or 6-inch-diameter casing to allow a larger pump to be installed, the most common casing diameter is 4 inches, which allows 4-inch screens to be used and provides adequate screen area for fluid flow. This diameter allows small submergible pumps to be used. The option of installing a pump in an injection well is useful during well development and during postleach restoration of the water quality, even though the pump is not left in the well during leaching. This option also permits later conversion of an injection well to a recovery well.

The most common casing material is polyvinyl chloride (PVC) plastic which has replaced stainless steel because PVC is much cheaper. A disadvantage of installing PVC during Wyoming winters is that the glue does not set properly when colder than 4° C (40° F).

An alternative which makes glue unnecessary is Yelomine⁴ PVC pipe manufactured by Certain-Teed Products Corp., St. Louis, Mo. It uses a patented connector in which a nylon strap is slipped around the joint in a special groove to hold the coupling secure. An O-ring inside the coupling prevents leaking. Yelomine is slightly more expensive than standard PVC, but it is claimed to be stronger. Wells deeper than 500 feet are sometimes cased with fiberglass which is stronger than PVC.



Screens

Just as for casings, plastic screens have replaced stainless steel because of its cheaper cost. There are several manufacturers of plastic well screen each claiming advantages. All of the screens have tapered slots with the narrowest part of the slot to the outside which minimizes plugging with sand grains (fig. 1). A grain small enough to enter the

⁴Reference to specific equipment (or trade names or manufacturers) is made for identification only and does not imply endorsement by the Bureau of Mines.

FIGURE 1. - Tapered screen slots minimize plugging from sond grains.

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narrowest part of the slot is unlikely to be trapped in the wider parts of the slot. If the slot is not tapered, grains are more likely to be trapped part way through. The type of screen having the greatest open area is wound over thin plastic ribs, and it is sold by Johnson Div., Universal Oil Products, St. Paul, Minn. A different design, which gives less open area but more strength, is wound over a plastic pipe containing closely spaced holes and it is available from Well Supply, Inc., and Wesco, Inc., both of Houston, Tex.

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The slot size should be chosen carefully to allow optimum well development. Too small an opening will not allow enough of the fine material from near the well to be flushed through the screen and pumped out. Too large an opening will allow material from the formation to continue to flow through the screen. A common recommendation is to choose a slot size that allows 60 wt-pct of the material to pass through. This slot size is usually from 0.008 to 0.025 inch (0.20 to 0.63 mm). Thus, cores must be taken for grain-size analysis (7, p. 179) before selecting the slot size.

An alternative to conventional screens is to case and cement the well to the bottom of the deposit, then use a water-jet device developed by the Bureau of Mines to perforate the casing and cement. This method has the advantage that the perforation pattern can be tailored exactly to the deposit. The perforator, described in a Bureau publication by G. A. Savanick (5), uses a 10,000-psi water jet to make small holes through the casing and cement that are small enough to provide sand control.

Another alternative is to case and cement to the bottom of the deposit, then remove the casing and cement by underreaming at the desired depths. If the formation is sufficiently consolidated, no screen is necessary. If the formation is poorly consolidated, a telescoping screen of smaller diameter than the casing is slid into position after underreaming.

DRILLING

Of the several methods of drilling, the most common is hydraulic rotary drilling where the drilling fluid is liquid. Foam and air drilling have also been used successfully.

Foam and air drilling are similar in many ways to hydraulic rotary drilling, except the drilling fluid that carries the cuttings up is foam or air instead of liquid. Since hydraulic rotary drilling is much more common, this circular will emphasize drilling with liquids.

Hydraulic Rotary Drilling

Hydraulic rotary drilling is well-known and described in reference $(\underline{7}, p. 47)$. The choice, use, and flushing of drilling fluid is very important. Any drilling fluid that is not removed during development will be forced into the formation during injection and hence it will contribute to clogging. Drilling fluids made from bentonite are especially prone to cause clogging because bentonite is hard to remove and swells.

Drilling fluids made from guar gum are less likely to cause clogging than bentonite, and they are often used in drilling injection wells. Examples of such fluids are Revert $(\underline{8})$, sold by Johnson Div. of Universal Oil Products and Loloss (3), sold by Baroid Services Div., NL Industries, Inc. The advantage claimed is that guar gum drilling fluids can be broken down to a fluid having the viscosity of water by enzymes or chemicals after drilling is completed. However, there are conditions where guar gum fluids will gel and resist breaking down. The literature describing Revert states that a combination of certain chemical constituents in the water such as boron, copper, aluminum, and calcium, coupled with a pH over 8, can cause gelling. The same literature suggests methods for treating the water to avoid gelling. The amount of the chemical constituents that can be present at a given pH before gelling occurs has not been published. When using the fluids it is important to follow all the manufacturer's directions including the warnings of the effects of trace chemical constituents and improper pH. This seemingly obvious advice is stated because the Bureau has encountered several instances of clogging where failure to pretest the water and insure its suitability may have been a contributing factor. In hot weather it may be advisable to preserve guar gum drilling fluids with formaldehyde to prevent them from breaking down before the drilling is completed.

Newer fluids are being recommended by some manufacturers. For example, Baroid now recommends Drispac or Quik-trol rather than Loloss for drilling injection wells. Drispac is a polyanionic cellulose polymer (3) which has been used successfully for drilling injection wells. Quik-trol is an organic polymer (3). Baroid indicates that these two drilling fluids are more effective than guar gum fluids at encapsulating clays and hence preventing the buildup of a fine clay suspension on the borehole wall.

Baroid stresses the need to control the solids content of the fluid by removing clay particles during drilling. Equipment is available for this purpose, and some of it is small enough to be used during injection well drilling. The buildup of solids was a problem at the IEC site which was attributed to the portable mud pits being too small to allow adequate settling of the suspended particles. It would have been preferable to use larger pits, but this was prevented by extremely wet conditions.

Drilling wells straight and vertical is important for several reasons. A crooked hole makes it difficult to lower the casing especially with a cementing basket. Casings have broken when excessive force was used. A crooked hole also makes it difficult to lower a submergible pump down the casing if the pump is long and its diameter is only slightly smaller than the casing. If the holes are not vertical, the well pattern at the ore depth will differ from the surface pattern. This may lead to poor distribution of the lixiviant.

Using as small a downward thrust (pulldown) as practicable at the top of the drill string will help insure a straight hole. Applying part of the necessary force downhole with two drill collars worked well for Tep-Cor at the IEC site. Downward thrust applied at the top of the drill string tends to make the drill go crooked, but weight applied near the bottom of the string helps the drill go straight and vertical. Most companies do not try to drill



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FIGURE 2. - Tailpipe with sediments accumulation.

the full-diameter hole in one pass. Drilling a pilot hole a little more than half the final diameter requires less downward thrust and yields a straighter hole. However, one company has found that using more drill collars and a high bit rpm allows straight holes up to 6-3/4-inch diameter to be drilled in one pass. The Bureau's experience suggests that, in an ordinary formation, a careful driller can avoid being more than about 6 feet out-of-vertical at a depth of 250 feet when using a pilot hole.

The final diameter must be large enough to accommodate the casing with its couplings and cementing basket if used. This is considerably larger than the nominal inside diameter (ID) casing size. For example, a 4-inch ID casing requires a borehole diameter of at least 6-3/4 inches. Tep-Cor preferred 7-3/8-inch-diameter boreholes to facilitate installing the casing. The outside diameter (OD) of the couplings is about 5 inches. There must be room for the cement to flow up the annulus between the casing and the formation to allow a good seal.

The hole must be drilled deeper than the screen bottom to allow for some material sloughing to the bottom of the hole and for a tailpipe to extend below the screen. The tailpipe is a piece of casing, usually 5 to 10 feet long, attached to the bottom of the screen and capped at the bottom end. This allows material to settle in the tailpipe without blocking the screen as shown in figure 2. Placing about a foot of plaster of paris in the cap helps prevent drilling through it.

Foam and Air Drilling

Foam or air drilling offers the promise of minimizing the lowpermeability skin on the borehole wall. However, it provides less support for the borehole wall and hence increases the risk of collapse.

Air drilling was used successfully in a Wyoming operation. The wells were drilled to a competent layer above the uranium-bearing zone using a guar gum based drilling fluid. A 6-inch-diameter casing was installed and cemented. Then a hole for a 4-inch-diameter screen was drilled through the uraniumbearing zone using compressed air as the drilling fluid. The hole was full of water, and the air and water made a froth that carried up the cuttings. A 4-inch-diameter screen was slid down the 6-inch casing to the desired depth. The screen was capped at the bottom and had a packer at the top to seal the space between the screen and casing.

This method produced wells having a low resistance to injection. Those who try this method should keep in mind that a poorly consolidated formation may collapse before the screen can be installed. Various manufacturers offer foam drilling fluids that provide better wall support than air and water.

COR ING

Coring poorly consolidated deposits is difficult. Part of the core may be washed out of the barrel during drilling. Also, the core may stick in the barrel so hard that forcing it out breaks it up. Double-tube core barrels (1, p. 181) prevent the drilling fluid from flowing over the core in the barrel and hence help keep the core from washing out. Split-tube core barrels have an inner tube that is in two parts allowing the core to be lifted out when the tube is open and thus eliminating the need to force the core out the the end of the barrel.

Excellent core recovery was obtained by Tep-Cor Drilling Co. at the IEC site with a simple solid-core barrel. The drilling fluid was Revert at a Marsh viscosity $(\underline{7}, p. 222; \underline{3})$ of 50 sec. This is slightly thicker than the 40-sec Marsh viscosity used during drilling, but it is near the viscosity range recommended for Revert $(\underline{8}, p. 4)$. Core drilling was done slowly to avoid forcing the core tightly into the barrel. Coring 10 feet took 1 to 2 hours. Essentially no pulldown force was applied, so the force on the NX-size bit was from the weight of two drill collars, each weighing 300 to 400 pounds, and 250 feet of drill string. To minimize core washout, the mud pump was slowed until it was just adequate to bring up the cuttings. Most of the 10-foot core sections could be pushed out of the barrel with a rod. If more force was needed, the mud pump was connected to the barrel and the core was pumped out. This step had to be done carefully because once the core started to move, it moved easily. If excessive pressure was used, the core could be ejected so rapidly that it went over the core table and fell on the ground.

For those who are new to coring, Acker (1) is a useful reference. Most types of coring and related drilling are discussed, and previous experience is not assumed.

LOGG ING

Well logging is performed on the uncased hole. Three logs aid in deciding the exact depth to set the screen and cementing basket. These logs are natural gamma, resistivity or resistance, and caliper.

The natural gamma log helps in deciding where the highest uranium grade is and hence where to set the screen as shown in figure 3. Uranium decay products emit gamma rays and, if the uranium has not moved away from its decay products, the areas of highest natural gamma rays correspond to the areas of



FIGURE 3. - Gamma log-well profile comparison.

highest uranium content. The gamma log is referred to as a "natural" log to distinguish it from induced gamma logs, where a radioactive source is in the probe and gamma rays from the artificially produced nuclides are measured.

A resistance or a resistivity log is used in deciding where to set the cementing basket, which must be set in a competent zone of shale or other well consolidated material to prevent seepage into the screened zone. A resistivity log measures the resistivity of the formation between the ends of the probe. A resistance log, which is more common, measures the resistance from a point on the surface to the downhole probe. These logs can help indicate the proper place for the basket because the resistivity of fine-grained material such as shale and clay is lower than that of coarser grained material such as sand.

The caliper log indicates the diameter of the hole, and it also indicates if sloughing has occurred. The caliper has spring loaded fingers that are extended once the tool has been lowered to the bottom of the hole (fig. 4). The caliper is then brought up the hole constantly measuring the hole diameter. The cementing basket must not be placed in a zone that has sloughed.

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FIGURE 4. - Caliper logging probe.

INSTALLING CASING AND SCREEN

After logging is completed, the casing and screen are installed. The first step is to measure and cut the casing so that the screen and cementing basket will be at the chosen depths. The tailpipe is then capped and attached to the bottom of the screen. Small holes should be drilled in the casing just below the cementing basket plug to allow air to escape as the assembly is lowered



FIGURE 5. - Casing operation using PVC pipe.



FIGURE 6. - Centralizer.

into the water. "Weep holes" of 1-inch diameter are drilled above the plug.

The hoist on the drill rig holds the screen and casing as they are lowered into the hole and connected as shown in figure 5. If glued casing connections are used, screws are also put through the couplings for extra strength.

A centralizer (fig. 6) is slipped over one or more of the casing sections to keep the casing centered in the hole permitting the cement to seal all sides. The centralizers as purchased have six staves (sidebars). At the IEC site, alternate staves were removed, because the staves were quite stiff and a large amount of force was required to push them down the hole with all six staves attached.

One should be careful not to overshoot the depth when lowering the casing. The basket may be ruined if the casing is pulled up more than the distance, about 2 feet, that the basket can slide on its section of casing.

The casing and screen should be installed as soon as possible after drilling and logging are completed. If installation is delayed, the risk of clay swelling and sloughing are increased. In one instance, a caliper log showed that clay swelling reduced the diameter of a 6-3/4-inch hole at one point to 5-1/2 inches. Instead of reaming out that point, the driller forced the casing down the hole. The cementing basket stuck at the narrow point, and so much thrust was applied to force the casing down that it broke below ground. The casing could not be retrieved, and the well was lost (fig. 7).

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FIGURE 7. - Wedging of the cementing basket caused by clay swelling.

FIGURE 8. - Screen misplacement caused by sloughing of well bore wall.

If a large amount of sloughing occurs, so much material can drop into the bottom of the hole that the tailpipe and hence the screen cannot be lowered to the desired depth as shown in figure 8. If sloughing occurs at the basket depth, the cement can flow around the basket.

CEMENTING

Proper cementing between the casing and the formation is vital. If this space is not sealed, ground water and leaching solution can move from one aquifer to another along the outside of the casing as shown in figure 9. This results in a loss or dilution of leaching solution and possible escape of pollutants. Portland type I cement is often used, with about 6 or 7 gallons of water per 94-pound sack of cement. Some companies have used up to 14 gallons of water per sack. However, cement tends not to stay in suspension with more than 10 gallons of water per sack. Also, shrinkage increases as water content increases. To reduce shrinkage and help insure a good seal, 1 to 4 pounds of bentonite per sack of cement can be added.

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FIGURE 9. - Control of fluid injection direction through cementation.

The method of placing the wet cement slurry is important. If it were merely poured along side the casing, adequate sealing would be unlikely. The cement would bridge the gap above spots where the casing was close to the formation.

The Texas Water Quality Board requires the casing method of cementing (7, p. 242). In the variation of this method used for in situ leaching wells, a cementing basket (fig. 10) is attached to the casing above the screen before the casing is lowered into the well. The basket comes on a short section of casing that contains plaster of paris and a plywood plug. The cementing basket is attached so that it will be at a shale or other competent layer above the ore. Holes of about 1-inch diameter called weep holes are drilled either in the casing attached to the basket or near the bottom of the next higher casing (fig. 11).

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FIGURE 10. - Cementing basket.

Weep hole Weep hole Coupling Plaster of paris Casing Cementing basket Plywood disc

FIGURE 11. - Cementing basket and plaster of paris plug prefabricated unit.

After the casing has been lowered into position, the wet cement slurry is pumped down the inside of the casing and flows out the weep holes above the cementing basket. The cementing basket prevents the cement from flowing down over the screen, and it forces the cement to flow up the annulus between the casing and the borehole wall as shown in figure 12. After a volume of cement sufficient to fill the annulus has been injected, water is pumped into the casing to force or "chase" most of the cement out of the casing, through the weep holes and up into the annulus. Volumes are chosen so that some cement is

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FIGURE 12. - Cementing operation.

left in the casing as shown in figure 13. After the cement has set, the excessive cement and the plug in the cementing basket section are drilled out. The well is then ready for development.

Incomplete sealing may result if much sloughing occurs above the cementing basket. Ordinarily, a small amount of sloughing at one point will not seriously impair the sealing, since the cement will isolate this spot. However, if substantial sloughing occurs, the seal may be poor over enough distance that some aquifer mixing may be possible. For this reason, it is desirable to minimize the time between lowering the casing and cementing. Letting the casing stand overnight in the hole without being cemented should be avoided whenever possible.







FIGURE 14. - Cementing basket placement.

If the cementing basket is not making good contact with a competent shale or other layer, the cement may be able to pass the basket and cover the screen. This can happen if there is sloughing at the basket, as in figure 14, or if the fingers of the basket are bent in during the setting of the casing and do not spring out again. There are cementing baskets with fingers that will not spring back after being pressed against the casing; these should be avoided.

An alternative to the casing method of cementing is to force the cement through a small pipe outside of the casing $(\underline{7}, p. 240)$, if there is sufficient space between the casing and the borehole wall. How-

.ever, most companies appear to favor the casing method.

DEVELOPING

Well developing is defined as "those steps in completing a water well that aim to remove the finer material from the aquifer, thereby cleaning out, opening up, or enlarging passages in the formation so that water can enter the well more freely" (7, p. 295). Proper well development is essential for both injection and recovery wells, but it may be impossible if the wrong drilling fluid is used, if the drilling fluid is used incorrectly, or if the screen slot size is incorrect.

Wells can be developed either by gravel packing or by natural development. Natural as used here only denotes the absence of gravel packing; it does not mean avoiding forcing water into and out of the formation. Gravel packing consists of placing graded material around the well bore in an annular space drilled or reamed for this purpose. Gravel packing has two disadvantages: It is more expensive than natural development and it makes removal of the fine material more difficult because it must move through the gravel pack. Gravel packing is seldom used in in situ uranium leaching wells; it may be beneficial in extremely fine sand deposits, but it is usually unnecessary.

The first step in development is a gentle washing of the screens with a simple jetting tool attached to the lower end of the drill string. This

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low-pressure operation should not be confused with high-pressure jet development. A thorough washing of a 10-foot-long, 4-inch-diameter screen will take 1 to 2 hours.

The next step is pumping to remove the drilling fluid and fine particles from the borehole wall. Only after pumping brings up clear water should more vigorous development such as jetting, airlifting, or surging be attempted. Vigorous development before pumping may force drilling fluid into the formation and make proper development impossible.

Developing with a high-pressure (200 to 300 psi) jet $(\underline{7}, p. 307)$ or airlifting after pumping can provide more vigorous water movement and break up sand grain bridges ($\underline{7}, p. 299$) that may have formed on the screen. Jetting is effective, but must be used carefully to avoid breaking the screen if screens with inner ribs are used. A rotating jetting device can catch on a rib and break it. Either a jetting device with no projections should be used, or the jetting device should not be rotated while jetting. Breakage would be less likely with a screen wrapped on a perforated pipe, but this type of screen does not allow the jetting action to be so effective. The force of the water jet itself does not break the screen. A Bureau of Mines laboratory test showed that even the ribbed-type screen did not break with a water-jet pressure of 675 psi.

Airlifting consists of injecting air fast enough into the bottom of the well through a small pipe so water is lifted out of the well. The resulting turbulence in the well bottom breaks up the sand bridges.

Mechanical surging (7, p. 299) consists of operating a plunger up and down in the casing. The resulting in-and-out flow is very effective at breaking sand bridges; however, surging is seldom needed. If it is used, it should be used with care. In large amounts of clay, the clay can stick to the screen and clog it. The screen can be broken if surging is done too vigorously, especially if it is partially clogged.

The use of chemicals can aid in development; for example, a small amount of flocculating agent appears to help remove guar gum based drilling fluids from the borehole wall and to help drop clay in the mud pit. IEC obtained good results adding 2 oz of Cyfloc-326, a flocculating agent available from IMCO Services Div., Halliburton Co., to the circulating fluid during development of 7-3/8-inch-diameter, 250-foot-deep wells that had been drilled with Revert. Flushing with a combination of hydrofluoric and hydrochloric acid has been used successfully in oil wells (6), and it has been suggested for improving injection wells for in situ leaching. The combination may be more effective than the presently used hydrochloric acid flushing.

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SUMMARY

From the preceding sections, it has been shown that there are many factors that should be considered if good injection wells are to be made. Factors that tend to be overlooked but that can have a great effect on the well include:

- The type of screen and slot size. 1.
- 2. The quality of the cementing basket.
- The type of drilling fluid. 3.
- 4. The method and thoroughness of development.

Neglecting any of these factors can lead to wells with too much fluid resistance to serve their intended purpose.

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Wave attenuation in partially saturated rocks

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A model is presented to describe the attenuation of seismic waves in rocks with partially liquid-saturated flat cracks or pores. The presence of at least a small fraction of a free gaseous phase permits the fluid to flow freely when the pore is compressed under wave excitation. The resulting attenuation is much higher than with complete saturation as treated by Biot. In general, the attenuation increases with increasing liquid concentration, but is much more sensitive to the aspect ratios of the pores and the liquid droplets occupying the pores, with flatter pores resulting in higher attenuation. Details of pore shape other than aspect ratio appear to have little effect on the general behavior provided the crack width is slowly varying over the length of the liquid drop.

INTRODUCTION

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The velocity and attenuation of seismic waves in crustal materials are strongly dependent upon pore fluid content and the details of pore geometry. The degree of wave interaction with fluids is in general determined by the shape, and hence compliance, of the pores within the solid matrix of mineral grains. Rocks with flatter pores are more sensitive to the details of the fluid and its ability to support or transmit compressional and shear loads; rounder, more rigid pores are less sensitive to the presence of fluids. In the low frequency limit, pore fluids influence the system through their density, compressibility, and distinct lack of rigidity; at higher frequencies, viscous and inertial interactions are introduced.

This dependence of velocity and attenuation on pore geometry and fluid properties can, in principle, serve as a diagnostic of material structure both in situ and in the laboratory. Nur (1971) and Solomon (1972), using equations from Walsh (1969), made estimates of upper mantle partial melt configuration from the velocities of teleseismic compressional and shear waves. Related experimental work on the dependence of velocity on partial melt was reported by Anderson and Spetzler (1970). Nur (1973) interpreted observed temporal velocity anomalies as diagnostic of dilatant strain and varying pore water saturation in the crust prior to certain earthquakes.

In exploration geophysics, a substantial effort has been made to develop more detailed theoretical and experimental correlations between longitudinal wave velocities, rock type, and fluid content in the shallow crust. The goal in oil and gas exploration is to be able to distinguish reliably between gas, oil, and water in situ, as well as to infer their relative concentrations, rock type, porosity, and permeability. Similar problems in geothermal exploration concern assessing water and steam content, as well as permeability and state of fracture.

Work by Domenico (1974), Kuster and Toksöz (1974a, b), and Elliott and Wiley (1975) indicates that the velocity of a liquid-saturated rock can differ substantially from that in the same rock with a partial saturation of a free gaseous phase. The two rocks in contact can account for a large reflection coefficient and an observed "bright spot". However, the dependence of velocity on the amount of gas saturation is very weak over the range 10 to 90 percent. The contrast in velocity is an indicator of gas, but a poor quantitative measure of economic value.

In this paper we present a model of one particular mechanism for wave attenuation in partially saturated liquid-gas systems. The model predicts that for certain rocks with at least a small concentration of very flat pores, even a small amount of water can dramatically enhance the dissipation of energy of compressional waves. Furthermore, the level of attenuation is directly dependent on the actual concentrations of liquid and gas, as well as on the fluid viscosity and pore shape. This can, in principle, serve as an independent data point on the state of saturation of porous rocks.

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FIG. 1. Schematic view of partially saturated, two-dimensional pore. Thickness of pore perpendicular to the page is equal to d, an approximation of the third dimension.

In the first section that follows, we will discuss some general considerations of fluid attenuation and introduce our model of partial saturation. In the second section, mathematical formulas are derived for calculating attenuation of waves. The remainder of the paper gives a discussion of the model results including simplified expressions for attenuation for specific pore geometries, limiting expressions at high and low frequencies, the ratio of attenuation for *P*- and *S*-waves, and comparison with other models of fluid attenuation.

FLUID ATTENUATION

The primary source of fluid attenuation in porous media (ignoring nonmechanical effects) is relative motion between the solid and liquid. Such motion results in shearing stresses in the fluid and, consequently, viscous dissipation of mechanical energy. In our model of attenuation, we examine the details of flow and energy dissipation on the scale of the individual pores. We approximate the rock as a macroscopically isotropic elastic solid containing a distribution of partially saturated cracks or pores of the type shown schematically in Figure 1. We assume that the liquid is segregated into one or more discrete "drops" within each pore that flow as the pore is deformed. For mathematical convenience, the separate pores are treated as two-dimensional cracks in plane strain with width d (into the page) equal to some function of the half-length c. Furthermore, the separate pores are assumed not to interact, and only flat cracks with aspect ratio $\alpha_c < 0.1$ are considered (where $\alpha_c = a_0/c$ and a_0 is the maximum pore half-width in the plane of the page). Rigorously, this might limit our applications to low porosity igneous rocks. However, conceptually, the notions of dissipative flow that we will develop are quite applicable to more closely spaced, equidimensional pores. We will also find that flat pores give a much larger

effect than the same volume of equant pores.

Our treatment of the details of flow in the individual pores will be reminiscent of Biot's (1956a, b) for the general porous solid except for the emphasis here on undersaturation. In this study, details of pore geometry will be retained, and both high and low frequencies are addressed.

MATHEMATICAL DERIVATION: NORMAL COMPONENT OF EXCITATION

Both *P*- and *S*-waves passing through our material exert oscillatory stresses which can be resolved into normal and shear components in the plane of each pore. In this section we find the attenuation resulting from the normal component of excitation on the individual pore; a later section treats the shear component. For a given wave and distribution of crack orientations, the total attenuation can then be found from a summation of both components over all pores. We will find, in fact, that the shear component of dissipation resulting from either compressional or shear waves gives a negligible contribution for most cases of interest involving water.

Seismic attenuation is estimated for a given fluid geometry by solving for the specific dissipation function Q^{-1} of the fluid-elastic composite, given by

$$Q^{-1} = \frac{\Phi}{2\pi W},$$

where Φ is the energy dissipated in the fluid phase during one cycle of sinusoidal oscillation and W is the peak energy stored during the same cycle. The spatial attenuation function can then be found from

$$\alpha_x = \frac{\omega}{2C_P Q},$$

where α_x is the attenuation coefficient for plane wave amplitude decay with propagation and C_P is the compressional phase velocity at frequency ω . The method of solution will be to solve for the fluid flow field in each single partially filled pore resulting from a prescribed oscillation of the pore walls. The elastic energy of the rock surrounding the pore will then be obtained for the same oscillation.

For this study, pore geometries are limited to long narrow two-dimensional cracks as shown in Figure 1.

LIST OF SYMBOLS

 $a(x), \tilde{a} =$ Pore half-width

- $a_0 = Maximum$ pore half-width
- A(x) = Fluid volume as a function of position in pore
 - c = Pore half-length
 - $C_p =$ Compressional wave phase velocity
 - d = Pore dimension in third dimension

D = Drop length

- E = Young's modulus
- f = Frequency
- $K_f =$ Fluid bulk modulus
- M = Modulus of rock
- P = Fluid pressure
- Q^{-1} = Specific dissipation function
- S(x) = Pore wall displacement as a function of position
 - u = Fluid velocity
 - U = Surface displacement of rock sample
 - V = Volume of rock sample
 - v = Volume of drop
 - V_p = Speed of sound in liquid

 $W, W_0, W_p = \text{Elastic strain energy}$

- α_c = Aspect ratio of pore
- α_f = Aspect ratio of drop
- α_x = Spatial attenuation function
- β = Fractional volume of liquid in rock
- δ = Maximum pore wall displacement
- ε = Pore strain
- $\eta = \text{Viscosity}$
- λ = Lame's coefficient for rock material
- μ = Shear modulus for rock material
- $\nu =$ Kinematic viscosity
- ξ = Poisson's ratio
- $\rho = Fluid$ density
- σ = Applied stress
- Σ = External surface of rock sample
- $\tau =$ Viscous shear stress
- Φ = Energy dissipated during one cycle

 ψ = Porosity

 ω = Frequency



FIG. 2. Liquid drop subject to oscillations of pore walls.

Surface tension is neglected except for the assumption that, during seismic oscillation, each fluid drop remains intact rather than breaking up into smaller drops or losing contact with one or both of the pore walls. In our analysis we find that the induced gradients of pressure within each drop are important in determining dissipation, while the absolute pressure is not. Since the effect of surface tension is to superimpose an increment of essentially uniform pressure within the drop, we ignore only a slight perturbation in the estimation of W. A much more important effect which we consider later is the effect of surface tension on the distribution of liquid throughout the rock. Because the pores are undersaturated, the flow is incompressible for most frequencies and geometries of interest (see Appendix A). (An extension to compressible flow at very high frequencies is discussed in the next section and in Appendix B.) Furthermore, by assuming that the crack half-width a(x) is a slowly varying function of x, the flow is essentially one-dimensional for small oscillations of the pore walls about the static position. Hence, the approximate equation of motion governing the fluid flow reduces to

$$\rho \frac{\partial u}{\partial t} = -\frac{\partial P}{\partial x} + \eta \frac{\partial^2 u}{\partial y^2}, \qquad (1)$$

where *u* is the *x*-component of velocity, ρ is the density, η is the viscosity, and *P* is the pressure of the fluid. [A discussion of the assumptions involved in obtaining the equation of motion (1) is given in Appendix A.]

The boundary conditions for the fluid are stated in terms of pore wall displacements (Figure 2). (The analysis is not limited to drops at crack tips. For drops away from the tips, the figure can be thought of as showing half the drop.) For very small strains, the pore half-width $\bar{a}(x, t)$ is assumed to oscillate about the static shape a(x) as

$$\tilde{a}(x,t) = a(x)[1 + \varepsilon e^{i\omega t}], \qquad (2)$$

where $\epsilon \ll 1$. The pore strain is given by $\epsilon = \delta/a_0$ where δ is the maximum pore wall displacement. Although the motion in (2) is in the y-direction, the y-component of fluid velocity is neglected in the onedimensional approximation. However, the oscillation in (2) results in a volumetric oscillation which causes a pressure gradient and a lateral displacement or flow of the fluid.

At any station x, with local pressure gradient $\partial P/\partial x$, the solution of equation (1) for (approximately) parallel-plate flow is given by

$$u(x, y) = \frac{-\partial P(x)}{\partial x} \frac{1}{i\omega\rho} \cdot \left[1 - \frac{\cosh\left(\sqrt{\frac{i\omega}{\nu}} y\right)}{\cosh\left(\sqrt{\frac{i\omega}{\nu}} a(x)\right)}\right], \quad (3)$$

where $\nu = \eta / \rho$. The weak x-dependence is contained in P(x) and a(x). The explicit time dependence is dropped here and in the remaining derivation since all quantities vary as $e^{i\omega t}$. Since the flow is incompressible, the net flow at x must be equal to the rate of change of volume $\mathring{A}(x)$ of the portion of the pore to the right of x. Hence,

$$\int_{-a(x)}^{a(x)} u(x, y) \, dy = - \mathring{A}(x), \qquad (4)$$

and from (3) and (4) we can solve for the pressure gradient

$$\frac{\partial P(x)}{\partial x} = \mathring{A}(x) \cdot \frac{i\omega\rho}{2a\left[1 - \frac{1}{a}\sqrt{\frac{\nu}{i\omega}}\tanh\sqrt{\frac{i\omega}{\nu}}a\right]},$$
ere (5)

where

$$\mathring{A}(x) = 2 \int_0^x \frac{\partial}{\partial t} \, \tilde{a}(x, t) \, dx.$$

By combining (3) and (5), the flow field is obtained,

$$u(x, y) = \frac{-\mathring{A}(x)}{2a(x)} \cdot$$

$$1 - \frac{\cosh \sqrt{\frac{i\omega}{\nu}} y}{\cosh \sqrt{\frac{i\omega}{\nu}} a} \cdot \frac{1 - \frac{1}{a} \sqrt{\frac{i\omega}{i\omega}} \tanh \sqrt{\frac{i\omega}{\nu}} a}{1 - \frac{1}{a} \sqrt{\frac{i\omega}{i\omega}} \tanh \sqrt{\frac{i\omega}{\nu}} a} \cdot$$
(6)

The energy dissipation Φ for the entire pore during one cycle is found by solving for the shear stress $\tau = \eta (\partial u / \partial y)$, and integrating the energy dissipation density over the period and the volume of fluid,

$$\Phi = \int_{V} \int_{T} \frac{1}{2\eta} \tau \cdot \tau^{*} dt dv$$
$$= \frac{3}{2} \frac{\pi \eta d}{\omega} \int_{0}^{D} \frac{\mathring{A} \mathring{A}^{*}}{a^{3}(x)} R(z) dx, \qquad (7)$$

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where * means complex conjugate, $z = a(x)(\omega/2\nu)^{1/2}$ and R(z) is given in Appendix B.

To find the peak mechanical energy stored in the rock-fluid system we consider a uniform oscillatory stress $\sigma = \sigma_0 e^{i(\omega(t+\phi))}$ applied to a sample of the material and the resulting surface displacement $U = U_0 e^{i(\omega t+\theta)}$. If the difference in phase between displacement and stress is small (i.e., $\theta - \phi \approx Q^{-1} \ll 1$), then the peak energy is approximately

$$W \cong \frac{1}{2} \iint_{\Sigma} \sigma_0 U_0 ds$$
$$\cong \operatorname{Re} \frac{1}{2} \iint_{\Sigma} \sigma^* U ds,$$

where the integral is over the external surface Σ of the sample and Re refers to the real part. To find the product

$$\frac{1}{2}\iint_{\Sigma}\sigma^*Uds,$$

and hence the peak energy, we use the Betti-Rayleigh reciprocity theorem. The theorem states that for a body acted upon separately by two sets of tractions, the work done by the first set of tractions acting through the displacement produced by the second set of tractions is equal to the work done by the second set of tractions acting through the displacements produced by the first set of tractions.

In the derivation that follows, we divide the rock into elements of volume, each containing a single pore. A uniform traction is applied to the boundary of each volume corresponding to the stress from the propagating wave. For cracks oriented at some arbitrary angle with the direction of propagation, the applied traction can be resolved into normal and shear components of stress in the plane of the crack. The crack compression from the normal component results in the fluid flow and attenuation derived above. The crack shearing from the shear component of stress results in the flow problem to be treated in a later section. (In most cases of interest, the shear dissipation will be negligible.) To find the stored energy for the arbitrarily oriented crack, both components of stress must be considered. Jaeger and Cook (1969, p. 313) show in detail how this energy varies with orientation for the simple case of a dry crack and how to sum over a random distribution of orientations. In our problem, the crack has a nonuniform internal fluid pressure distribution given by equation (5) which will modify the energy from the simple dry case. We will only solve in detail for the case of cracks oriented perpendicular to the principal stresses of excitation, in order to determine the firstorder fluid effects on propagation. However, in principle, variation with orientation can be found by repeating the derivation which follows, keeping careful note of the resolved components of stress, in a fashion analogous to Jaeger and Cook. We expect that this would result in only a small perturbation of our results. In a later section we do, however, estimate the P- and S-wave attenuation for random crack orientations at low frequencies, for which the expressions for strain energy simplify.

Walsh (1965a, b) discusses the difficulties and uncertainties associated with choosing the uniform stress versus a uniform strain boundary condition, as well as the difference between the penny-shaped crack and a two-dimensional crack in plane strain or plain stress. He concludes, as we do, that the differences resulting from these various assumptions are negligible compared to the overall level of approximation in the analysis.

To apply the reciprocity theorem, consider the two sets of tractions shown in Figure 3. The system on the left is loaded by an externally applied stress corresponding to the peak stress of the seismic wave. The pore wall displacement S(x) is due to both the external stress σ , tending to close the crack, and the instantaneous internal fluid pressure P(x) tending to keep the crack open. The system on the right has the same external stress σ^* applied to both the external and internal surfaces. In this case, the system behaves like a solid elastic block without the cavity or fluid. Applying the reciprocity theorem, we can write

$$-2d \int_{-c}^{c} P(x) \frac{\sigma^{*}}{M} a(x) dx + \frac{\sigma \sigma^{*}}{M} V$$
$$= \iint_{\Sigma} \sigma^{*} U ds - 2\sigma^{*} d \int_{-c}^{c} S(x) dx, \quad (8)$$

where V is the volume of the block, M is the elastic modulus of the solid rock, Σ is the external surface of the volume (excluding pore surfaces), and dimensions c and d are as given in Figure 1. Since



FIG. 3. Applying the reciprocity theorem to a rock under two sets of applied stress. On the left, only the induced pore pressure is applied to the pore. On the right, the applied stress σ^* is also applied to the pore, making the rock deform as though uncracked.

the theorem applies to clastic bodies it is necessary to treat the pores as external surfaces and the pore pressure as an externally applied load. The integral on the left is negligibly small and can be dropped (see Appendix D). For the case of plane wave propagation of a compressional wave, $M = \lambda + 2\mu$ where μ is the shear modulus and λ is Lame's coefficient for the intrinsic rock material. Rearranging equation (8) and taking the real part, we get

$$\operatorname{Re} \frac{1}{2} \iint_{\Sigma} \sigma^* U ds = \frac{1}{2} \frac{|\sigma|^2}{M} V + \operatorname{Re} \sigma^* d \cdot \int_{-c}^{c} S(x) dx,$$

or

$$W = W_0 + W_p. \tag{9}$$

The term on the left is recognized as the approximate peak mechanical energy of the composite system W, which we are seeking. The terms on the right are the peak strain energy W_0 of a comparable rock without porosity, plus the energy contribution W_p due to the presence of the pore.

In order to relate the displacement S(x) to the applied stress σ , it is convenient to consider a crack with uniform pore pressure \overline{P} (see Appendix C). For very small stresses σ and \overline{P} (as for a wave), the resulting small pore displacement and its integral W_p can be written as

$$S(x) \simeq \frac{2(\sigma - \overline{P})c(1 - \xi^2)}{E} \cdot \left[1 - \left(\frac{x}{c}\right)^2\right]^{1/2},$$
(10)

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$$W_{p} \approx \operatorname{Re} \frac{\pi \sigma^{*} (\sigma - P) c^{2} d(1 - \xi^{2})}{E}, \quad (11)$$

where ξ is Poisson's ratio and E is Young's modulus. With nonuniform pressure P(x), the energy W_p can still be written in the form (11) if the pressure \overline{P} is chosen as

$$\overline{P} = \frac{2}{\pi c} \int_{-c}^{c} P(x) \left[1 - \left(\frac{x}{c}\right)^{2} \right]^{1/2} dx, \quad (12)$$

where P(x) is obtained from equation (5) (see Appendix C). Setting $S(0) = a_0 \varepsilon$, we can solve for σ in terms of \overline{P} and ε or $\sigma = \overline{P} + \varepsilon \alpha_c E/2(1 - \xi^2)$. Finally, combining this with equations (9) and (11) and setting $\lambda = \mu$ and $\xi = 1/4$, we arrive at the total strain energy in terms of ε and \overline{P} :

$$W = \frac{8}{27} \mu V \alpha_c^2 \varepsilon^2 \left(1 + \frac{9}{4} \frac{\psi}{\alpha_c} \right) + \frac{\mu V}{6} \left[\left(\frac{|\bar{P}|}{\mu} \right)^2 + \frac{8}{3} \alpha_c \varepsilon \left(1 + \frac{9}{8} \frac{\psi}{\alpha_c} \right) \operatorname{Re} \left(\frac{\bar{P}}{\mu} \right) \right]. (13)$$

Here ψ is the porosity and α_c is the crack aspect ratio.

The specific dissipation function Q^{-1} now can be given by combining equations (7) and (13),



FIG. 4. The frequency dependence of Q^{-1} for the parallel walled pore in compression.

where Y(z) is given in Appendix B. Using equation (12), we get finally the equivalent uniform pressure that appears in the formula for W,

$$|\overline{P}| = \frac{\omega^2 \varepsilon \rho}{\pi} c^2 \gamma Y(z),$$

Re $\overline{P} = \frac{\omega^2 \varepsilon \rho}{\pi} c^2 \gamma Z(z),$ (17)

$$Q^{-1} = \frac{\Phi}{2\pi W} = \frac{\frac{3}{2}\pi\eta \frac{d}{\omega} \int_{0}^{\nu} \frac{\mathring{A}\mathring{A}^{*}R(z)}{a^{3}(x)} dx}{\frac{8}{27} \mu V \alpha_{c}^{2} \varepsilon^{2} \left(1 + \frac{9}{4} \frac{\psi}{\alpha_{c}}\right) + \frac{\mu V}{6} \left[\left(\frac{|\overline{P}|}{\mu}\right)^{2} + \frac{8}{3} \alpha_{c} \varepsilon \left(1 + \frac{9}{8} \frac{\psi}{\alpha_{c}} \operatorname{Re}\left(\frac{\overline{P}}{\mu}\right) \right].$$
(14)

RESULTS: THE PARALLEL-WALLED PORE

Consider the specific example of a pore where a(x) is approximately a constant (i.e., $a(x) = a_0$) over the region occupied by the drop of length 2D. Here, R(z) is independent of x and

$$\check{A}(x) = +2x\varepsilon a_0 i\omega e^{i\omega t}$$

Equation (7) can easily be evaluated to give the energy dissipated per cycle,

$$\Phi = \frac{4\pi\eta\omega d\varepsilon^2 D^3}{a_0} R(z).$$
(15)

The pressure distribution P(x) is obtained by integrating equation (5) and taking the modulus

$$|P(x)| = \left| \int \frac{\partial P}{\partial x} dx \right|$$

= $\frac{\omega^2 \varepsilon \rho}{2} (D^2 - x^2) Y(z),$ (16)

where γ and Z(z) are also given in Appendix B. The attenuation Q^{-1} can be found by placing these simplified forms in equation (14).

A plot of Q^{-1} versus ω for the parallel walled pore is given in Figure 4. The most striking feature is the sharp peak at $\omega = \omega_0 (\omega_0 \text{ is the frequency at maximum$ attenuation), and the rapid fall off at both high fre $quencies, where <math>Q^{-1} \simeq \omega^{-3/2}$, and low frequencies, where $Q^{-1} \simeq \omega$. The peak and high-frequency falloff result from the fluid compressibility which becomes important at very high pressures. We include this effect by modifying the continuity condition, equation (4), in the above derivation (see Appendix B). For most applications, however, the frequencies of interest are well within the limits of incompressible flow.

Let us examine more closely the asymptotic behavior. Table 1 gives the high and low frequency

	$\omega \leq \frac{2\nu}{a^2}$ (Poisseuille)		$\omega \gg \frac{2\nu}{a^2}$ (inertial)
	$\omega \ll \frac{1}{D} \sqrt{\frac{K}{\rho}}$	(incompressible)	$\omega \ge \frac{1}{D} \sqrt{\frac{K_f}{\rho}}$ (compressible)
R	I	$\frac{a_0}{3}$	$\sqrt{\frac{\omega}{2\nu}}$
Y	$\frac{3\eta}{\rho\omega a_0^2}$	1	. —
Z	6 5	1	
Ф	$\frac{4\pi\eta\varepsilon^2 dDa\omega}{\alpha_f^2}$	$\frac{4\pi\eta\omega\varepsilon^2D^3d}{3}\sqrt{\frac{\omega}{2\nu}}$	$\sqrt{2\eta\rho} \frac{\pi d\varepsilon^2}{\omega^{3/2}} \left(\frac{\kappa}{\rho}\right)^{3/2}$
<i>P</i>	$\frac{3\eta\varepsilon\omega}{2a_0^2}\left(D^2-x^2\right)$	$\frac{\omega^2 \varepsilon \rho}{2} \left(D^2 - x^2 \right)$	$eK_f\left[1-e^{-\omega\sqrt{p/K_f(D-x)}}\right]$
w	$\frac{8}{27} \mu V \alpha_c^2 \varepsilon^2 \left(1 + \frac{9}{4} \frac{\psi}{\alpha_c} \right)$	$\frac{8}{27} \mu V \alpha_c^2 \varepsilon^2 \left(1 + \frac{9}{4} \frac{\psi}{\alpha_c} \right)$	$\frac{8}{27} \mu V \alpha_c^2 \varepsilon^2 \left(1 + \frac{9}{4} \frac{\psi}{\alpha_c} \right) + \frac{\mu V}{6} \left[\frac{8}{3} \alpha_c \varepsilon \left(1 + \frac{9}{8} \frac{\psi}{\alpha_c} \right) \left \frac{P}{\mu} \right + \left(\left \frac{P}{\mu} \right ^2 \right) \right]$
Q ⁻¹	$\frac{\frac{27}{16}}{\mu\alpha_c^2\alpha_f^2\left(1+\frac{9}{4}\frac{\psi}{\alpha_c}\right)}$	$\frac{9}{16} \frac{\eta \omega \beta a_0}{\mu \alpha_j^2 \alpha_c^2 \left(1 + \frac{9}{4} \frac{\psi}{\alpha_c}\right)} \sqrt{\frac{\omega}{2\nu}}$	$\propto \omega^{-3/2}$

Table 1. Limiting forms of frequency dependent terms.

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forms of Φ , *P*, *W*, and Q^{-1} based on the limiting forms of R(z), Y(z), and Z(z). The new parameters are β , the volume concentration of liquid in the rock, K_f , the fluid bulk modulus, and $\alpha_f = a_0/D$, the aspect ratio of the drop.

Physically, the low-frequency expressions $(\omega \ll 2\nu/a^2)$ correspond to Poisseuille flow. That is, the inertial terms are negligible, and the flow is governed by the balance between viscous shear forces and the pressure gradient driving the flow. These viscous shear stresses are proportional to ω ; the average dissipation goes as ω^2 ; and the dissipation during one period, $T = 2\pi/\omega$, varies as ω .

The fluid pressure P, varies as $\eta \omega \varepsilon D^2/a^2$ at low frequencies. The pressure-shear balance is obvious here since the peak velocity is approximately $\omega \varepsilon D$, the shear stress is approximately $\eta \omega \varepsilon D/a$, and the integrated shear force over the drop length is approximately $\eta \omega \varepsilon D^2/a$. This equals a change in pressure force of approximately Pa over the length of the drop. For the case of water, the low-frequency pressure is usually small compared with the stress in the rock. Hence, at low frequencies (incompressible flow), the energy W is approximately the energy of a dry porous rock, independent of ω .

The condition for Poisseuille flow, and therefore a condition on the low-frequency form of Φ in Table 1, corresponds to z < 1, $\omega < 2\nu/a^2$, or $f < \nu/\pi a^2$. For a water system $\nu = 0.01$ cgs, so that f < 0.003/a, where a is in centimeters and f is in Hz. For the case of joints or fractures where $a \simeq 1$ mm, the low-frequency expressions are restricted to frequencies below 0.3 Hz; for pores or microcracks where $a \simeq 0.1$ mm, the restriction is f < 30 Hz. It would seem that for exploration frequencies the lowfrequency approximation is generally adequate. However, where unusually wide cracks or high frequencies are encountered (in the laboratory, for example) the other forms should be used.

The viscosity always appears with frequency as the product $\eta \omega$ in the Poisseuille flow expressions (in Table 1). This is a characteristic of viscous flow that can be particularly useful. For example, in the laboratory, we can define $\eta \omega$ as an effective frequency $\omega' = \eta \omega$ and measure the frequency dependence of liquid-solid systems by varying either the real frequency ω or the fluid viscosity.

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Computed values of Q^{-1} for some specific rocks, Boise sandstone, Bedford limestone, and Troy granite at 50 percent water saturation $(\beta = \psi/2)$ and f = 1.6 Hz, are shown in Table 2. These are computed using the low-frequency formula and aspect ratio distributions given by Toksöz et al (1976). We assume for simplicity and for comparison of aspect ratios that all pores are oriented alike, and that each pore is exactly half-filled with water. The contributions from the first two pore shapes from each rock type are not computed because the quantitative reliability of the model is low for such large aspect ratios. However, the trend indicates that smaller aspect ratios dominate the overall behavior, almost independent of the porosity of each aspect ratio group. Hence, the total rock attenuation is insensitive to the assumed distribution of fluid except in the flattest pores. All three rock types show a similar sensitivity to saturation and a dominance of flatter pores or cracks in determining the overall attenuation. Although the three rocks are very different in nature, the population of small aspect ratio cracks is somewhat similar in each. It should be noted that if smaller aspect ratios or higher frequencies are to be considered, the higher frequency expressions in Table 1 must be used.



FIG. 5. Nearly parallel-walled pore in shear.

ψ	α _c	αŗ	β	Q-1
Boise sandstone				
1.8×10^{-1}	1			
6.9×10^{-2}	1. $\times 10^{-1}$			
$1. \times 10^{-4}$	2.5×10^{-3}	5. $\times 10^{-3}$	5. $\times 10^{-5}$	5.4×10^{-7}
1. × 10-4	2. $\times 10^{-3}$	4. $\times 10^{-3}$	5. $\times 10^{-5}$	1.3×10^{-6}
1.5×10^{-4}	1.5×10^{-3}	3. $\times 10^{-3}$	7.5×10^{-5}	6.2×10^{-6}
2. × 10 ⁻⁴	1. $\times 10^{-3}$	2. $\times 10^{-3}$	$1. \times 10^{-4}$	4.2 × 10 ^{−5}
$1. \times 10^{-4}$	5. $\times 10^{-4}$	$1. \times 10^{-3}$	5. $\times 10^{-5}$	3.3×10^{-4}
2. $\times 10^{-5}$	$1. \times 10^{-4}$	$2. \times 10^{-4}$	1. $\times 10^{-5}$	4. $\times 10^{-2}$
Bedford limestone				
$1. \times 10^{-1}$	1.			
2. $\times 10^{-2}$	$1. \times 10^{-1}$	•		
2.5×10^{-3}	$1. \times 10^{-2}$	2. $\times 10^{-2}$	1.2×10^{-3}	5. $\times 10^{-8}$
5. $\times 10^{-4}$	5. $\times 10^{-3}$	$1. \times 10^{-2}$	2.5×10^{-4}	1.7×10^{-7}
5. $\times 10^{-4}$	4. $\times 10^{-3}$	8. $\times 10^{-3}$	2.5×10^{-4}	4.1×10^{-7}
7. $\times 10^{-4}$	3. $\times 10^{-3}$	6. $\times 10^{-3}$	3.5×10^{-4}	1.8×10^{-6}
6. $\times 10^{-4}$	2. $\times 10^{-3}$	4. $\times 10^{-3}$	3. $\times 10^{-4}$	7.9 × 10⁻ ⁶
4. × 10 ⁻⁴	1.5×10^{-3}	3. $\times 10^{-3}$	2. $\times 10^{-4}$	1.7×10^{-5}
5. $\times 10^{-4}$	$1. \times 10^{-3}$	2. $\times 10^{-3}$	2.5×10^{-4}	1. × 10 ⁻⁴
Trov granite				
$1. \times 10^{-3}$	1			
5. $\times 10^{-4}$	$1. \times 10^{-1}$			
1.5×10^{-3}	$1. \times 10^{-2}$	2. $\times 10^{-2}$	7.5×10^{-4}	3. $\times 10^{-8}$
5. $\times 10^{-5}$	5. $\times 10^{-4}$	$1. \times 10^{-3}$	2.5×10^{-5}	1.7×10^{-4}
7.5×10^{-5}	4. $\times 10^{-4}$	8. $\times 10^{-4}$	3.5×10^{-5}	5.8×10^{-4}
1. × 10 ⁻⁴	2.5×10^{-4}	5×10^{-4}	5×10^{-5}	5.4×10^{-3}
5. $\times 10^{-5}$	$1. \times 10^{-4}$	$2. \times 10^{-4}$	2.5×10^{-5}	i × 10 ⁻¹
		••		

Table 2. Numerical examples of attenuation for three rock types at f = 1.6 Hz and uniform 50 percent water saturation.

The higher frequency behavior of dissipation and attenuation, Table 1, is governed by the increasing importance of fluid inertial stresses with respect to viscous stresses. In particular, the pressure at intermediate frequencies $(2\nu/a^2 \le \omega \le (1/D)\sqrt{K_f/\rho})$ is a balance between pressure gradient $\simeq P/D$ and inertial stress $\simeq \rho(\omega^2 \varepsilon D)$, where $\omega^2 \varepsilon D$ gives the acceleration. At very high frequencies ($\omega \gg$ $(1/D)\sqrt{K_f/\rho}$, inertial forces greatly stifle the flow so that it becomes easier to compress the fluid (with pressure $\sim \epsilon K_f$) than to accelerate it along the pore. The transition between incompressible and compressible flow, and hence the peak in the attenuation curve, occurs when the fluid inertial stress $\sim \omega^2 \varepsilon \rho D^2$ is comparable with the fluid compressive stress $\sim \varepsilon K_f$ or $\omega \sim (1/D) \sqrt{K_f/\rho}$.

SHEAR COMPONENT OF EXCITATION

Consider once again the nearly parallel-walled pore of width $2a_0$ over the region occupied by the drop of length 2D. This time the pore is excited by a pure shear in the plane of the pore as shown in Figure 5. This is essentially the same mechanism considered by Walsh (1969) for saturated pores. The equation of motion is

$$\frac{\partial u}{\partial t} = \nu \frac{\partial^2 u}{\partial y^2},$$

with the boundary conditions on velocity of:

$$u = \begin{cases} i\omega\delta e^{i\omega t} & y = +a_0 \\ -i\omega\delta e^{i\omega t} & y = -a_0 \end{cases}$$

at the upper and lower pore walls, respectively. The flow field can easily be found:

$$u(y,t) = \frac{i\omega\delta\sinh\left(y\sqrt{\frac{i\omega}{\nu}}\right)}{\sinh\left(a_0\sqrt{\frac{i\omega}{\nu}}\right)} e^{i\omega t}.$$
 (18)

The energy dissipated in the entire pore during one cycle is found exactly as in the compressional problem and is given by

$$\Phi_{\rm shear} = \frac{2\omega^2 \pi \eta \delta^2 D d}{\nu} \sqrt{\frac{\nu}{2\omega}} \ .$$

$$\frac{\sinh\sqrt{\frac{2\omega}{\nu}}a + \sin\sqrt{\frac{2\omega}{\nu}}a}{\sinh^2\sqrt{\frac{2\omega}{2\nu}}a\cos^2\sqrt{\frac{\omega}{2\nu}}a + \cosh^2\sqrt{\frac{\omega}{2\nu}}a\sin^2\sqrt{\frac{\omega}{2\nu}}a},$$
(19)

or, in the limits of high and low frequency,

$$\Phi_{\rm shear} = \frac{4\pi\omega\eta\varepsilon^2 Dad}{\frac{4\pi\omega^2\eta\delta^2 Dd}{\nu}\sqrt{\frac{\nu}{2\omega}}} \quad \omega \ge 2\nu/a^2.$$
(20)

The relative importance of dissipation in shear and compression for this geometry is found by taking a simple ratio Φ (compression)/ Φ (shear) with identical pores and fluid and equal amplitudes of pore displacements. Using equation (20) and Table 1, we have

$$\frac{\Phi_{\text{compression}}}{\Phi_{\text{shear}}} = \begin{cases} 1/\alpha_f^2 & \omega \ll 2\nu/a^2 \\ 1/3 \alpha_f^2 & 2\nu/a^2 \ll \omega \ll \frac{1}{D} \sqrt{K_f/\rho}. \end{cases}$$
(21)

It is clear that for small aspect ratios, the dissipation in shear will be many orders of magnitude smaller than for compression in either limit. The interpretation of this is simple. The fluid velocity in the shear case is approximately the pore wall velocity $\simeq \omega \delta$. This gives an average fluid shear stress of $\eta \omega \delta/a$. On the other hand, the fluid velocity in the compressional case is on the order of $\simeq \omega \delta/\alpha_f^2$, with a fluid shear stress $\simeq \eta \omega \delta/\alpha_f^2 a$. The flow in compression is amplified by the aspect ratio.

We should emphasize that these analyses of dissipation in shear and compression refer to the shear and compressional components of stress resolved on each individual crack. The results are not identically the dissipation that would be associated with shear (S) and compressional (P) wave propagation. For either type of wave, each crack depending on its orientation, would have both a shear and compressional contribution to energy dissipation in the fluid and strain energy stored in the elastic matrix. These are discussed in the next section.

P- AND S-WAVE ATTENUATION

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To estimate low-frequency *P*- and *S*-wave attenuation we assume a random distribution of crack orientations and use the results of the parallel-walled pore. A crack at arbitrary orientation to the principal stresses encounters both shear and normal excitation. However, based on the results of the previous sections only the normal component of fluid excitation contributes significantly to dissipation. In addition, at low frequencies, the induced fluid pressure is small enough that the pores deform under stress as though dry. Hence, the maximum pore strain ε , using equation (10), is approximately related to the resolved normal stress σ_n by

$$\varepsilon = \frac{2(1-\xi^2)}{E\,\alpha_c}\,\sigma_n.$$

Substituting this into the expression for low-frequency dissipation shown in Table 1 gives

$$\Phi = \frac{16\pi\eta\omega dD^3(1-\xi^2)^2}{a\alpha_c^2 E^2}\,\sigma_n^2.$$
 (22)

The crack orientation is defined by spherical coordinates θ and ϕ . θ is the angle between the crack normal and greatest principal stress axis. ϕ is the azimuthal angle of rotation about the stress axis.

For a *P*-wave, the normal stress is rotationally symmetric about the direction of propagation and is given by

$$\sigma_n = \sigma [\cos^2 \theta + \xi' \sin^2 \theta / (1 - \xi')].$$

Here ξ' is the effective Poisson's ratio of the porous rock and σ is the normal stress in the direction of propagation (Walsh, 1966). The total dissipation Φ_P is given by the sum of the expression (22) over all N cracks:

$$\Phi_{P} = \frac{16\pi\eta\omega(1-\xi^{2})^{2}}{E^{2}}\sigma^{2}\sum_{N}\frac{dD^{3}}{a\alpha_{c}^{2}}\cdot \left[\cos^{2}\theta + \frac{\xi'}{1-\xi'}\sin^{2}\theta\right]^{2}.$$
 (23)

For very large N, the summation in (23) can be

approximated with an integral over a continuous distribution of crack orientation. In addition, we assume that the dimensions d, D, a, and α now represent appropriate averages for the distribution:

$$\Phi_{P} = \frac{16\pi\eta\omega(1-\xi^{2})^{2}\sigma^{2}dD^{3}}{a\alpha_{c}^{2}E^{2}} \frac{N}{4\pi} \cdot \int_{0}^{2\pi} \int_{0}^{\pi} \left[\cos^{2}\theta + \frac{\xi'}{1-\xi'} \cdot \sin^{2}\theta\right]^{2}\sin\theta d\theta d\phi.$$
(24)

The peak strain energy in a volume of rock V is

$$W = \frac{\sigma^2 V}{2E'} \frac{(1 - 2\xi')(1 + \xi')}{(1 - \xi')},$$

where E' is the effective Young's modulus of the porous rock. Finally, the *P*-wave attenuation becomes



FIG. 6. The ratio Q_{ν}/Q_s versus effective Poisson's ratio ξ' at low frequencies.

$$Q_{P}^{-1} = \frac{16\eta\omega dD^{3}}{5\,a\alpha_{c}^{2}E} \left(\frac{N}{V}\right) \left(\frac{E'}{E}\right) \cdot \frac{(1-\xi^{2})^{2} \left[1+\frac{4}{3}\frac{\xi'}{1-\xi'}+\frac{8}{3}\left(\frac{\xi'}{1-\xi'}\right)^{2}\right](1-\xi')}{(1+\xi')(1-2\xi')} .$$
(25)

Similarly, for an S-wave the normal stress on a crack is given by (Walsh, 1966)

$$\sigma_n = \sigma(\cos^2\theta - \cos^2\phi\,\sin^2\theta)$$

where σ is the principal stress. Combining this with equation (22) and summing over all cracks gives the S-wave dissipation,

$$\Phi_{S} = \frac{16\pi\eta\omega(1-\xi^{2})^{2}\sigma^{2}dD^{3}}{a\alpha_{c}^{2}E^{2}}\frac{N}{4\pi} \cdot \int_{0}^{2\pi}\int_{0}^{\pi} [\cos^{2}\theta - \cos^{2}\phi \sin^{2}\theta]^{2} \cdot \sin\theta d\theta d\phi$$

The peak strain energy is given by

$$W=\frac{\sigma^2 V}{E'}(1+\xi').$$

The S-wave attenuation becomes

$$Q_{\overline{S}}^{-1} = \frac{32 \eta \omega dD^3}{15 a \alpha_c^2 \overline{E}} \left(\frac{N}{V}\right) \left(\frac{E'}{E}\right) \frac{(1-\xi^2)^2}{(1+\xi')}.$$
 (26)

Although it is difficult to test these absolute values of Q_P and Q_S , it is interesting to take their ratio:

The ratio of Q_P/Q_S is plotted versus ξ' in Figure 6. The fact that $Q_P/Q_S < 1$ emphasizes that this is physically a local compressional mechanism of attenuation. Although the expressions (25) and (26) apply only at low frequencies, the ratio in equation (27) should be at least approximately correct to much higher frequencies.

Laboratory measurements on nominally dry rocks usually show $Q_P/Q_S \approx .5$, in fair agreement with our prediction in Figure 6. For example, for dry Quincy granite at low stress $\xi' \approx .1$ (Birch et al, 1942, p. 73), while $Q_P/Q_S \approx .5$ (Birch and Bancroft, 1938). Similarly, for Solenhofen limestone $\xi' \approx .25$ (Birch et al, 1942, p. 76) while $Q_P/Q_S \approx 0.6$ (Peselnick and Zietz, 1959). One could argue that dry rock measurements should not be compared with these results. However, because of capillarity some nominally dry rocks might contain small amounts of water in flat cracks. For example, Born (1941) found that when previously dried samples of Amherst sandstone were exposed to air their attenuation

$$\frac{Q_P}{Q_s} = \frac{2(1-2\xi')}{(1-\xi')\left[3+4\left(\frac{\xi'}{1-\xi'}\right)+8\left(\frac{\xi'}{1-\xi'}\right)^2\right]}$$
(27)



FIG. 7. Logarithmic decrement ($\sim Q^{-1}$) versus frequency for Amherst sandstone (Born, 1941).



FIG. 8. Two simple drop geometries. The upper drop is a linear or triangular wedge. The lower drop has parabolic shape.

increased due to absorbed moisture. The added increment of attenuation was frequency-dependent $(\Delta Q^{-1} \propto \omega)$, as expected from shear losses in a fluid phase, whereas Q^{-1} for the dried samples was independent of frequency. This is shown in Figure 7. A core of gypsum that was only air dry showed a similar frequency-dependent Q (Born, 1941).

Winkler (1977, personal communication) found that $Q_P/Q_S > 1$ for dry Massilon sandstone, but when almost fully saturated $Q_P/Q_S < 1$.

OTHER GEOMETRIES

The parallel pore is particularly useful in understanding the characteristics of the model because the integral in equations (6) and (13) for compressional dissipation can very easily be evaluated. For other simple pore geometries, the integral can also be evaluated if we work in the low frequency regime such that $R(z) \approx 1$.

Consider the two geometries shown in Figure 8. In each case the pore half-width is given by $a(x) = a_0(x/c)^n$, n = 1, 2, and the maximum pore displacement is δ . Using formula (6), we first note that

 $A(x) = \frac{2a_0}{c^n} \frac{x^{n+1}}{n+1} e^{i\omega t},$

or

$$\mathring{A}\mathring{A}^* = \frac{4\omega^2\delta^2}{c^{2n}} \frac{x^{2n+2}}{(n+1)^2}.$$

(28)

The dissipation Φ is then

$$\Phi = \begin{cases} \frac{3\pi\eta\omega\varepsilon^2\nu}{\alpha_f^2} & n=1\\ \frac{4\pi\eta\omega\varepsilon^2\nu}{\alpha_f^2} & n=2 \end{cases}$$
(29)

where v is the volume of the drop. This result compared with Table 1 for the parallel pore suggests that for low frequencies the fluid dissipation can be approximated for a variety of geometries by

$$\Phi \simeq g \frac{n\omega\varepsilon^2 v}{\alpha_f^2} , \qquad (30)$$

where g is a geometric factor which we have found to vary from π to 4π for the specific geometries studied. This rather weak dependence on geometry suggests that the results derived for the parallel pore have general applicability, particularly for order-ofmagnitude behavior.

COMPARISON WITH OTHER MODELS

Perhaps the most comprehensive single treatment of wave propagation incorporating dissipative fluid motion was presented by Biot (1956a, b). His formulation assumes a fully saturated porous material and includes the effects of fluid compressibility and coupled fluid and solid stress. At low frequencies, the relative fluid flow is assumed to resemble Poisseuille flow in a flat or circular duct, while at higher frequencies inertial terms are also included (laminar flow is always assumed). This microscopic flow field is used only to establish a frequency dependent proportionality between the average flow and the stresses transmitted to the solid rock. Details of pore shape and local flow are neglected thereafter, and are lumped into parameters which relate only the averaged solid and fluid motions on a scale much greater than the pore size.

The elimination of local flow, and the condition of complete liquid saturation treated by Biot, severely limit the amount of flow and dissipation that can occur under wave excitation. White (1965, p. 133) shows that for the saturated medium, the only sources

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of relative fluid motion from the passing wave are viscous drag due to acceleration of the solid with respect to the fluid and pressure gradients between the peak and trough of the passing wave. His numerical example of a water-saturated sandstone shows negligible dissipation.

In our model we specifically neglect the large-scale acceleration and diffusion and look only at the local flow. In this sense our mechanism of dissipation is more a point property. In addition, the undersaturation provides a strong local heterogeneity, which causes locally high pressure, gradients and flow.

At low frequencies, Q^{-1} is proportional to ω in both Biot's model and ours, although the magnitude; of attenuation is much greater in ours. At higher frequencies the dependence is quite different. Biot's expression for Q^{-1} varies as $\omega^{-1/2}$, while ours varies in a complicated fashion toward $\omega^{-3/2}$ at very high frequencies.

Another model of attenuation in porous media is by White (1975). His treatment resembles Biot's in that lumped parameters describe the material and flow properties (on a scale much greater than a pore dimension. Only low frequency viscous flow is considered. White includes undersaturation by considering regions of dry rock containing many pores imbedded in regions of saturated rock also containing many pores. High pressure gradients and flow occur at the contact between wet and dry rock and result in large attenuation. At low frequencies White's expression for Q^{-1} varies as ω_{i} , while at higher frequencies (still within the Poisseuille range) Q^{-1} varies as ω^{-1} . The only physical comparison we can make between the two models is to suggest that the contact region between wet and dry in White's model is somewhat similar to our description of the individual partially saturated pores.

DISCUSSION

We have presented a simple model to describe the attenuation of seismic waves in rocks with partially liquid saturated flat cracks or pores. In this study, the presence of at least a small fraction of a highly compressible gaseous phase permits the fluid to flow freely when the pore is compressed under seismic excitation. This leads to viscous shearing in the fluid and high energy dissipation. In general, the attenuation increases with increasing liquid cohcentration. However, only partially saturated pores contribute, as well as saturated pores connected to open pores. As successive regions saturate, the attenuation will fall off. In the limit of complete saturation, the flow is stifled and the attenuation is expected to essentially



FIG. 9. Attenuation versus saturation for several materials and fluids. Bereatsandstone from Gardner et al (1964); Alundum rods from Wyllie et al (1962). All samples excited in extensional oscillation, except, for sample with FC-75, which is in torsion.

disappear as is predicted by Biot's formulation. Likewise, the dissipation from pure shear distortion of the pores, whether completely saturated or not, is negligible.

The attenuation or Q^{-1} is found to be extremely sensitive to the aspect ratios of the pores and the liquid droplets occupying the pores, with flatter pores and drops resulting in higher attenuation. Details of pore shape other than aspect ratio appear to have little effect on the general behavior, provided the crack width is slowly varying over the length of the liquid drop.

An important factor in interpreting attenuation measurements is the actual distribution of liquid within the rock. Since only the flattest cracks are important, it is the state of flat crack saturation, rather, than the total rock saturation, that determines attenuation. The distribution will depend, for the most part, on capillarity. Wetting fluids will tend to occupy the flattest pores, while nonwetting fluids might be more randomly distributed. The distribution and, hence, attenuation might also depend on saturation history. For example, if one flat crack after another is sequentially wetted as fluid is added to a rock, we might expect the low frequency attenuation Q^{-1} to increase linearly with fluid content (see Table 1). This is due to the linear increase in the fluid content β_{i} . while the average aspect ratios of wetted cracks and droplets do not change. On the other hand, if all flat

cracks are gradually filled simultaneously, then we might expect Q^{-1} initially to increase roughly as the third power of fluid content. This is due to the steady decrease of droplet aspect ratio in addition to the increase of β as fluid is added.

Measurements of attenuation under partially saturated conditions have been reported by a number of authors (Born, 1941; Wyllie et al, 1962; Gardner et al, 1964; Usher, 1962). Some of the results are shown in Figure 9. All these curves show a monotonic increase of attenuation with increasing saturation, as we might expect. The data for water in sandstones show a faster, nonlinear increase- with saturation than for the nonaqueous liquids in alundum rods. This is perhaps due to a greater number of very thin cracks in the sandstones, and greater wetting with water.

Since small amounts of water can decrease Q, it is interesting to consider also the effect on elastic. moduli. At low frequencies, a partially saturated rock' behaves as though dry (neglecting the effects of surface tension and chemical softening), while at extremely high frequencies droplets of water behave as rigid bridges, effectively shortening flat cracks and stiffening the rock. Comparison of measured static and dynamic moduli of nominally dry rocks shows that high-frequency moduli can be as much as 100 percent greater (Simmons and Brace, 1965), particularly on igneous rocks which have a large relative population of flat cracks. We might expect at least part of the difference to result from the fluid stiffening. To estimate the magnitude of the effect, we can use the dispersion relation given by Kjartansson (1977),

$$\frac{M_1}{M_2} \approx \left(\frac{f_1}{f_2}\right)^{2/\pi Q} \tag{31}$$

where M_1 and M_2 are two moduli measured at two frequencies f_1 and f_2 . Using this relation, we assume that Q stays roughly the same over the band of interest. For static measurements at $f_2 \le .1$ Hz and dynamic measurements $f_1 \approx 10^6$ Hz, this gives $f_1^2/f_2 > 10^7$. For Q = 100, this gives $M_1/M_2 \approx 1.1$. For $Q \approx 50$, $M_1/M_2 \approx 1.2$. These are less than some of the observed differences, but in the right direction. This estimate, as obtained from equation (31), is a conservative one, based on the assumption of frequency-independent Q. To further investigate the static-dynamic discrepancy, it will be useful and necessary to measure the moduli as a function of both frequency and degree of partial saturation. Such measurements could well unravel the physical

mechanism of attenuation in partially saturated porouš rocks,

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APPENDIX A THE FLUID EQUATION OF MOTION

In most of our treatment of fluid flow within the individual pores of a rock, we assume that the fluid behaves as though incompressible. Usually the principal requirement for this to be approximately true is that the fluid speed be small compared to the speed of sound V_p (Batchelor, 1967, p. 174). Our results indicate that the peak fluid velocity is on the order of $\omega \varepsilon D$. Then for incompressible flow, we demand

$$\omega \varepsilon D \ll V_p = \left[\frac{K_f}{\rho}\right]^{1/2}.$$

For water $V_p \simeq 10^3$ m/sec and for strains $\varepsilon < 10^{-4}$, this becomes

$$\omega D \ll 10^7 \text{ m/sec.}$$
 (A-1)

A second requirement we can impose is that the volumetric strain due to fluid compression be small compared with the volumetric strain imposed as a boundary condition, i.e.,

$$\frac{P}{K_f} \ll \frac{\delta}{a_0} = \varepsilon$$

Our results give a peak fluid pressure of

$$P \simeq \begin{cases} \frac{3}{2} \frac{\eta \omega \varepsilon D^2}{a_0^2} & \omega \text{ small} \\ \\ \frac{1}{2} \omega^2 \rho D^2 \varepsilon & \omega \text{ large} \end{cases}$$

Then the requirement becomes

$$\frac{\eta \omega \varepsilon D^2}{a_0^2 K_f} \ll \varepsilon \Rightarrow \frac{\eta \omega D^2}{a_0^2} \ll K_f \qquad \omega \text{ small,}$$
$$\frac{\omega^2 \rho D^2 \varepsilon}{K} \ll \varepsilon \Rightarrow \omega^2 D^2 \ll \frac{K_f}{\rho} = V_\mu^2 \qquad \omega \text{ large.}$$

These are more restrictive than (A-1). For water $K_f = 2 \cdot 10^{10} \text{ dyne/cm}^2$ and $\eta \simeq 10^{-2} \text{ dyne sec/cm}^2$, we require:

$$\frac{\omega}{\alpha_f^2} \ll 2 \cdot 10^{12} \text{ sec}^{-1} \qquad \omega \text{ small,}$$

$$\omega D \ll 10^5 \text{ cm/sec} \qquad \omega \text{ large.}$$

Within these bounds of incompressibility, the equation of motion for the fluid is (Batchelor, 1967)

$$\rho \frac{Du_i}{Dt} = -\frac{\partial P}{\partial x_i} + \eta \nabla^2 u_i,$$

where $D/Dt = \partial/t + u \cdot \nabla$. We will assume that η is constant with time and position.

For a two-dimensional pore, $u_z = \partial/\partial z = 0$. Furthermore, if the pore width is slowly varying, i.e., $1/a \cdot \partial a/\partial x \ll 1$ and the pore strains are very small, then the flow is approximately unidirectional, and we can neglect the terms $u(\partial u/\partial x)$ and $\partial^2 u/\partial x^2$. Hence, the equation of motion becomes

$$\rho \, \frac{\partial u}{\partial t} = - \, \frac{\partial P}{\partial x} + \eta \, \frac{\partial^2 u}{\partial y^2} \, .$$

APPENDIX B FREQUENCY-DEPENDENT EXPRESSIONS AND THEIR LIMITING FORMS

The frequency dependence of Φ and P(x) is found as follows. The flow field is given by equation (6):

$$u(x, y) = \frac{-\mathring{A}(x)}{2a(x)} \cdot$$

$$\frac{1 - \frac{\cosh\sqrt{\frac{i\omega}{\nu}}y}{\cosh\sqrt{\frac{i\omega}{\nu}}a}}{1 - \frac{1}{a}\sqrt{\frac{\nu}{i\omega}}\tanh\sqrt{\frac{i\omega}{\nu}}a}$$

The shear stress $\tau = \eta (\partial u / \partial y)$ is then

$$\tau(x, y) = \frac{\eta \mathring{A}(x)}{2a} \cdot \frac{\sqrt{\frac{i\omega}{\nu}}}{\left[1 - \frac{1}{a}\sqrt{\frac{i\nu}{i\omega}} \tanh\sqrt{\frac{i\omega}{\nu}}a\right]} \cdot \frac{\sinh\sqrt{\frac{i\omega}{\nu}}a}{\cosh\sqrt{\frac{i\omega}{\nu}}a}.$$

The average dissipation rate per unit volume of fluid is given by

found by noting that at large z, $\sinh z \approx \cosh z$ and at small z by expanding the trigonometric and hyperbolic functions in power series and dropping higher order terms. Hence the definition of large and small z is $z \ge 1$ and $z \ll 1$, respectively, or in terms of ω : $\omega \ge 2\nu/a$, $\omega \ll 2\nu/a$.

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The complex pressure P(x) is obtained by taking the integral of equation (5):

$$\frac{\partial P}{\partial x} = \frac{\mathring{A}(x)i\omega\rho}{2a\left[1 - \frac{1}{a}\sqrt{\frac{\nu}{i\omega}} \tanh\sqrt{\frac{i\omega}{\nu}}a\right]},$$
$$P(x) = P_0 + \int_0^x \frac{\partial P}{\partial x}dx.$$

For the parallel drop, we set $\mathring{A}(x) = 2x\varepsilon a_0 i\omega$, and assume for simplicity that the pressure at the edge of the drop, x = D, is zero. This gives

$$P(x) = \frac{\omega^2 \varepsilon \rho}{2} \left(D^2 - x^2 \right) \cdot \left[1 - \frac{1}{a} \sqrt{\frac{\nu}{i\omega}} \tanh \sqrt{\frac{i\omega}{\nu}} a \right]^{-1}$$

$$\frac{1}{2\eta}\tau\tau^* = \frac{\omega\rho}{8a^2}\frac{\mathring{A}\mathring{A}^*}{T(z)}\cdot\left[\frac{\sinh^2\sqrt{\frac{\omega}{2\nu}}\,y\,\cos^2\sqrt{\frac{\omega}{2\nu}}\,y+\cosh^2\sqrt{\frac{\omega}{2\nu}}\,y\sin^2\sqrt{\frac{\omega}{2\nu}}\,y}{\cosh^2 z\,\cos^2 z+\sinh^2 z\,\sin^2 z}\right],$$

where

$$T(z) = 1 - \frac{1}{z} \cdot \left[\frac{\tanh z + \tanh z \tan^2 z - \tanh^2 z \tan z + \tan z}{1 + \tanh^2 z \tan^2 z} \right] + \frac{1}{2z^2} \left[\frac{\tanh^2 z + \tan^2 z}{1 + \tanh^2 z \tan^2 z} \right],$$

Finally, integrating over the volume and period gives

$$\Phi = \int_0^D \frac{\pi d\eta \mathring{A} \mathring{A}^* z}{4a^3 \omega T(z)} \cdot \\ \cdot \left[\frac{\sinh 2z - \sin 2z}{\cosh^2 z \, \cos^2 z + \sinh^2 z \, \sin^2 z} \right] dx$$
$$= \frac{3}{2} \frac{\pi \eta d}{\omega} \int_0^D \frac{\mathring{A} \mathring{A}^*}{a^3} R(z) dx,$$
$$R(z) = \frac{z}{6T(z)} \cdot \\ \cdot \left[\frac{\sinh 2z - \sin 2z}{\cosh^2 z \, \cos^2 z + \, \sinh^2 z \, \sin^2 z} \right].$$

The asymptotic expressions given in Table 1 are

The modulus and real part of P are

$$|P| = \frac{\omega^2 \varepsilon \rho}{2} (D^2 - x^2) Y(z),$$

Real (P) = $\frac{\omega^2 \varepsilon \rho}{2} (D^2 - x^2) Z(z),$

where

$$Y(z) = \left[(\cos^2 z + \sinh^2 z)^2 - \frac{1}{2z} \cdot (\cos^2 z + \sinh^2 z) \cdot (\sinh 2z + \sin 2z) + \frac{1}{8z^2} (\sinh^2 2z + \sin^2 2z) \right]^{1/2} / F(z).$$

$$Z(z) = \left[\cos^2 z + \sinh^2 z - \frac{1}{4z} (\sinh 2z + \sin 2z) \right] / F(z),$$

$$F(z) = \left[\cosh z \cos z - \frac{1}{2z} \cdot (\sinh z \cos z + \cosh z \sin z) \right]^2 + \left[\sinh z \sin z - \frac{1}{2z} \cdot (\cosh z \sin z - \sinh z \cos z) \right]^2,$$

$$z = a \sqrt{\frac{\omega}{2\nu}}.$$

To find the equivalent pressure \vec{P} for the case of a drop centered in the pore, we substitute these values into equation (12):

$$\begin{cases} |P| \\ \text{Real } P \end{cases} = \frac{\omega^2 \varepsilon \rho}{2} \begin{cases} Y(z) \\ Z(z) \end{cases} \frac{2}{\pi c} \cdot \\ \cdot \int_{-D}^{D} (D^2 - x^2) \left[1 - \left(\frac{x}{c}\right)^2 \right]^{1/2} dx \\ = \frac{\omega^2 \varepsilon \rho c^2}{\pi} \gamma \begin{cases} Y(z) \\ Z(z) \end{cases} , \end{cases}$$

where

$$\gamma = \left[\left(\frac{1}{4} + \frac{1}{2} \frac{D^2}{c^2} \right) \frac{D}{c} \sqrt{1 - \left(\frac{D}{c} \right)^2} + \left(\frac{D^2}{c^2} - \frac{1}{4} \right) \sin^{-1} \frac{D}{c} \right].$$

The high and low frequency limits of Y(z) and Z(z) are found in the same manner as R(z).

We include the effect of fluid compressibility in the parallel pore by using a modified form of the continuity condition given by equation (4):

$$\int_{-a}^{a} U(x, y) dy = -\left[\mathring{A}(x) - \frac{2a_0}{K_f} \int_{0}^{x} \mathring{P}(x) dx \right],$$

where K_f is the fluid bulk modulus. Now the total rate of flow past a given plane (x = const) is equal to the difference between the volume change of the pore and the fluid volume change due to compression. Substituting for U from equation (3), this gives.

$$\frac{2a_0}{i\omega\rho} \left[1 - \frac{1}{a_0} \sqrt{\frac{\nu}{i\omega}} \tanh \sqrt{\frac{i\omega}{\nu}} a_0 \right] \frac{\partial P}{\partial x}$$
$$= 2x\varepsilon a_0 i\omega - \frac{2a_0 i\omega}{K_f} \cdot \frac{1}{2\kappa} \cdot \frac{1}{2\kappa} \int_0^x P dx. \quad (B-1)$$

For frequencies well above the Poisseuille range $(\omega \ge 2\nu/a^2)$, this becomes

$$\frac{\partial P}{\partial x} = -x\varepsilon\omega^2\rho + \frac{\omega^2\rho}{K_f}\int_0^x P(x)dx,$$

with solution (corresponding to zero pressure at the edge of the drop):

$$P = \varepsilon K_f \left[1 - \frac{\cosh \alpha x}{\cosh \alpha D} \right]$$

$$\approx \begin{cases} \frac{\omega^2 \varepsilon \rho (D^2 - x^2)}{2}, \ \alpha D \ll 1 \ \text{(incompressible)} \\ \varepsilon K_f (1 - e^{-\alpha (D - x)}), \ \alpha D \gg 1 \end{cases}$$
(B-2)

where $\alpha = \omega \sqrt{\rho/K_f}$. Viscous effects can be retained if the term in brackets [] in (B-1) is a weak function of x, giving a modified form of (B-2) with

$$\alpha \sim \omega \cdot \left[\rho / K_f \left(1 - \frac{1}{a_0} \sqrt{\nu / i \omega} \tanh \sqrt{\frac{i \omega}{\nu}} a_0 \right) \right]^{1/2}$$

Substituting the pressure gradient into (3), we obtain the flow field and, finally, the dissipation:

$$\Phi = \frac{2\pi\eta d\varepsilon^2 K_f}{\omega\rho(\cosh 2\alpha D + 1)} \cdot \sqrt{\frac{\omega}{2\nu}} \left[\frac{\sinh 2\alpha D}{\alpha} - 2D \right]$$
$$\approx \begin{cases} \frac{4\pi\eta\omega\varepsilon^2 dD^3}{3} \sqrt{\frac{\omega}{2\nu}} & \omega \ll \alpha D\\ \sqrt{2\eta\rho}\pi d\varepsilon^2 \left(\frac{K}{\rho\omega}\right)^{3/2} & \omega \gg \alpha D. \end{cases}$$

APPENDIX C SHAPE APPROXIMATIONS IN CALCULATING ENERGIES

The separate calculation of Φ and W assumes a certain degree of uncoupling between the details of the fluid flow field and strain field in the rock around

the pore. In a rigorous approach the pore strain ε in equation (2) is a function of x and is coupled to the fluid pressure distribution P(x).

The general form for the dissipation Φ is given by The equation (7) as a function of \mathring{A} where

$$\mathring{A}(x) = 2 \int_0^x \frac{\partial}{\partial t} \, \bar{a}(x, t) \, dt.$$

This can be rewritten using (2) as

$$\mathring{A} = 2i\omega e^{i\omega t} \int_0^x a(x) \varepsilon(x) dx.$$

In our calculations for specific geometries, we simplify the integral by replacing $\varepsilon(x)$ by an appropriate average constant value ε , such that

$$\mathring{A} \simeq 2i\omega\varepsilon e^{i\omega t}\int_0^x a(x)dx$$

We further assume that this constant value of ε is approximately the strain that would occur for a uniformly pressurized pore deforming as equation (10).

In general, the pore wall displacement S(x) resulting from uniform confining pressure and uniform pore pressure will depend on the details of crack shape. However, Mavko and Nur (1977a) have shown for a broad class of two-dimensional flat crack shapes that, for very small increments of loading as we might expect from a passing wave, the incremental change of pore shape is elliptical in form, i.e.,

$$\frac{\partial a(x)}{\partial \sigma} = \frac{2c(1-\xi^2)}{E} \sqrt{1-\left(\frac{x}{c}\right)^2}$$

Then we can approximate S(x) by

$$S_{n}(x) = \frac{\partial a}{\partial \sigma} \left(\sigma - \overline{P} \right) = \frac{2(\sigma - \overline{P})c(1 - \xi^{2})}{E} \cdot \sqrt{1 - \left(\frac{x}{c}\right)^{2}},$$

.

which is equation (10). The maximum displacement is $S(0) = 2(\sigma - \overline{P})c(1 - \xi^2)/E$. Comparing with equation (2), the maximum displacement is $a_0\varepsilon$ so that we set

$$\frac{2(\sigma-P)c(1-\xi^2)}{E} \approx a_0 \varepsilon.$$

Equation (8) shows that the energy W depends only on the integral of crack displacement

$$\overline{S} = \int_{-c}^{c} S(x) \, dx.$$

Hence, for calculating W any approximation of pore wall deformation S(x) is valid as long as it has the correct average value \overline{S} . Mavko and Nur (1977b) have shown that for a broad class of two-dimensional flat cracks, the integrated displacement due to pressure distribution P(x) is exactly the same as for a uniform pressure \overline{P} , where \overline{P} is an appropriately weighted average of P(x), equation (12).

APPENDIX D PORE PRESSURE APPROXIMATION IN CALCULATING ENERGY

The pore pressure term in equation (8) can be shown negligible as follows. Since the bulk modulus of water K_f is much less than M, the modulus of rock, then

$$2d \int_{-c}^{c} P(x) \frac{\sigma^*}{M} a(x) dx \ll 2d \cdot \int_{-c}^{c} P(x) \frac{\sigma^*}{K_f} a(x) dx.$$

In Appendix A, we require for the incompressible analysis to be valid that $P \ll \varepsilon K_r$, then

$$2d \int_{-c}^{c} \frac{P(x)}{K_f} \sigma^* a(x) dx \ll 2d \int_{-c}^{c} \sigma^* \varepsilon a(x) dx.$$

(If we allow for compressible flow, $P < \varepsilon K_f$, and this inequality still holds.) But by equation (2), $\varepsilon a(x) \simeq S(x)$:

$$2d \int_{-c}^{c} \sigma^{*} \varepsilon \, a(x) \, dx \simeq 2d \, \sigma^{*} \int_{-c}^{c} S(x) \, dx.$$

Therefore,

$$2d \int_{-c}^{c} P(x) \frac{\sigma^*}{M} a(x) dx \ll 2d\sigma^* \int_{-c}^{c} S(x) dx.$$



No. 48, April 1978

Water Jet Perforation of Well Casings

Objective

Reduce the cost of modifying uranium well casings so that leaching solutions can pass through, but sand grains are blocked.

Approach

The well casing and sur-

rounding cement are perforated at the mineralized zone by impinging them with high pressure water jets.

How It Works

A nozzle assembly is attached to a high pressure (15,000 psi) pipe and lo-



Figure 1. Tightening high pressure tube unions of water jet perforator in the well.

wered into the well casing, which typically is schedule 40 PVC (polyvinyl chloride). The high pressure pipe line is extended down into the casing until it reaches the mineralized zone. The upper end of the pipeline is then connected by a high pressure hose to the outlet of a 10,000 psi pump. Turning the pump on for 5 seconds causes a high velocity water jet to cut through the well casing and the surrounding cement. Figure 1 shows a high pressure pipe being installed in a well casing.

Cutting small diameter holes in the casing allows the leachant to enter the casing and be pumped to the surface. However, the holes are small enough to prevent most sand grains from entering. Numerous holes are usually cut through the casing. The 3-nozzle assembly shown in Figure 2 cuts three holes, one above another.

Use of the water jet perforator eliminates the need for placing well

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Figure 2. Nozzle assembly for making three perforations simultaneously. Notice the oval shaped plates which center the assembly in casing.

screens in the hole and has the advantage of allowing the perforation pattern to be tailored exactly to the characteristics of the deposit.

Test Results

A prototype of the system has been successfully tested by Bureau of Mines personnel in the wells of four companies doing in situ leaching of uranium ore. The following corporations were cooperators: Mobil Oil (Energy Minerals Division) - 12 wells, Rocky Mountain Energy - 6 wells, Union Carbide - 46 wells, and Wyoming Mineral - 10 wells. During this testing the system was used,

principally to establish new wells, but was also used to perforate the well screens of older wells that had become clogged and had not responded to acid stimulation. Figure 3 shows a perforated screen.



Figure 3. Well screen perforated with the water jet.

All 74 applications to date have been successful. In addition, experience has shown that the water jet enhances the permeability of the uraniferous sur roundina sand, by selectively removing clay particles from a 1-foot-wide band around the casing. Varving the vertical hole pattern in the recovery well casing allows more uniform flow to the pump; other hole pattern changes can be used

to modify the flow of leachant through the field.

The water jet perforating system was developed and tested by personnel of the Bureau's Twin Cities Mining Research Center. Dr. George Savanick was the project leader.

For More Information

Copies of a paper describing this work are available. The paper, "Water Jet Perforator for Uranium Leaching Wells" was given at the Conference on Uranium Mining Technology, University of Nevada, Reno, April 25-29, 1977.

The prototype equipment water jet perforation is available to mining companies for trial use through cooperative agreements with the Bureau of Mines. Persons wanting more information about this development or trial use of the equipment should contact the:

Technology Transfer Officer Twin Cities Mining Research Center

Bureau of Mines P.O. Box 1660 Twin Cities, Minnesota 55111

Patent Status

A patent application on this development has been filed with the United States Patent Office.

UNIVERSITY OF UTAH RESEARCH INSTITUTE EARTH SCIENCE LAB.

White Pine Experiments With Cyanide Leaching of Copper Tailings

D. H. ROSE, V. LESSELS and D. J. BUCKWALTER

SUBJ

MNG WPEL

> At White Pine Copper Co.'s operation in the Upper APeninsula of Michigan, the company has been losing more than four lbs of copper in each ton of sand tailings. With an average rate of 12,000 tpd of sand going to the tailing pond daily, the company has been losing more than 14 million lbs of the red metal annually.

> With an eye aimed toward lessening this loss, White Pine engineers in 1959 initiated a study on techniques for recovering this "lost" copper from the sands. Inasmuch as the flotation operation was considered to be optimized, a logical approach seemed to be leaching. For various reasons ammonia, ferric chloride, acid, and biological leaching were ruled out as impracticable. This led to a consideration of cyanide leaching as practiced in the precious metals industry.

> In an early investigation at the White Pine laboratory, sand tailings were treated with a solution of calcium cyanide under oxidizing conditions, and the copper dissolved readily; however, cyanide recovery was not sufficiently high to make this leaching method economic. In August 1960, the study was brought to the Institute of Mineral Research at the Michigan Technological University as a sponsored project. Laboratory experimentation there eventually developed a process whereby cyanide was conserved by the exclusion of air, and about 90% of the copper was dissolved with very little loss of either cyanide or sulfide ions. Leaching methods, copper precipitation, cyanide regeneration, and optimum concentration levels were also investigated. This work led to a process on which a patent entitled Treatment of Sulfidic Material was granted (U.S. Patent No. 3,224,835) in December 1965.

PILOT PLANT TESTS

Due to success on the bench scale at the Michigan Technological University, a recommendation was made to White Pine Copper Co. that a pilot plant

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Fig. 1-Flowsheet of White Pine Copper's Cyanide Process.

be built to demonstrate the feasibility of the cyanide leaching process. Pilot plant tests were desirable because of the lack of operating plant data on cyanide leaching of copper sulfide ores. It was deemed necessary to investigate both the mechanical and chemical feasibility of the process on a pilot plant scale, to confirm the predictions based

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Fig. 2—Diagram of experimental leaching tank.

on the laboratory results, and, further, to obtain data for design of a prototype plant.

Construction of a 12-24 tpd pilot plant located in the mill building at White Pine was completed in August 1963, and pilot plant tests were carried on from that time until June 1964.

Chemistry of Process: The chemistry of the process involves the following reactions:

Leaching

 $Cu_{cS} + 3Ca(CN)_{a} \longrightarrow 3Ca^{**} + 2Cu(CN)_{a} + S^{=} [1]$

Precipitation

$$3Ca^{++} + 2Cu(CN)_{s}^{\pm} + S^{\pm} + 3H_{2}SO_{s} \longrightarrow 3CaSO_{s} \downarrow + Cu_{2}S \downarrow + 6HCN [2]$$

Regeneration.

$$H' + CN^{-} (in solution) \longrightarrow HCN (gas in N_2)$$

2HCN + CaO \longrightarrow Ca(CN)₂ + H₂O
[3]

Flowsheet and Equipment: A schematic diagram of the pilot plant flowsheet is shown in Fig. 1.

The leaching tank consisted of a closed cylindrical vessel 8 ft in diam and 10 ft high, with a filter 6 in. above the conical bottom, and a glass covered viewing port near the top of the tank. A diagram of the leaching tank is shown in Fig. 2. In operation the tank was filled with sand by means of a revolving distributor positioned just below the tank cover. A barometric leg attached to the underside of the filter permitted use of vacuum to increase the percolation rate. The leached sands were flushed into a 12-in. discharge pipe extending up through the center of the tank just to the filter level; water jets were placed around the periphery of the tank to completely remove the sands.

The sulfuric acid precipitator consisted of a closed stainless steel tank 24 in. in diam by 36 in. high containing a sealed Lightning agitator. Pregnant leach solution was pumped into the tank con-

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tinuously. Sulfuric acid was metered to the tank by a pH controller on the precipitator overflow. The acid slurry from the precipitator was filtered and washed on a 24-in. laboratory Eimco filter with an enclosed stainless steel filter drum.

The acid filtrate storage tank was a cylindrical steel, rubber-lined, two-cubic meter tank also equipped with a sealed Lightning mixer.

The cyanide regeneration equipment consisted of three towers packed with 1-in. Berl saddles and connected in series so that nitrogen could be passed upward through each tower. The first two towers, for stripping, were 10 in. in diam by 15 ft high and made of stainless steel. Acid filtrate containing HCN was passed downward through the first tower, then pumped to the top of the second tower and passed downward countercurrent to the stream of nitrogen. The solution stripped of cyanide was discharged to waste through a trap at the bottom of the second tower. The cyanide-laden nitrogen was then passed upward counter-current to a downward stream of lime water in the third, or absorption, tower to



Fig. 3—Conductivity curve for a sample test.



Fig. 5—Filter unit in the pilot plant.

This proved successful chemically, but the crystalline CaCO_a fouled the equipment and pipelines to such an extent that continuous operation became impossible.

To regenerate calcium cyanide solution, the acid filtrate was run through the stripping and absorption towers previously described. Regenerated leach solution could be concentrated to as high as 45 g NaCN eq/l. This is a significant step in the process in that it makes it possible to eliminate either dilution water or wash water from the system, and the proper balance of solution volumes and concentrations can thus be maintained. When the HCN in the acid filtrate was sufficiently high, the filtrate was realkalized with lime and returned directly to the leach solution storage tank along with the "Recycle" solution. By running all three stages of leaching, precipitation, and regeneration simultaneously, the process was continuous.

All equipment and storage tanks of the plant were vented to a central scrubbing system to avoid contamination of the air by cyanide vapor. As a further precaution, air in the plant was analyzed continuously at 12 different points by an automatic HCN analyzer connected to a warning alarm.

Table I. Leach Solution Distribution and	ď
Concentrations	د

_	Yolumé, Gal	NaCN Eq., g/L	Copper, g/L
Rich	1122	16.5	5.4
Reèvele	515	17.2	1.5
Ends	760	3:2	0.7
Reĉvele	515	17.2	1.5
Eñds	760	3.2	0.7

OPERATING RESULTS, REAGENT CONSUMPTION, AND COSTS

The over-all copper recovery in pilot plant tests was 91.65%, while cyanide losses averaged 0.362 lbs (NaCN eq. per pound of copper recovered. The cyanide losses were distributed as follows: leaching, 29.1%; precipitation and filtering, 27.2%; and stripping and regeneration, 43.7%.

During the first stages of testing it was found that losses due to formation of cyanide, thiocyanate and ferrocyanide were not serious; consequently, they were not determined routinely. However, they are included in the above total cyanide loss because they were accounted for in the final cyanide balance.

Consumption of other reagents per pound of copper recovered were: lime, 2.06 lbs; spent sulfuric acid (75%), 3.60 lbs; and sodium bisulfide, 0.099 lbs.

Reagent costs per lb of recovered copper were about 9¢ to 10¢, depending upon shipping costs. By altering the present flotation flowsheet so as to combine the cleaner flotation tails with the coarser . fraction of sand tails, the amount of leach plant feed would be decreased to about 7000 tpd while the copper content would be raised to about 7 lbs per ton of sand. Reagent costs for a feed of this character would still be about 9¢ to 10¢ per lb of copper recovered.

CONCLUSIONS

Use of this process to recover copper from flotation tailings depends upon the following conditionswhich prevail at White Pine:

1) The tailing to be leached possesses little value, so far as conventional beneficiation processes are concerned, for other than road material.

a) Recovery by flotation to produce smelter feed appears to be at its economic limit.

b) The amount of acid-soluble material and lack of pyrife in the flotation tailings makes conventional acid-ferric sulfate or bacterial leaching unattractive.

c) Ammonia leaching of cuprous sulfide is ineffective compared with extraction by cyanide.

2) Preparation of feed for leaching is inexpensive.

a) No grinding of larger sizes is required to make copper available for leaching in a limited time.

b) Removal of fines to obtain necessary flow characteristics of the leach bed is easily accomplished.

 Copper is rapidly soluble and contaminants are not.

4) Washing is rapid and thorough.

Reagent costs per lb of copper are well-defined Operating labor costs in a well-instrumented plant should compare with those in a conventional plant. Maintenance costs should not be excessive. However, capital costs per ton of material treated will be high; a 7000-tpd cyanide plant may cost \$1300 to \$1400 per ton compared to \$600 to \$1000 per ton for a flotation plant of the same capacity.

Economic analysis indicates that an otherwise valueless feed material containing as little as 7 lbs of copper per ton is potentially profitable when treated in a 7000-tpd plant.

MINING ENGINEERS

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Wanted: Rotary Drilling Technology for In Situ Mining Systems

Gerald W. Laswell, Conam Co.

The pace of in situ mining must rapidly accelerate if the. US is to continue to compete in world markets for metallic ores and fossil fuels. In recent years, in situ techniques have found an increasing number of applications, particularly in copper recovery. Some well-known in situ operations include:

Cities Service Co.'s Miami mine in Miami, Ariz.,

■ Ranchers Exploration and Development Co.'s Old Reliable and Big Mike mines located near Mammoth, Ariz., and Winnemucca, Nev., respectively, and

■ McAlester Fuel Co.'s Zonia operations, near Kirkland Junction, Ariz.

In situ mining research is also being conducted by the US Bureau of Mines and Duval Corp. at the Sierrita pit, south of Tucson, Ariz. Kennecott Copper Corp. and the Energy Research and Development Administration

SUBJ MNG WRDT (ERDA) are continuing R & D efforts in the application of nuclear blasting to recover in situ copper. Finally, ERDA is conducting an in situ coal gasification experiment near Gillette, Wyo. Here, the long-term goal is to recover methane from sub-bituminous coals from a depth of 910 m (3000 ft).

Pros and Cons of In Situ Mining

Resources that cannot be recovered by conventional mining methods can be evaluated for possible recovery by in situ mining. Utilization of these methods allows a high degree, of recovery with minimal cost and labor. Unfortunately, the same factors that hinder conventional methods often preclude in situ, recovery programs utilizing conventional mining methods. These factors include: (a) ecological impact; (b) slow financial returns; (c) a resource body too deep to strip for exposure and fragmentation; (d) an unstable formation, prohibiting underground mining techniques; (e) excessive water requirements; and (f) difficulty in controlling the resource recovery media.

Furthermore, while a 4.15-million-ton blast by the McAlester Fuel Co., indicated that drilling blastholes from the surface was a valid concept, some shortcomings were identified. Tight and block spots were located, thus preventing optimum flow of the leach liquid; and the number of blastholes needed was costly.

A review of the results and problems points directly to situations that have arisen in other drilling industries, and thereby to solutions and concepts derived from oil well and industrial drilling.

What is In Situ Rotary Drilling?

In its simplest form, rotary-drilled in situ mining consists of blastholes drilled into the resource body and loaded with sufficient explosive to fragment the host rock by expanding it into drilled void holes. Recovery liquids or gases are routed to the resource through drilled and cased injection holes and the liquid is retrieved from other drilled and cased recovery holes.

Unfortunately, the equipment, technology; and expertise to perform such a drilling program can rarely be found in mining organizations. For that matter, the unique aspect of in situ drilling will tax the other drilling industries as well, but the in situ planner can utilize the abilities of the various drilling industries, and the options open to him and his drilling contractor are practically unlimited. Failure to consider new and unusual techniques can condemn an in situ recovery program to marginal success or outright insolvency.

Available Equipment and Technology

Due to the complex operational steps required for in situ recovery, there is not a drill on the market that can fulfill all of the requisites. Likewise, the downhole tools presently available are at best borderline for hard-rock applications. There is the expertise within the drill equipment companies to develop specific drills and downhole tools, but as yet market incentive has not appeared. In the meantime, the only workable solution is to modify existing equipment and substitute wherever possible.

For shallow in situ blastholes and voids less than 180 m (600 ft) deep, there are several drill types that can be used as the basic machine, including conventional blasthole drills and water well drills of the 1700/category.

Blasthole drills must be upgraded in hösting, steel breaking, and torque for in situ use. The water well machines have to be altered to accommodate larger diameter pipe, and need modification to facilitate rapid movement from lible to hole. Both types need increased air compressor capability.

The result of these-modifications is a drill that can produce, a 270-mm-diam (10³/4-in.) hole to depth, with adequate air to underream a chamber, and still retain the mobility of a blasthole drill.

These are costly adaptations, and a drilling contractor must be expected to recoup a reasonable return, because a drill thus modified is worthless for other contract applications. Another obstacle facing contractors is the material and component shortages needed to modify drills. Long delivery dates for structural steel and other parts must be anticipated and programmed into the project timing.

For deep in situmining below 180 m (600 ft), the drill options are more limited. While the oil well industry has developed the necessary drills, these units cannot be moved rapidly. Construction industry drills in this class are even more sedentary. These drills can be upgraded into a more mobile unit, but the cost is high and the overall mining plan must be able to justify the modifications. The dollar value of the resource dictates equipment limitations and project feasibility.



Fig. 1—Failing's 3000 Series drill offers maximum an-site mobility for deep in situ mining applications.



fig. 2—[—]Tigre Tierra's Aardvark 125 can produce holes from horizontal to vertical, while installing casing out to 3000 ft.

Injection and Recovery Holes

In many programs, the blasthole drill design will also be used for installing injection and recovery casing. In others, a conventional water well machine will suffice. Due to the fragmented nature of the host rocks, casing installation will often require specialized machines such as surface percussion drills, which can drive the casing while rotary drilling through the broken rock; angle drills, capable of drilling from horizontal to vertical holes, thus hitting the target from advantageous drill sites, or hitting a number of targets from a single site; or internal casing drills that install the casing inside the drill pipe. With these, casing can be installed through any formation.

Idealizing an In Situ Drill

The ideal in situ drill would be a modular unit, fabricated so that the correct combination of horsepower and air components could be added or removed as needed. This concept has found wide acceptance in the oil industry, but has rarely been applied to mine drilling.

Among the many innovations that are not being utilized in mining are three concepts that have in situ drilling applicability. They are:

Underreaming, or chambering—a useful method for special oil well applications. Existing tools are not designed for continuous operation in abrasive or hard-rock drilling. They are not selective; i.e., they could only be used in the hole when needed. They are also unable to expand to the desired diameter ratios.

Even with all these drawbacks, chambering is the key to successful in situ drilling. While these tools are costly and have a short life, they can drastically reduce the number of loaded and void holes for a given project. Reduction of the number of blastholes significantly cuts operational time and reduces the number of drill sites and roads.

Chambering in softer rock such as uranium sands with presently available "drag-type" underreamers can effectively open a 710-mm (28-in.) cavity from a 270-mmdiam (10³/4-in.) pilot hole. This order of magnitude approaches the ratios needed for efficient in situ drilling.

Research and development continues for selective hardrock tools. It is anticipated that an adequate chambering tool will arrive before in situ drills. Tri-State Oil Tools offers a production underreamer that overcomes many operational problems inherent to hard-rock application. While at present this tool can only double the annular area of the blasthole, it is a significant step towards the development of a true tool, and further improvements are expected.

Dual-concentric drillpipe---while fully developed, has, not been completely accepted. It complements in situ drilling by drastically lowering the air volume requirements needed to clean a large borehole or chamber. By containing the airflow down to the bit and returning the air and cuttings through its inner tube, maximum air efficiency is attained. Since no air is returned up the outside of the drill pipe, large-diameter pipe is not needed, and drill hoisting/racking requirements are decreased.

Dual pipe is mainly used for drilling blast and void holes, but also lends itself to hydrology and leach fluid testing. With its unique construction, it can airlift the fluids to the surface without pulling the drill pipe, running casing, or installing pumps. Thus, fluid testing can be accomplished in a single pass.

Dual pipe is in short supply as of November 1975, and delivery time is about eight months, with special sizes taking even longer. Downhole tricone percussion—should not be confused with the ordinary harmer drill. These large tools employ a lower energy level than hammers, while incorporating the efficiencies of a tricone rock bit. They have double the penetration rates through hard rock, yet maintain suitable rates through soft or broken material. These bits can be rented from several oil field supply companies.

Other downhole tools that should also be considered include directional control systems and pressure grouting tools. Directional control systems enable the driller to maintain a straight hole or "deviate" the hole to a specific target, as needed. This can be accomplished with calculated placement of stabilizers above the drill bit and with motorized rock bits (see Fig. 6). High-pressure grouting, to prevent unwanted waterflows or loss, has reached a very sophisticated level. This service is available from many cementing companies, that also offer hydraulic fracturing services. While hydraulic fracturing appears to have some merit as an in situ technique, it has no means for directional flow control.

Selecting a Circulation Media

Any drilling method is only as good as its ability to remove the cuttings from the borchole and cool the rock bit or tools. Selection of a correct circulation media is dictated by the rock formation, the equipment available, access to water, and program time schedules. The general classifications of circulation fluids are:

Drilling mid-a mixture of bentonite and water, usually with other additives. Best when drilling in adverse



Fig. 3—A field proven hard-rock underreamer developed by Tri-State Oil Tool Industries, Inc. produces a chamber double the annular area of the blasthole.

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r, usudverse formations such as water-sensitive shales. It has the slowest penetration rate.

Water—less costly than mud, but risky in all but the most stable formations. It is subject to loss in low-psizones, but is faster than mud.

Aerated fluid—air injected into mud or water. It reduces hydrostatic head at the bit, thereby reducing fluid loss to formation. Its use requires a low-volume, highpressure air compressor in addition to pump and fluid, and it has faster penetration than water.

Eoam—a strange concoction of water, bentonite, foaming agents, guar gum, and inhibitors. Pumped slowly and aerated, the result is a slow-moving foam resembling an aerosol shave cream. A very effective system for largediameter drilling, it is faster than aerated fluid, but cannot be recycled and in some cases, is not biodegradable.

Mist drilling—when conventional air drilling encounters damp, sticky formations or actual water flows, small quantities of foaming agents, water, and inhibitors are injected with the air. It requires a small, high-pressurepump in addition to high-volume air compressors, and is faster than foam drilling.

Air—When drilling conditions permit, straight air drilling is the ultimate drilling circulation system, having the best penetration rate. There is no water to haul, chemicals to buy, or pumps to maintain. The economic value of air decreases as hole sizes increase. For large-diameter holes, compressed air in conventional systems is costly. Using a 114-mm (4½-in.) drill assembly, it only takes $25 \text{ m}^3/$ mm (900 scfm) to drill a 200-mm-diam (7%-in.) blast-



Fig. 4—Walker-Neer's "Con-cor" drilling process employs dual-concentric drillpipe that reduces air volume requirements and is suited for blast- and void-hole production.



Fig. 5—Downhole tricone, percussion tool from indersoll-Rand's Compression Services, boasts lower energy requirements and comparable penetration rates, when matched with conventional rotary drilling.

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Fig. 6—Dyna-Drill, developed by Smith International, utilizes a directional control system that enables the driller to maintain a straight hole or deviate the hole to a specific target as needed.

hole, but 142 m³/min (5000 scfm) to drill a 445-mm-diam $(17\frac{1}{2})$ -in.) blasthole.

Air, like all other factors affecting in situ drilling, must be evaluated according to its merits and shortcomings.

The Right Combination

While a wealth of techniques, tools, and services are available to improve in situ drilling, the favorable aspects

of each occasionally detract from the effect of the others. Thus a careful evaluation of the costs and effects of each component and its effect on other components is necessary. A technique that complements one drill assembly will not necessarily improve a different drill assembly. Likewise, a combination of tools and techniques that is optimum for one in situ mining system may be totally ineffective for another.

Taking an extreme example, chambering with jet piercing was the salvation of the taconite industry a few years back. Attempts at utilizing jet piercing in other hard-rock mining operations were costly failures. Now it appears that a modified form of jet piercing could be an answer to chambering for oil shale in situ retorting, due to the spallable characteristics of the marlstone combined with the combustion of the kerogen components. In effect, a technique acceptable for extremely hard rock was inadequate for hard rock, but excellent for soft rock. There is no universal rule for finding the correct combination of in situ equipment and techniques. Each in situ mining program must be carefully examined. All applicable data must be utilized, such as core and sample drilling records, hydrology, topography, and geology. Ideally, a pilot program would be drilled; detonated, sampled, produced, and evaluated before a production drilling program is initiated.

If in situ mining is to become a major mining method, it cannot wait for equipment development. Effective programs can be accomplished now with innovative drill program and equipment planning. Even though the state of the art of drilling and chambering has not reached the level required, it is adequate and will improve as demand continues. The benefits of a drilled program can justify a reduced level of efficiency by eliminating all underground manpower and equipment. Even programs that utilize underground mining methods can benefit from some degree' of surface drilling. In some cases, drilling in conjunction with underground mining is the only answer.

In situ drilling is not new. The vast sulfur programs in Texas and Louisiana are a prime example: they were developed almost entirely with oil well drilling technology. The chambered drill hole gives us access to ores that have been condemned by all other methods. The pure in situ project does not fear strip mining bills or other unreasonable controls.

Acknowledgment

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About the Author Gerald W. Laswell, a drilling consultant with the Conam Co. (No. 730-37 Street, Bouider, Colo. 80303) is a member of SME-AIME and the Canadian Institute of Mining and Metallurgy, Mr. Laswell has authored numerous papers on experimental drilling. His accomplishments include the development of the "differential value circulation system," which directly contributed to the successful drilling of shatts for nuclear emplacement; development of dual-concentric thip sample/ drilling methods; and refinement of the dielectric technique of mineral sample analysis. Prior to his present position, Mr. Laswell was project leader of the Servco blasthole chamber tool project.



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DURING HYDROMETALLURGICAL PROCESSING OF PYRRHOTITE-CONTAINING CONCENTRATES

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T. N. Matevich, V. I. Goryachkin, A. I. Slavskaya, M. I. Mantsevich, and A. S. Ladygo

The autoclave technology in the first stage of the Nadezhda Metallurgical Plant at the Noril'sk Mining and Metallurgical Combine provides for dumping most of the iron in the raw material in the form of neutralized hydrated pulp, which is the principal factor in losses of valuable constituents [1]. Compared with standard pyrometallurgical technology used for copper-nickel ores, hydrometallurgical processing of pyrrhotite concentrate containing (in %) 2-3 Ni, 0.5-1.2 Cu, and > 0.1 Cu (with an Fe-Ni ratio of > 16) substantially reduces the amount of non-ferrous metals lost with the waste products [2]. Nevertheless, the losses of Ni, Cu, and Co remain high, amounting to \sim 3.5 2.0, and 0.3-0.6 kg respectively per ton of waste iron.

Improving the technology by including a sorption stage in the scheme practically eliminates losses of non-ferrous metals with the solutions; the main subject of attention was therefore the reduction of the metal content of solid matter in the waste tailings.

No provision was made in the Nadezhda Plant first stage for processing the iron tailings by generally-known methods [3] to obtain commercial iron with final extraction of the valuable constituents, because it involves a substantial capital outlay and difficulty in rendering the gaseous and liquid production waste harmless and offers little economic advantage under the specific conditions prevailing at that enterprise. The greatest potential for increasing non-ferrous metals extraction therefore lies in improving process schedules in the principal operations provided for in the design (oxidizing leaching, aggregation of sulfur and sulfides into granules, flotation etc.) [1].

Examination of the forms in which the non-ferrous metals occur in the initial pyrrhotite concentrate indicates that a high extraction rate is possible.

The nickel content of the ore concentrate pyrrhotite fraction fluctuates from 2.2 to 7.7% and the copper content reaches 5.3% [4]; the percentage content of metals isomorphically included in the pyrrhotite lattice is 0.03-0.04 Ni, 0.03-0.08 Co, and 0.01-0.5 Cu (5]. A comparatively small amount of nickel is linked with the non-ore minerals [4, 6, 7]; the magnetite contains 0.08-0.1% Ni and 0.005-0.008% Co which, according to [6], are included in its composition isomorphically.

A study of the composition of waste tailings samples from laboratory and pilot-plant flotation experiments using chemical, mineralogical, x-ray microspectral, phase, and other methods of analysis¹ reveals the following distribution of nickel, copper, and cobalt among the constituents: from 10 to 185 is linked with gangue minerals and magnetite, up to 20% is in water-soluble compounds, and \sim 70% of the losses of each metal is attributable to oxidized forms and natural and secondary sulfides. Films of iron oxides were found to be present on the unextracted sulfide surfaces, rarely reaching several microns in thickness. In most cases, the films are much thinner and can be detected only by precise methods (ESKhA electron diffraction) [8].

Studies have shown that the extraction of nickel, copper, and cobalt is governed to a great extent by the conditions in the principal operation: oxidation of the initial concentrate aqueous pulp by oxygen in the autoclave.

The results of experiments with leaching of the initial concentrate in water, followed by flotation of the oxidized pulp, show that the tailings copper and nickel content drops to 0.10-0.15% as the extent of pyrrhotite decomposition and the leaching time increase (to 5-6 hr). This is caused by passage of the metals into solution, and also by a gradual improvement in the floatability of the sulfides due to the probable elimination of oxide films and formations from their surfaces. Sulfide surface passivation develops rapidly during the initial period of oxidation at a solution pH> 4.0. As a rule, 80-90% oxidation of pyrrhotite in concentrate of typical composition reduces the losses of each metal with solid matter in the tailings to 3-5%.

According to sedimentometric analysis, there is a sharp increase in the proportion of copper and nickel in the fine tailings classes (< 10 μ) when the extent of concentrate decomposition increases; this is apparent from the Figure. It is significant that the content of these metals in the fine classes is also higher than in the coarse classes; this trend is particularly clear in the finest tailings fractions; thus, one

¹The study was conducted with the direct participation of staff from Gintsvetmet: E. I. Bogoslovskaya, V. A. Kukoev, K. D. Leont'eva, V. M. Demidova, V. V. Kazakova, and L. G. Samokhvalova.

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Effect of Sulfate Additions in Oxidizing Leaching* of Pyrrhotite Concentrate Upon the Level of Non-Ferrous Metal Losses with the Waste Tailings

flota f. t. was	Sp. losses with flotation-tail- ings solid (kg/ 't,waste iron)of		
NÍ	Co		
4,1 2,8 2,4 2,6	0,37 0,30 0,28 0,28		
¢	0 0,75		

*Leaching conditions: t = 110 C; PO; = 5 atm; T = 3 hr. Initial concentrate composition, 8: 2-2.5 Ni, 0:6=1.6 Cu, 52-56 Fe, 30-32 S; flotation by the routine provided in the design [1].

of the samples of representative composition² contained the following (in %):

Fraction	Cu.	Ni
< 5 µm	0.09	0.46
< 1 µm	0.18	0.50
< 1, µm*,,	0.40	0.60

Coating the walls of the vessel, average particle size fractions of a micron.

The following methods, which can be implemented in stage I at the plant, were tested for final extraction of non-ferrous metals from the tailings:

- centrifuging with quartz sand as the abrasive additive at 80°C and mixing for 1 hour:

- contact with molten sulfur at the rate of 100% of solids weight at 140-170°C for 1 hour;

- releaching at 160°C, PO = 5 atm for 1 hr. Processing a sample of tailings containing 0.14% Cu and 0.46% Ni showed that consecutive application of these operations reduced the copper and nickel content to 0.01 and 0.13%, respectively. Centrifuging with sand released 28.6% Cu and 13.1% Ni into the solution, contact with molten sulfur extracted 42.8% Cu and 19.5% Ni into the sulfur granule, and releaching extracted 21.5% Cu and 39.1% Ni into the solution. Cobalt extraction was at the same level as nickel extraction. The total extraction after the three operations was ~ 93 % Cu and 73% Ni for this sample of tailings. Pulp flotation after centrifuging with sand reduces metal losses with the tailings

Pulp flotation after centrifuging with sand reduces metal losses with the tailings somewhat, but the concentrate obtained contains a considerable amount of iron oxides. Similar results were obtained in flotation of tailings pulp following treatment with sand and molten sulfur.

It is apparent from the results given in the Table that acidifying the solution prior to leaching or adding iron and magnesium sulfates to it substantially improves the composition of the oxidized pulp flotation tailings in terms of nickel and cobalt; this factor has comparatively little effect upon copper extraction. As in leaching in water, the leanest tailings -- with respect to non-ferrous metals content -- correspond to maximum pyrrhotite decomposition.

Thus, the nickel and copper lost with the tailings are in the form of sulfides, water-soluble sulfates, and also secondary oxidized relatively insoluble compounds. Over 50% of non-ferrous metals losses are attributable to sulfides; no more than 15% Cu and Ni is lost with the gangue, while the water-soluble compounds account for 7-30% of all losses. As a rule, the sulfides are covered with films of oxidized compounds which impede their flotation. Most of the non-ferrous metals are lost with the fine tailings classes (< 10 μ), which contain increased amounts of copper and nickel. Increasing the extent of pyrrhotite decomposition during leaching helps to reduce losses of Cu, Ni, and Co with the tailings.

The following steps are recommended as ways to reduce the losses of these metals with the solid matter in iron tailings:

- addition of sulfate ion (in the form of sulfuric acid, recirculating oxidized pulp, and solutions containing iron and magnesium sulfates) to the pulp at the oxidiring leach stage at the rate of over 0.5% of the initial concentrate mass, pyrrhotite decomposition being at least 80%;

The initial solid solids! sample from the tailings contained 0.1% Cu and 0.14% Ni.

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tribution t (1, 4) of nickel (a) and copper (b) in pulp flotation tailings after leaching pyrrhotite concentrate. Fraction, µm: 1, 3 - -10; 2, 4 + +20.

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- aggregating sulfur and sulfides from the oxidized pulp into granules in the absence of an oxidizing agent at temperatures up to 160-170°C.

These measures will reduce the percentages in the waste tailings as follows: to 0.04-0.1 Ni, to 0.010 Co, and to 0.02-0.05 Cu, which amounts to 1.6, 0.2, and 0.8 kg of each metal per ton of iron removed respectively.

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million will be incurred on research work; sy million on general expenses and working opital; \$55 million on construction conmets and equipment; and \$10 million on current interest charges. The: \$55 million of capital works is apportioned as to of capital works is apportioned as to of sis: 3 million on wharves and loading finities; \$21 8 million on surface works and reament plant at the mine; \$7 million on shafts, machinery, etc.; \$53 million on detric power station; and \$56 million on busing and personal services by the time the project is completed.

The capital will be provided as follows: fio I million representing the capital of the Compagnie des Potasses du Congo; \$25.9 million by advances from the company's preholders; and loans from three financial mitutions amounting to \$45 million, of the the World Bank will provide \$30 million, the European Bank for Investment p million and the Banque Nationale de his \$6 million.

Winning of Useful Elements from Minerals by Leaching Underground*

IN Nature, the processes of leaching of different elements from rocks has been widely developed by flowing water underground. And it is now well known that certain bacteria are geological agents; which transform minerals. By artificially creating analogous conditions within an ore deposit it is possible to leach some mineral deposits in situ.

Underground leaching implies selective solution and transport by water or other solvents moving within an ore layer. The circulation of solvents through the

*This article first appeared in full in Gornly Zhournal, January 1967.



pores and fissures of an ore layer takes place by the action of a special system of forcing and drainage. ONENCE LAD

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Most of the tasks in the hydrodynamics of underground leaching can be solved on the basis of the existing theories of the elasticity of a bed (worked out by M. Maskatov, V. N. Shelkatchev, N. N. Veriguin, M. D. Millionshikov and others). Most of the problems in the kinetics of leaching can be solved on the basis of the already developed theory of filtration-solution of the dispersed material in sandy-clayey or fissured rocks.

It is known that in dissolving underground salts by sceping water, regular stages occur, and a residue is left.

Underground leaching opens wide possibilities for complex extraction from ores. All the valuable components in the orebody can be recovered either simultaneously or successively.

This method of working mineral deposits is already profitable, even for recovering metals and other valuable components from pillars; mine wastes and lean ores, as well as in winning particular ore blocks with specially difficult water conditions.

Recovery of copper by underground leaching has industrial significance in U.S.A., Mexico, Japan and the U.S.S.R. The cost of copper obtained by this method is one third to one fifth of that by underground mining and smelting of ore. In the U.S.S.R., reliable experience of leaching this metal has accumulated in the mining areas of Degtiarskiy, Suselskiy, and elsewhere. The ore was leached through holes drilled from the surface. However, the recovery of copper by this method has not widely expanded. Recovering copper from Permian sandstones on the west slopes of the Urals has been given priority in the U.S.S.R. Plans for this work have been available for a long time.

World annual output of rock salt by solution mining, is 25 to 30 million ton. In the U.S.S.R. and Bulgaria, the cost of rock salt obtained by this method is one tenth that of conventional methods.

Combined Methods

The physical-chemical and microbiological methods for winning some metals and other-substances can complement each other and be combined with conventional mining. For example, it is possible to successfully combine washing theore out through boreholes with leaching, or to combine underground leaching with drilling and blasting, or inderground leaching with microbiological methods.

Existing plans and research results show that underground leaching with the ore broken in situ by nuclear blasts appears profitable even with large low grade deposits. For example, in the U.S.A., it has been estimated that it is already economic to work copper deposits with less than 0.5 per cent copper if the ore reserves exceed 10 million ton.

The intensity of leaching and the grade of recovery can be substantially increased by introducing appropriate bacteria into the solvent directed to the ore layer. Micro-organisms are known that accelerate the processes of oxidation and dissolving of metals and other useful minerals by 10 to 20 times, or more.

Types of bacteria have been obtained which enable up to 70 per cent of the metal to be recovered from sulphide ores of copper, cobalt and iron. Methods exist for recovering molybdenum and zinc from sulphide and oxidised ores by bacteria, also for removal of iron from ferrous titanium ores. In Yugoslavia, micro-organisms have been used for dissolving the uranium minerals. Microbiological solution methods have also riven positive results in winning cobalt. copper, uranium and other elements from low-grade ores. In the U.S.S.R., tests are being made for adopting thionine bacteria to intensify a solution action on copper-sulphide minerals.

Chemical Methods

The recovery of useful minerals by chemical and physical methods is often lower than in underground mining, But this is temporary, because to date much two little attention has been paid to studying, developing and improving solution mining methods.

An analysis of the experience and the results of the researches brings out the following technical layouts for underground leaching of different deposits: Fig. 1. System of vertical or inclined boreholes for pressure and discharge. 1; 2 = water resistants; 3 = waterbearing horizon; 4 = ore bed; 5 = discharge borehole; 6 = pressure borehole.



- (i) Different systems of vertical or inclined pressure and discharge boreholes drilled from the surface (Fig. 1).
- (ii) Rows of pressure and discharge boreholes, but connected into drain rows placed along the ore layer.
- (iii) Working shallow deposits by means of irrigation and drainage channels or drifts.
- (iv) Underground layouts with a system of rooms and boreholes drilled from them.
- (v) Underground layouts with preliminary loosening of the ore blocks intended for leaching, using nuclear or conventional blasting with storage of ore (Fig. 2).
- (vi) Combined layouts consisting of Sunderground drainage rooms and pressure boreholes drilled from the surface (Fig. 3).

The choice of the layouts for underground leaching depends entirely on the depth of the deposit and on the geological, tectonic and hydrogeological conditions.

For deep mineral deposits it is evidently more rational to leach by pressure and discharge boreholes drilled from the surface. From the point of view of underground hydraulics in sedimentary deposits composed of sandy-clayey rocks; methods (i) and (ii) are more profitable with forcing and drainage holes in rows. Adoption of a ring-shaped leaching system must be limited to deposits with orebodies of small, separate layers.

According to the movement of the solvent within the orebody, chosen to suit the type of the deposit, its permeability, structure and special features, the following technical layouts for underground leaching are found:

(1) With continuous action;

- (2) With pulsating action;
- (3) Combined layout.

Fig. 2. Layout of underground leaching of useful minerals in chambers. I = ore bed; 2 = shaft; 3= block of loosened ore being subject to leaching; 4 = flow of filtrated solutions; 5 = sublevel drift for collecting solutions; 6 = room for receiving solutions; 7 = absorption columns and other enrichment equipment for extracting metals from solutions; 8 = room for receiving fresh solvent; 9 = equipment for preparing the solvent; 10 = pipes for feeding the solvent for irrigation; 11 = pipes for feeding fresh reagent; 12 = pipe for irrigator; 13 = host rock.



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Fig. 4. Laboratory equipment for studying underground leaching. I = filtration device; 2 = high pressure container; 3 = watermeasuring glass; 4 = flask with compressed nitrogen; 5 = reducingvalues; 6 = container for selection of filtrate; 7 = electrodes for $measuring <math>E_h$ and pH; 8 = buffer container; 9 = receiving container; $I_0 = connecting hoses; II = collecting container; I2 = mano$ meter; I3 = three-way cock; I4 = places for sampling.

Fig. 3, right. Combined system consisting of vertical boreholes for pressure and drainage of drifts and crosscuts.

1 = pressure boreholes; 2 = drainage drifts; 3 = shaft; 4 = waterresisting rocks; 5 = water-bearing horizon; 6 = ore bed.

* In the layout for continuous action, the maximum development of convective eaching is secured. It is mainly adopted in deposits with a high content of leachablematerial, and a characteristic oxidising geochemical medium. Possible solvents for leaching are: fresh natural waters, water-gas mixtures, acid solvents (0.5 -3 per cent) and carbonate solutions. Accelerators introduced into the solvent include air, O₂, CO₂, NO₂ and others. For the same purpose, gas can be blown through the deposit, according to the system gas - solvent - gas; heating the deposit is also possible.

Leaching of elements directly from an ore bed, apart from the ore composition, is greatly affected by the composition of the roof and foot wall, as well as by the chemical composition of underground waters confined to the ore layer and its country rock. For this reason, the solvent, when percolating through an ore body, will always contain more components than the same solvent in hydrometallurgical processing for example.

The type of mineralisation and the . composition of orebodies is often very variable. Therefore, the technical parameters of underground leaching must be determined by laboratory and field investigations for each orebody. The layout of a laboratory installation for determining the parameters (coefficients of convective and diffusion leaching, etc.) as well as the hydrodynamic parameters of an ore bed (piezoconductivity, conductivity) is shown in Fig. 4. This installation has been successfully applied



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Economic [.] res	ults of v	vinning u	seful miner	als using v	arious method	s*
				- <u>I D -</u>		1

Working method	Relative cost of winning	Relative intensity of winning	Recovery ful subs from c (per c	Comments			
, j	r tou	or winning	Real	Possible			
Conventional system of under- ground mining (drilling, blast- ing, mechanical loading and haulage)	I		75-90	Up to 98	According to A. V. Boudko		
Underground mining of sulphur by smelting and raising it by air- lift	0-3-0-5	Over 1	Up to 30		Up to 30 fr		According to sources from U.S.A.
Underground leaching of copper in blocks mined out	0.2-0.4	0.3-0.2	Up to 70	Up to 80	The same		
Underground dissolving salt through boreholes drilled from the surface	Occasion- ally 0-2-0-3	Up to 0'5	3-10	Up to 30	The same		
Underground leaching sedimen- ary deposits of rare elements	0:5-0:75	Over 1	Up to 70	Up to 90			
Underground leaching non- industrial copper deposits (up to 0.5 per cent Cu) with loosening ore blocks by nuclear blasts	0-6-0-75	Over 1	40	Up to 80	According to the laboratory work of		
Working sedimentary deposits of rare elements by a combined, method — washing out and leach- ing through boreholes drilled from the surface.	0'3-0'5	Over 1	During Up to 80		K. N. Ivanov		
Underground leaching of copper by bacterial solvents	Up to 0-15	5 1-6 cent					
Underground leaching sedimen- ary uranium deposits	ġ :3−0: 5		During 550 days 66 per cent	80-90	According to sources from U.S.A.		

* The results achieved in underground mining are indicated by 100 per cent.

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in the U.S.S.R. for investigating ore deposits. Determination of an oxidisingreducing medium within an ore bed has the highest significance in the problem of underground leaching. The presence of a reducing medium within a bed to be leached, for example, can point at the need for oxidising agents.

Underground leaching and solution can be impeded by two natural factors: low permeability to water of the ore bed and the presence of tectonically fissured zones causing excessive leakage of the solvent. But the effect of these factors can be greatly reduced or eliminated by installing hydrodynamic grout curtains, loosening of ore layers by conventional or nuclear blasts, etc.

Most mineral deposits are in water bearing horizons. Therefore, it is usually necessary to investigate in detail the interrelationship of the ore layer or its water bearing horizon with adjacent aquifers. In this way leakages in or out of the leached bed are prevented.

Despite the economical and technical advantages, no more than 2-3 per cent of ores throughout the world are won by using physical-chemical and microbiological methods.

A. I. KALABIN, Doctor of Geological and Mineralogical Sciences.

Abstracts

A Survey of the Literature

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COMMISSIONER OF MINES

GOVERNMENT OF JAMAICA

Qualifications: A qualified mining engineer with experience in the administration of Mining Laws and Regulations.

Duties: (A) Responsible for the efficient operation of the functions of the Department of Mines to ensure that maximum benefits are secured from the Island's mineral resources.

- (B) Administration of the Mining Law, Quarries Law, the Petroleum Law and ancillary legislation.
- (C) To advise the Government on the policy to be applied to the mining industry including its taxation policy.
- (D) To investigate and promote schemes for the development of the Island's mineral potential.

Age Limits: Under 55 years.

Terms of Appointment: On contract for one tour two-three years. Salary £3,510 p.a. Terminal gratuity 20% of total emolument. Free passage and medical attention. Generous leave and educational allowance.

Applicants, who should be nationals of the United Kingdom or Irish Republic, should apply quoting RC 242/92/01 and giving full names, age, qualifications and experience to:

> The Appointments Officer, Ministry of Overseas Development, Room 301, Eland House, Stag Place, Victoria, London, S.W.1.

teristic figures have to be investigated pied of the their applicability in practice. This is done fir impormeans of a reference plane, similar toⁿ, are detectonic plane, the mathematical element of which are precisely known. By comparing TABJAN, with mathematical values or values forming app in the practical drawing of mine maps are more plans, the errors to be expected are identias a function of the density of points in 20:: the g

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Experimental arrangements set up r Vibrat results obtained by the large opencast methicfactor of Spreetal are described which eres and mainly concerned with the rational contribution of extractive equipment. Other fields down v applications in mine surveying are drivp ain cussed. (German text.)

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exte The multiple-moment method describe acci in the present paper is a random to method permitting obligatory statements 1 Par be made at a statistical safety of 95 per cer Th on any irregular processes or quantities, 12-for each accuracy desired. This mod **Spc** me method of work study, when used approp ately to the occasion, is suited for filler information gaps in maintenance wer below ground. fil

Compared with other methods, specadvantages presented by it include: time ar cost saving, universal application, ar simple handling. (German text.)

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UNIVERSITY OF UTAN RESEARCH INSTITUTE EARTH SCIENCE LAB. SUBJ MNG WWT ; 4189381 PATENT NO.-ORFASE ATTE IN WITH SPACES, ONEY NOID II 9 8 3 4 8 FOLDED, STAPLED OR OTHERWISE MUTH ATED. DO NOT ATTACH AD "ITIONAL THICKNESS OF PAPER TO THIS COUPON It will be accepted by the U. PATENT and TRADEM ARK OFFICE in lieu of 50° m payment for exples of U.S. Patent E S Do Not Write In This Box Adatess Coupons Only Box 9 300184 Patent and Trademark Office NDD IF Coursen No. 0982212 Washington, D.C. 20231 1 orm PTO-194b Series of 1979

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United States Patent [19] Laferty et al.

[54] WASTE WATER TREATMENT

- [75] Inventors: John M. Laferty, Wheatridge; Gary
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 Zundel, Lakewood, all of Colo.
- [73] Assignee: Amax Inc., Greenwich, Conn.
- [21] Appl. No.: 940,055
- [22] Filed: Sep. 7, 1978
- [51] Int. CL² C02C 5/08
- [58] Field of Search 210/28, 37 B, 38 B, 210/44, 50-54, 63 R, 73 R, 62, DIG. 31

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Primary Examiner-Charles N. Hart

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 [11] 4,189,381 [45] Feb. 19, 1980

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Attorney, Agent, or Firm-Michael A. Ciomek; Eugene J. Kalil

[57] ABSTRACT

Waste water containing over 2 ppm Mo and at least one heavy metal impurity selected from the group consisting of Fe, Mn, Cu, Zn, Pb, and Cd, and also containing cyanide ion (CN) is treated by passing waste water having an adjusted pH value ranging from about 3 to 4 through an ion-exchange resin column selective to the removal of Mo and provide an ion-exchange effluent containing at least one of said heavy metal impurities and said cyanide ion. The pH value of the effluent is then adjusted to a range of about 7 to 11 sufficient to precipitate the heavy metal impurity baving the highest pH requirement for precipitation, following which the precipitate is flocculated and the effluent containing the flocculated precipitate then subjected to electrolysis using insoluble electrodes to form electrolytic oxygen and hydrogen and effect electroflotation of the flocculated precipitate and form a froth thercof which is separated from the effluent by skimming.

6 Claims, 1 Drawing Figure



U.S. Patent



1 WASTE WATER TREATMENT

This invention relates to the treatment of industrial waste water for recycling to surface waters and, in 5 particular, to the treatment of waste water obtained in mineral recovery processes, such as in the flotation recovery of molybdenite.

BACKGROUND OF THE INVENTION

Large amounts of water are employed in flotation processes which generally require a water recycle system utilizing active tailing dams and water storage facilities to collect mill water and then subsequently return the water for reuse into the flotation system.

While the system employed enabled total containment of the waste water during certain parts of the season, this was not always possible during the annual spring runoff of melted snow. Thus, the annual rapidly increasing runoff into the tailing system made it neces- 20 sary to discharge some of the industrial water from the system into surface waters in order to keep the total system in balance.

The water effluent or waste water obtained in molybdenite flotation generally contains small concentrations 25 of heavy metals, such as molybdenum, copper, zinc, iron, and the like, as a result of solubilization during the flotation process. The mill water may also contain combined cyanide in concentrations of less than about two or one part per million introduced in the mill circuit as 30 sodium cyanide which is used as a copper depressant. Such waters present a pollution problem if discharged into the surrounding environment.

It would thus be desirable to provide a waste water treatment process to remove substantially said heavy 35 metals in accordance with the prevailing target amounts for such waters.

OBJECTS OF THE INVENTION

It is an object of the invention to provide a process 40 for treating waste water containing heavy metals and produce an effluent with the heavy metal ions and cyanide ion substantially reduced.

Another object is to provide a process for removing heavy metal ions from industrial waste waters, for ex- 45 ample, industrial waste waters of the type obtained in the flotation recovery of molyodenite.

These and other objects will more clearly appear from the following disclosure and the accompanying drawing which is a flow sheet showing one embodiment 50 for carrying out the process of the invention.

STATEMENT OF THE INVENTION

One embodiment of the invention is directed to an environmental pollution control process for treating 55 waste water containing over 2 ppm Mo and at least one heavy metal impurity selected from the group consisting of over 2 ppm Fe, over 1 ppm Mn, over 0.05 ppm Cu, over 0.2 ppm Zn, over 0.01 ppm Pb, and over 0.015 ppm Cd, as well as over 0.025 ppm CN ion, particularly 60 waste water obtained in the flotation recovery of molybdenite. The process comprises passing waste water having an adjusted pH value ranging from about 3 to 4 through an ion-exchange resin column selective to the removal of Mo to a level not exceeding 2 ppm and 65 provide an icn-exchange effluent containing said at least one heavy metal impurity, adjusting the pH value of said effluent to a range of about 7 to 11, the pH value

selected being sufficient to precipitate that heavy metal impurity having the highest pH requirement for precipitation, cosgulating and flocculating said precipitate, and then subjecting the flocculated precipitate-containing effluent to electrolysis using insoluble electrodes to form electrolytic oxygen and hydrogen and effect electroflotation of the flocculated precipitate by virtue of the presence of bubbles of electrolytic oxygen and hydrogen and form a froth thereof, the froth containing

10 the heavy metals being thereafter separated from the effluent. The effluent is then filtered to provide a clean tailing liquor containing not more than 2 ppm Mo and not more than 2 ppm Fe, 1 ppm Mn, 0.05 ppm Cu, 0.2 ppm Zn, 0.01 ppm Pb, 0.015 ppm Cd, and 0.025 ppm 15 CN.

The waste water obtained from the molybdenite flotation process may typically contain the following in parts per million or mg/1.

FEED ANALYSIS										
Fe	Mn	Cu	Zn	РЪ	Мо	Cd	CN			
3-7	5-7	0.025-0.16	0.2-0.4	>0.01	2-24	0.015	0.2-0.5			

The effluent after treatment is deemed to be substantially cleaned of impurities when it contains a maximum of the following:

	TABLE 1										
0			E	FFLUE							
	Fe	Mn	Cu	Zn	Ръ	Мо	Cd	CN			
	2	1	0.05	0.2	<0.01	2	0.015	≦0.025			

DETAILS OF THE INVENTION

In carrying the invention into practice, the waste water containing molybdenum and at least one other heavy metal ion is adjusted to a pH of about 3 to 4 and the waste water then passed through an ion-exchange column containing an ion-exchange resin selective to the removal of molybdenum from solution. A preferred ion-exchange resin is a weak-base amine type anion exchange resin. This type of resin has a high capacity for molybdenum absorption and, moreover, has a high affinity for hydroxyl ions which allow for effective elution of molybdenum from the resin with smaller alkaline requirements.

One example of an ion-exchange resin is one sold under the trademark IRA 99, formerly Amberlite XE-299. This resin is a macro-reticular weakly basic anion exchange resin with a tertiary amine functional group attached to a copolymer of styrene-divinyl benzene as a polymer matrix. With this type of resin, laboratory loadings of up to about 12 pounds of molybdenum have been obtained at a cumulative percent recovery of over 90%. The resin in the hydroxyl form does not have a high capacity of adsorbing molybdenum but does have a high capacity in the bisulfate or chloride form. Sulphuric acid is preferred as the regenerant in that it is cheaper and also that it avoids contamination of the effluent water with chloride ions.

Tests have shown that an average molybdenum concentration of 2 parts per million could be obtained in waste water from a feed concentration ranging from about 2 to 24 parts per million, the average resin loading being about 3.66 lbs/ft³ of resin at these molybdenum feed concentrations. The average resin loadings at these

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feed concentrations would be higher when using a pulsed column.

Molybdenum resin elution efficiencies in excess of 98% were obtained using sodium hydroxide as the eluant, the resulting sodium molybdate solution containing 5 about 16 to 19 grams of molybdenum per liter.

A series of tests were conducted in which the feed waste water had a pH value of about 3.5 and contained an average of about 22.2 ppm Mo. Over a period of 8 days, the feed solution was processed by passing it 10 through the resin bed at a 24-hour operating schedule basis, the average feed rate for the 8 days being about 41.4 gallons per minute per square foot of resin bed (cross sectional area). The average molybdenum content of the feed was reduced from 22.2 ppm to 1.3 ppm, 15 the average bed loading being about 3.9 lbs. Mo per ft.³ of resin, about 94.1% of the total molybdenum being recovered. It was surprisingly noted that the resin removed from about 50% to 70% of the cyanide ion.

At a downflow rate of about 41 gallons per minute 20 per sq. ft. of resin, the pressure drop through the resin bed was 40 lbs/in.² which was found to be within the allowable maximum of 40 lbs/sq.in. as recommended by the resin manufacturer to avoid excessive physical resin degradation. 25

Following substantial removal of the molybdenum from the feed solution, the resulting effluent is then processed to remove the heavy metals present. This is achieved by adjusting the pH value of the effluent to a level within the range of 7 to 11, the level chosen being that sufficient to precipitate that heavy metal impurity having the highest pH requirement for precipitation, for example, manganese. Thus, the heavy metals present having a low pH requirement are assured of being precipitated.

The desired pH value (e.g., 10.8) is obtained by em-³⁵ ploying lime as the base, although other bases may be employed to neutralize the acid and precipitate the heavy metals as hydroxides. After lime precipitation, the precipitate is flocculated by the addition of a polymer flocculating agent, e.g., polyelectrolytes, such as one sold under the trademark DOW MG-700 and PER-COL 728 sold by Allied Colloid, Inc. The preferred flocculants are polyacrylamides, for example, non-ionic or weakly anionic polyacrylamide of the following formulation: 45

$(CH_2 = CHCONH_2)_X$

where X denotes the number of mer units making up the polymer, the high molecular weight polymer being 50 preferred.

In a preferred embodiment, before the flocculant is added, the precipitate slurry is conditioned in an electrocoagulation cell for upwards of several minutes, e.g., 1 or 2 or 3 minutes, by contacting said slurry with bubbles of electrolytic hydrogen and oxygen generated in an electrolytic cell using insoluble electrodes. The coagulated slurry is then treated as follows:

The slurry is flocculated and then subjected to electroflotation in an electrolytic cell using insoluble elec- 60 trodes, the amount of current employed being sufficient to generate substantial amounts of electrolytic oxygen and hydrogen which in the form of micro bubbles effect flotation of the agglomerated heavy metal precipitate. This process is referred to in the trade as the Swift 65 Lectro Clear process.

The froth produced in the cell is skimmed off and the final effluent either recycled into the molybdenite flota-

tion process or disposed of by discharging it into environmental waters following flotation, assuming little or no cyanide present.

In a pilot plant unit designed for an average flow of 10 gallons per minute, the residence times for the various stages of treatment comprised 10 minutes for lime neutralization, one minute for treatment in the electrocoagulation cell via contact with electrolytic hydrogen and oxygen to condition the precipitate for the flocculation step and the addition immediately thereafter of the polymer flocculant followed by electroflotation at at residence time of 25 minutes to effect flotation of the flocculated precipitate.

The process steps employed are illustrated in the accompanying flow sheet which shows waste water 10 going to acid treatment 11 where the pH value is adjusted within the range of 3 to 4, e.g., 3.5, following which the acidified waste water is passed through an anion-exchange column 12 to remove molybdenum and provide an effluent impoverished in molybdenum, that is, not exceeding 2 ppm.

The effluent is then neutralized with lime at 13 to a pH value of about 10.8 to precipitate heavy metal hydroxides which are thereafter treated at 14 in an electrocoagulation cell, a polymer flocculant thereafter added, including a surfactant, and the flocculated precipitate subjected to electroflotation. A preferred surfactant is one designated by the trademark 85L sold by Stauffer Chemical Co.

This is achieved by charging the flocculated slurry into an electrolytic cell 15 operated with insoluble electrodes where the slurry is subjected to electroflotation using generated micro bubbles of oxygen and hydrogen as the means of forming a froth which is skimmed off as shown.

In the event any residual cyanide ions are present in excess of the safe limit (i.e., in excess of 0.06 ppm), a treatment step 16 is added in which sodium hypochlorite (NaOCI) or other 'oxidizing agent is added in amounts ranging up to about 50 ppm to oxidize the cyanide ion. Following this treatment, the effluent is passed through a Baker Sand filter 17 before being sent to disposal.

Most of the processes employed for the detozification of waste water of cyanides utilize the oxidation approach to remove free cyanide and transition metal coordination cyanide complexes.

One method utilizes chlorine gas injected into the waste water stream, the waste water being first rendered alkaline by adjusting its pH value to a range of about 10.5 to 11. Laboratory tests conducted at 10° C. at pH values of 9.5 and 10.5, respectively, on waste water containing 0.18 ppm of CN ion gave the following results:

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• •	C	N CONCE	NTRATIO	N	
pH	9	5	10.5		
Residence Time	15 min	30 min	15 min	30 min	
20 ppm Ch2 ·	0.07	0.05	0.06	_	
30 ppm Cl ₂	0.13	0.05	0.05	—	
50 ppm Cl ₂	0.04		0.02		
Feed	0.18	0.18	0.18	0.18	

As will be noted, more efficient results are obtained with the higher pH level, the addition of 50 ppm chlorine gas at 10.5 pH reducing the cyanide concentration

20

to a level of about 0.02 ppm in 15 minutes. It was difficult to achieve the same result on a large scale, although the cyanide concentration could be substantially reduced.

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Laboratory tests on the use of hypochlorite salts 5 indicated such salts to be also useful in lowering the cyanide content. The use of NaOCl was extensively studied and found to perform well. A feed solution containing 0.19 part per million cyanide (CN) was treated with 10 ppm and 20 ppm NaOCl concentration 10 at various pH levels above 7 and the following results obtained:

TABLE 3

	17	ROLD	2				
pH	1	3.8	10.6		11.0		
NaOCI Concentration	10 ppm	20 ppm	10 ppm	20 ppm	10 ppm	20 ppm	
30 minutes		0.08	0.04	0.03	0.03	0.01	
60 minutes		0.05	0.03	0.02	0.03	0.02	
90 minutes	-	0.07	0.04	0.02	0.03	0.02	_

Tests were also conducted on a large scale (pilot plant) and the effect of pH, residence time, and NaOCl concentration studied. NaOCl concentrations of 5 ppm, 10 ppm, 20 ppm, and 40 ppm were studied. The average cyanide concentration in the effluent during a 66-hour ²⁵ run was about 0.052 mg/liter or 0.052 ppm. Increasing the amount of hypochlorite addition did not materially affect the cyanide degradation. Concentrations as high as 40 ppm of NaOCl resulted in no significant decrease in effluent cyanide levels as compared to 5 ppm NaOCl ³⁰ solution at residence times of 33 minutes, 48 minutes, and 78 minutes. The best results were obtained at pH values over 10.

For a period of about 11 days, a feed water having a pH value of about 10.6 and an average CN ion concen-35 tration of about 0.2 ppm was treated with 20.9 ppm NaOCl at a residence time of about 33 minutes to provide an effluent averaging up to about 0.06 ppm cyanide. It was observed that the combined effects in the process of cyanide removal in the ion exchange step and 40 the subsequent treatment with hypochlorite followed by filtering produced an effluent with the desired cyanide limits.

It was also observed that to assure substantially complete removal of the precipitated heavy metal hydrox- 45 ides following skimming of the electroflotation product, a sand filter should be employed in order to polish or insure quality of the effluent.

A total circuit analysis of a pilot run is given in Table 4. 50

		17	ARCE	:4				_	
	Milligra	Heavy Ams Per	Metals Liter	or ppn	n	_	CN mg/l	-	
Fe	Mn	Zo	Cu	Cd	Мо	ρH	(ppm)		
4.3	6.4	0.29	0.19	0.01	5.9	6.5	0.28	- 33	
_	6.2	0.28	0.17	0.01	1.1	3.5	0.08		
0.65	1.0	0.05	0.05	0.01	0.6	10.5	0.035		
0.10	0.10	0.022	0.013	0.01	0.6	10.5	0.01	- 60	
	Fe 4.3 0.65 0.10	<u>Milligra</u> Fe Mn 4.3 6.4 — 6.2 0.65 1.0 0.10 0.10	17 Heavy Milligrams Per Fe Mn Zn 4.3 6.4 0.29 - 6.2 0.28 0.65 1.0 0.05 0.10 0.10 0.022	I A BLE Heavy Metals Milligrams Per Liter Fe Mn Zn Cu 4.3 6.4 0.29 0.19 - 6.2 0.28 0.17 0.65 1.0 0.05 0.05 0.10 0.10 0.022 0.013	IABLE 4 Heavy Metals Milligrams Per Liter or ppr Fe Mn Zn Cu Cd 4.3 6.4 0.29 0.19 0.01 - 6.2 0.28 0.17 0.01 0.65 1.0 0.05 0.05 0.01 0.10 0.10 0.022 0.013 0.01	IABLE 4 Heavy Metals Milligrams Per Liter or ppm Fe Mn Zn Cu Cd Mo Fe Mn Zn Cu Cd Mo Fe Mn Zn Cu Cd Mo G 0.19 0.01 5.9 - - - - G 0.28 0.17 0.01 1.1 0.65 1.0 0.05 0.01 0.6 0.10 0.6 0.10 0.6 0.01 0.6 0.10 0.6 0.10 0.6 0.10 0.6 0.10 0.6 <td colsp<="" td=""><td>IABLE 4 Heavy Metals Milligrams Per Liter or ppm Fe Mn Zn Cu Cd Mo pH 4.3 6.4 0.29 0.19 0.01 5.9 6.5 - 6.2 0.28 0.17 0.01 1.1 3.5 0.65 1.0 0.05 0.05 0.01 0.6 10.5 0.10 0.10 C.022 0.013 0.01 0.6 10.5</td><td>IABLE 4 Heavy Metals CN Milligrams Per Liter or ppm mg/l Fe Mn Zn Cu Cd Mo pH (ppm) 4.3 6.4 0.29 0.19 0.01 5.9 6.5 0.28 - 6.2 0.28 0.17 0.01 1.1 3.5 0.08 0.65 1.0 0.05 0.05 0.01 0.6 10.5 0.035 0.10 0.10 C.022 0.013 0.01 0.6 10.5 0.01</td></td>	<td>IABLE 4 Heavy Metals Milligrams Per Liter or ppm Fe Mn Zn Cu Cd Mo pH 4.3 6.4 0.29 0.19 0.01 5.9 6.5 - 6.2 0.28 0.17 0.01 1.1 3.5 0.65 1.0 0.05 0.05 0.01 0.6 10.5 0.10 0.10 C.022 0.013 0.01 0.6 10.5</td> <td>IABLE 4 Heavy Metals CN Milligrams Per Liter or ppm mg/l Fe Mn Zn Cu Cd Mo pH (ppm) 4.3 6.4 0.29 0.19 0.01 5.9 6.5 0.28 - 6.2 0.28 0.17 0.01 1.1 3.5 0.08 0.65 1.0 0.05 0.05 0.01 0.6 10.5 0.035 0.10 0.10 C.022 0.013 0.01 0.6 10.5 0.01</td>	IABLE 4 Heavy Metals Milligrams Per Liter or ppm Fe Mn Zn Cu Cd Mo pH 4.3 6.4 0.29 0.19 0.01 5.9 6.5 - 6.2 0.28 0.17 0.01 1.1 3.5 0.65 1.0 0.05 0.05 0.01 0.6 10.5 0.10 0.10 C.022 0.013 0.01 0.6 10.5	IABLE 4 Heavy Metals CN Milligrams Per Liter or ppm mg/l Fe Mn Zn Cu Cd Mo pH (ppm) 4.3 6.4 0.29 0.19 0.01 5.9 6.5 0.28 - 6.2 0.28 0.17 0.01 1.1 3.5 0.08 0.65 1.0 0.05 0.05 0.01 0.6 10.5 0.035 0.10 0.10 C.022 0.013 0.01 0.6 10.5 0.01

After electroflotation and removal of precipitate.

As will be noted, the feed was substantially reduced in impurities in accordance with the target goals set. 65 Thus, following the ion-exchange step at a pH value of 3.5, the molybdenum content was reduced from 5.9 ppm to 1.1 ppm. Following precipitation of the heavy metals and the removal thereof by electrofiotation, the effluent was substantially reduced in Fe, Mn, Zn, Cu, and Cd, in addition to Mo. Following hypochlorite treatment with a small but effective amount of the hypochlorite at a pH value of 10.5 and filtering through sand at the rate of 5 gallons per minute per square foot of filter, the heavy metals in the filtered effluent and the cyanide were further reduced, the cyanide ion being reduced to 0.01 ppm. Before disposing of or recycling the cleaned effluent, the pH value is adjusted to about 6 to 8.5.

The heavy metal precipitate separated at 18 in the flow sheet is preferably subjected to a "chem-fix" step before disposing of it into the environment. One method of chem-fixing is to mix the heavy metal precipitate with portland cement using sodium silicate as a binder to enable storage of the material in the environment without polluting the environment.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and the appended claims.

What is claimed is:

1. An environmental pollution control process for treating waste water containing over 2 ppm Mo and at least one heavy metal impurity selected from the group consisting of over 2 ppm Fe, over 1 ppm Mn, over 0.05 ppm Cu, over 0.2 ppm Zn, and over 0.015 ppm Cd, and containing over 0.025 ppm CN ion which comprises:

passing said waste water having an adjusted pH value ranging from about 3 to 4 through an ion-exchange resin column selective to the removal of Mo to a level not exceeding about 2 ppm to provide an ion-exchange effluent containing said at least one heavy metal impurity and said CN ion,

- adjusting the pH value of said effluent to a range of about 7 to 11, the pH value selected being sufficient to precipitate that heavy metal impurity having the highest pH requirement for precipitation,
- subjecting said precipitate to electrocoagulation and flocculation and provide a flocculated dispersion of said precipitate,
- subjecting said flocculated precipitate-containing effluent to electrolysis using insoluble electrodes to form micro bubbles of electrolytic oxygen and hydrogen and effect electroflotation of said flocculated precipitate and form a froth thereof,
- skimming off said froth to provide a substantially clean effluent containing residual amounts of cyanide in excess of 0.025 ppm,
- adding a small but effective amount of an oxidizing agent selective to the oxidation of said contained cyanide sufficient to reduce it to a value not exceeding about 0.025 ppm,

and then filtering said effluent,

whereby a cleaned liquor is obtained containing not more than 2 ppm Mo and not more than 2 ppm Fe, 1 ppm Mn, 0.05 ppm Cu, 0.2 ppm Zn, 0.015 ppm Cd, and 0.025 ppm CN ions.

2. The process of claim 1, wherein the oxidation of the CN ion is carried out at a pH value of at least about 10.

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3. The process of claim 1, wherein the filtering of the effluent is effected through a send filter.

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4. The process of claim 1, wherein the filtered effluent is adjusted to a pH value of about 6 to 8.5 before it is disposed of.

5. The process of claim 1, why rein the oxidizing agent

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is selected from the group consisting of alkali metal and alkaline earth metal hypochlorites.

6. The process of claim 1, wherein the amount of the 5 oxidizing agent added ranges up to about 50 ppm.

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