MINING SERVICES

TECHNICAL INFORMATION SHEET

DOWELL CHEMICAL SEAL RING

Chemical Seal Ring is a unique grouting material successfully being used in demanding applications to seal against the migration of aqueous fluids and low-pressure gases. Its chief applications are in conjunction with cement grouts for sealing shaft liners. Shafts drilled or sunk through soluble formations (rock salt and potash) as well as shale, sand and lime formations have been sealed using staged applications of cement and Chemical Seal Ring. Critical applications requiring a total seal have used DOWELL Chemical Seal Ring. Chemical Seal Ring has been used in conjunction with the Strategic Petroleum Reserve Programs, nuclear emplacement shafts, evaporite mine shafts and mined storage cavern shafts.

Chemical Seal Ring is truly unique. It is mixed as a slurry with controlled setting properties. It is placed by either pumping through grout or tremie pipes or draining or pouring from buckets lowered to a Galloway work stage. It fills the void to be sealed with a set material with most of the properties of a natural rubber. An additional prime property is that unconfined Chemical Seal Ring imbibes aqueous fluids, including brines, and physically becomes larger. Thus, confined Chemical Seal Ring provides a tighter, positive seal when contacted with aqueous fluids.

TYPICAL PHYSICAL PROPERTIES

Slurry

Form and Color — Pourable, Yellow-Green

Density — 9.95 lb/gal at 70°F

Cured Solid

Form and Color — Gunmetal Gray Rubber

Density — 9.95 lb/gal

Tensile Strength — 80 psi ultimate; ¼-in. thickness

Elongation — 137% ultimate

Hardness — 30 Durometer A

Tear Resistance — 14.7 lb/in. of thickness

Swelling Capacity — greater than 50% dimensional increase when exposed to aqueous fluids

COMPOSITION

Chemical Seal Ring slurry consists of a dispersion of a water-sensitive, high-molecular-weight polymer in a hygroscopic organic liquid. A water-soluble chromium compound crosslinks the polymer dispersion.

A cured Chemical Seal Ring resists biodegradation, and is considered to have a permanency at least equal to that of cement.

DISCUSSION

Repeated efforts with conventional cements and plastic grouts failed to provide the water-tight seal required for the nuclear placement shaft drilled into the Tatum Salt Dome. Chemical Seal Ring was developed to solve this and similar types of problem applications.

In the Tatum Salt Dome application, conventional cements were used to fill most of the annular space between the steel shaft liner and rock-salt formation. Chemical Seal Ring slurry was pumped to form a water-expanding gasket opposite the rock-salt formation in a zone below the aquifers. This successful application in 1964 has been followed by similar demanding uses throughout the

DOWELL DIVISION OF DOW CHEMICAL U.S.A., AN OPERATING UNIT OF THE DOW CHEMICAL COMPANY, HOUSTON, TEXAS 77042

Free World. The properties of Chemical Seal Ring which made these applications successful include the following.

- A pumpable slurry with controllable setting times between 40° to 100°F.
- The slurry neither shrinks nor expands upon setting.
- Set Chemical Seal Ring imbibes aqueous fluids (even saturated brines) with dimensional enlargement that provides a positive water-tight seal.
- Set Chemical Seal Ring is flexible and geologic shifts have not been reported to have damaged the seals.

Chemical Seal Ring has been cast in molds to form water-expandable gaskets. The shape of the gasket can be varied and extenders, such as fine sand, have been used. Applications of such gaskets include plugs for core holes and as water-expandable packers for groundwater monitoring wells.

SERVICE

Dowell provides Chemical Seal Ring service which comprises job design, materials, personnel, mixing and pumping of the slurry to the operator's surface conveyance (bucket, tremie or grout pipe). When water exists in the void to be sealed, a liquid wash (compatible with Chemical Seal Ring) is used ahead to displace the water. The wash is also used to displace Chemical Seal Ring slurry from tremie or grout pipe.

CASE HISTORIES

- Nuclear detonations in Nevada and Amchitka were stemmed with Chemical Seal Ring.
- Potash mine shafts sunk through the Blaremore (Canada) aquifer are routinely being sealed with Chemical Seal Ring.
- Rock-salt mines in Louisiana are completed with Chemical Seal Ring to prevent flooding by overlying water zones.

AVAILABILITY

Chemical Seal Ring material and some uses are patented by Dowell and the material is available from any service district within the United States. It is available from Dowell-Schlumberger service locations throughout the non-Communist world.

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DOWELL CHEMICAL SEAL RING

and

DOWELL CHEMICAL SEAL RING GASKET

Technical Report

DOWELL Division of The Dow Chemical Company
Tulsa, Oklahoma 74114

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INTRODUCTION

Dowell Division of The Dow Chemical Company developed Chemical Seal Ring to provide fluid-tight seals between shaft walls and shaft linings. It has been used successfully to seal tunnel liners, casing in gas storage wells, mine-shaft liners and casing in oil and gas wells. It has also been used as a tamp (stemming material) in nuclear emplacement holes and has been a key material in preventing the escape of radioactive gases into the atmosphere. The unique properties of Dowell Chemical Seal Ring suggest its use for a wide range of applications.

Two formulations of the material for Dowell Chemical Seal Ring have become the most widely used: the 300 system which is used for slurry placement, and the 201 system which is cast into gaskets, sheets, strips, water stops, or into almost any desired shape. The physical properties of both systems are shown in Table I.

TABLE I

PROPERTIES OF DOWELL CHEMICAL SEAL RING FORMULATIONS

Property	Thickness, Inches	ASTM Method	201 System	300 System
Tensile Strength, Ultimate, psi	1/8	D412-6	61	60
Tensile Strength, Ultimate, psi	1/4	D412-6	80	56
Elongation, Ultimate, percent	1/8	D412-6	118	330
Elongation, Ultimate, percent	1/4	D412-6	137	335
Secant Modulus at 2% Elongation, psi	1/4	D638-64T[2]	151	33
Shear Strength, psi of Shear Area	1/2	D732-46[3]	192	58
Tear Resistance, lbs/in of Thickness	1/8	D1004-66[4]	13.1	7.8
Tear Resistance, lbs/in of Thickness	1/2	D1004-66[4]	14.7	7.1
Hardness, Durometer A	1/2	D2240-64T	30	10
Thermal Conductivity, BTU in/hr ^{o}F ft^2	1	Dow Heat Flow Meter Method (Modified)	3.3	2.0
Compressive Strength, psi at:				
5% Deformation	1	D695-63T[5]	7.3	1.3
10% Deformation	1	D695-63T[5]	15.0	2.7
25% Deformation	1	D695-63T[5]	44.0	8.0
Compressive Modulus, psi	1	D695-63T[5]	146	27
Resistivity, ohm-cm	1/4	D257	2.7×10^7	5.2×10^7
Compressibility, in/in/psi	-	-	-	7.02×10^{-6}
Density, gm/cu cm	-	-	1.367	1.194
lbs/gal	-	-	11.40	9.96
lbs/cu ft	-	-	85.27	74.50

I. Description of Dowell Chemical Ring (300 system)

Chemical Seal Ring is an elastic, polymeric seal. It can be mixed and placed as a slurry which sets into a rubber-like material. Figure 1 shows a sample of Chemical Seal Ring which has swelled to more than 150 percent of its original volume by imbibing water. It is still an integral, sealing material in its swollen state. This single property sets Dowell Chemical Seal Ring apart from other sealing materials.

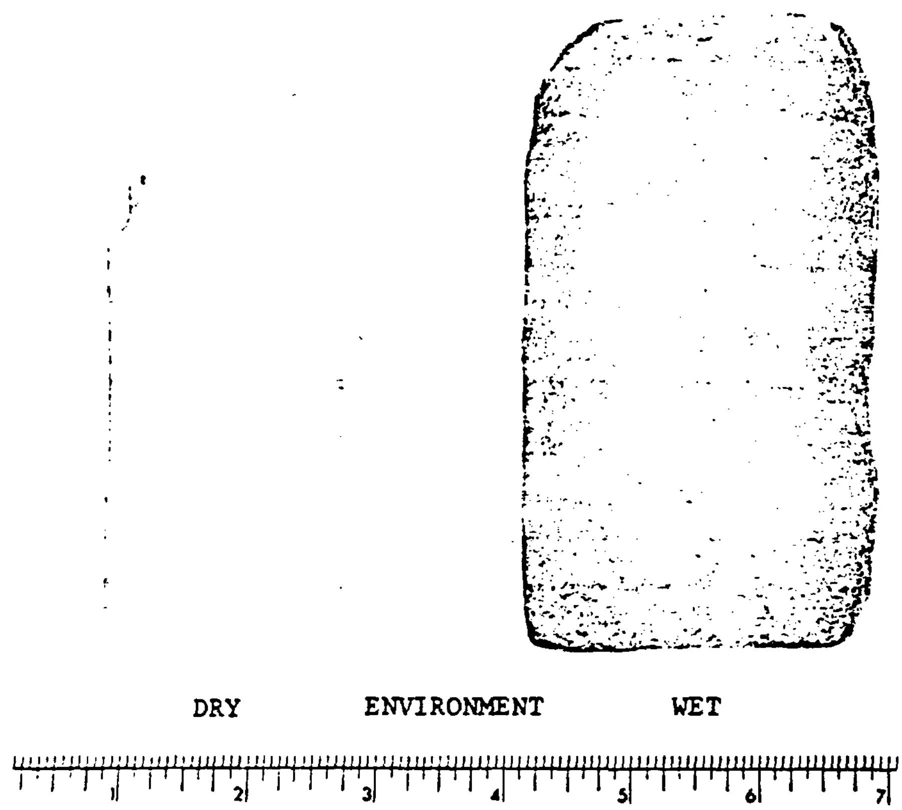


Figure 1. Sample of Dowell Chemical Seal Ring which has swelled to more than 150 percent of its original volume by imbibing water.

Life expectancy of set Chemical Seal Ring is of interest. Since the material is relatively new, by time standards, there is no method for determining how long it will actually last. Accelerated tests have been under way in concentrated environments of acid, caustic, brines, ozone, ammonia, hydrocarbons and fresh water for periods ranging from 90 days to four years. In all these tests, Chemical Seal Ring has maintained its integrity and sealing properties without apparent deterioration. Extrapolated values from these tests show that the material should last indefinetely. In fact, the chemistry of the

Is data report available ?

reaction by which Chemical Seal Ring is formed indicates permanency. The cross-linkage of the molecules is permanent and the material should be inert to further reaction.

In an actual case, Dowell Chemical Seal Ring was placed in a shaft in the Tatum Salt Dome in 1964. It has remained intact under the most severe conditions that could be imposed. This particular application is described later as a case history.

at 1350' with our sealing program approach

In casing and shaft-lining applications, Chemical Seal Ring normally is used in conjunction with more conventional sealants, such as cement. The cement provides support for the liner while Chemical Seal Ring provides the seal. Temperature and pressure changes during cementing operations cause the liners to expand and contract. This expansion and contraction often causes a micro-annulus, or channel, to form between the liner and the cement or the shaft wall and the cement. Great quantities of water or other fluids can flow through even the smallest channels. Chemical Seal Ring, spotted in the proper place in the cement column, is pliable enough to accommodate expansion and contraction while providing a positive seal. Further, any water flowing through the channel will be imbibed by the Chemical Seal Ring, causing it to swell and seal even tighter.

II. Description of Dowell Chemical Seal Ring Gasket (201 system)

Dowell Chemical Seal Ring Gaskets are manufactured from a unique polymer which swells in water. This polymer is chemically cross-linked during formation of the gasket. The result is a three-dimensional network of polymer molecules which has adequate physical strength, yet retains the property of swelling in water.

When a Dowell Chemical Seal Ring Gasket is confined in the flanged joints of a tunnel or mine-shaft lining, the rubber-like nature of the material makes it possible to assemble an air-tight, as well as a water-tight, structure. This property can help, for instance, to minimize air-compressing costs while driving a tunnel under a river. Furthermore, any tendency for water to leak through joints containing Chemical Seal Ring Gasket is immediately counteracted, since gasket material swells tighter and blocks the leakage path.

Several important features of Dowell Chemical Seal Ring Gasket stem from the nature of the chemicals used in its manufacture. A corrosion inhibitor prevents rust wherever Dowell Chemical Seal Ring Gasket is in contact with iron. A standard method of flame testing (ASTM D1692-59T) shows that Dowell Chemical Seal Ring Gasket is self-extinguishing. "Samples tend to burn only on the exterior and would not flame-propogate after removal of the flame source."

The pressure-sealing ability of Dowell Chemical Seal Ring Gasket depends on good seal design practices. Figure 2 is a schematic drawing of test apparatus used to pressure test Chemical Seal Ring Gasket in the laboratory. Under conditions shown here (without back-up shims), gasket successfully sealed pressures of 1200 psi for extended periods with no leak. With a back-up shim, pressures in excess of 4500 psi were sealed.

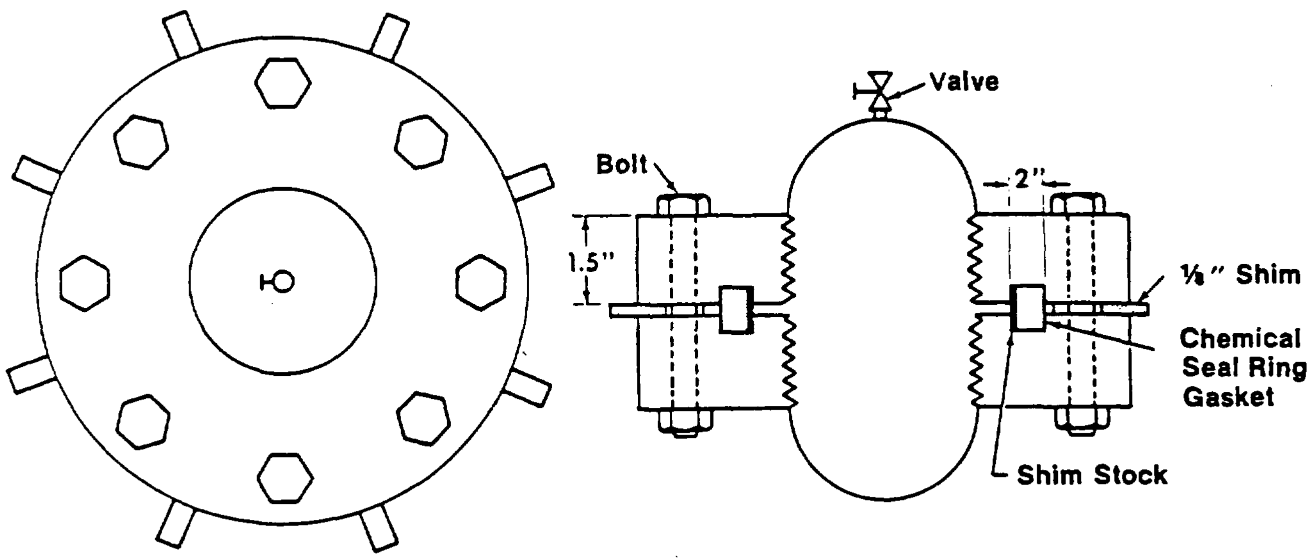
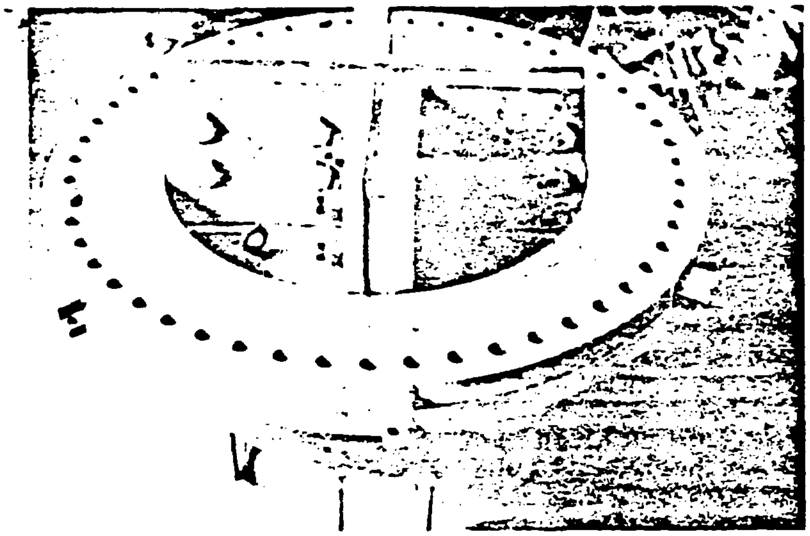


Figure 2. Schematic drawing of apparatus used to pressure test Dowell Chemical Seal Ring Gasket in the laboratory.

Figure 3 is a photograph of a full-scale model of the T-joints that will exist in a tunnel or mine-shaft lining built up of segments and rings. The T-joint is considered the critical leakage location. Long-term tests of such joints are presently being conducted by Commercial Shearing and Stamping Company, a leading supplier of underground supports with over 47 years of experience in the design and manufacture of steel supports for tunnels, shafts, and caissons throughout the free world. The joints are presently holding 1400 psi water pressure with no leaks or failures. These tests have now been in progress for months and are continuing.

Should a shaft lining containing Dowell Chemical Seal Ring Gasket ever leak after installation, several methods of repair exist. First, because the material swells in water, it is self-healing and further repair efforts may not be required. Time-lapse movies of very large, deliberately formed, leakage paths (Figure 4) have been made while water was pumped through them. Chemical Seal Ring Gasket not only withstood the flow of water, but swelled to shut off the leak. Swelling continued thereafter so that the self-repaired leak would hold more and more pressure.



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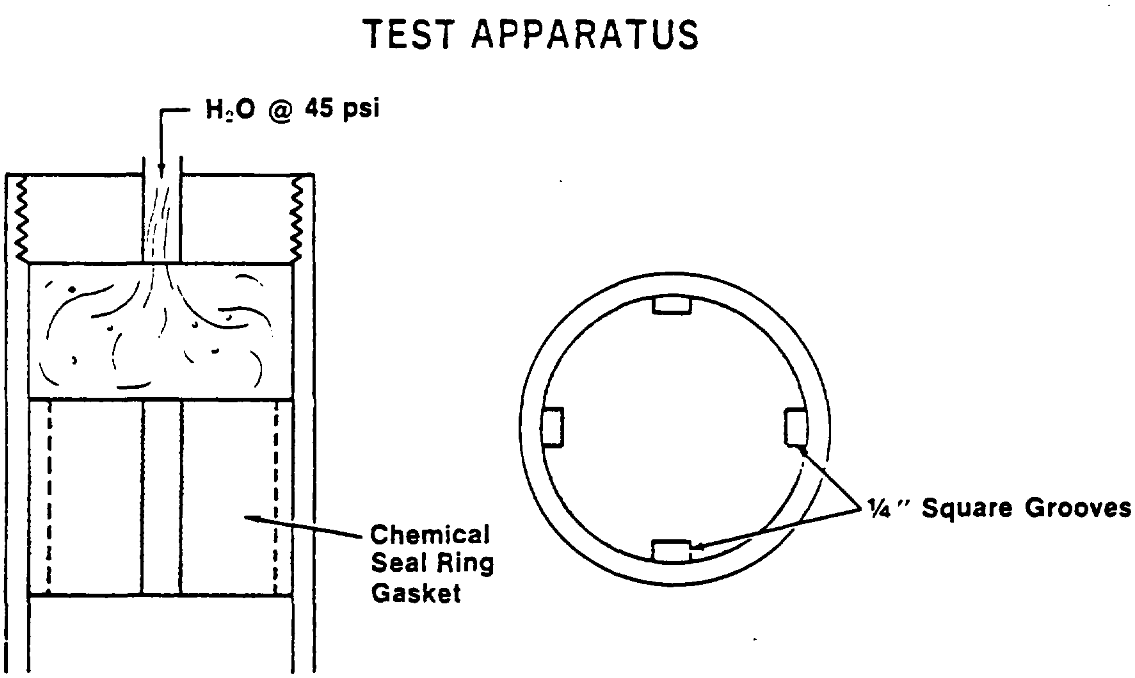

Figure 4. Test apparatus used to determine self-healing properties of Chemical Seal Ring.

Should extensive damage ever occur, leaks can be repaired by grouting with Chemical Seal Ring slurry or by conventional cementing procedures.

Figure 5 shows examples of the infinite number of sizes and shapes of Chemical Seal Ring Gaskets. Since nearly every application requires gaskets designed specifically for a particular purpose, the gaskets are not maintained in stock. Chemical Seal Ring Gaskets are packaged in protective wrapping so that only sheltered storage is required to shield them from moisture to facilitate their handling.

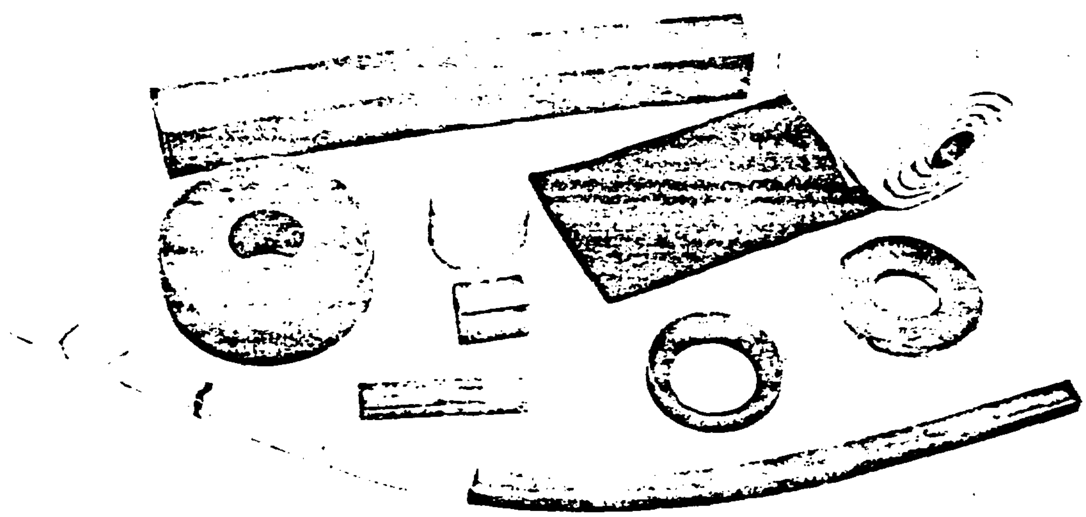

Figure 5. Examples of the infinite number of sizes and shapes of Dowell Chemical Seal Ring Gasket.

III. Technical Discussion

Mixing

Dowell Chemical Seal Ring is mixed by adding a powdered polymer to a premixed fluid phase. The polymer disperses readily and is easily mixed with a minimum of stirring or agitation. Conventional oilfield mixing and pumping equipment and specially designed continuous-mix units can be used. Even hand-drill-driven paddles in a 50-gallon drum have been used to mix small quantities of Chemical Seal Ring.

Viscosity -

Chemical Seal Ring slurry viscosity varies with the formulation, but is relatively low. The five-minute viscosity of a typical slurry is about 4 poises. By comparison, a cement grout (5.2 gallons of water per sack of cement) has a viscosity of approximately 15 poises.

Heat of Reaction

Setting of the Chemical Seal Ring is not an exothermic reaction. The heat of reaction is negligible; viz., it is too low to measure by ordinary laboratory tests. Monolithic pours thus create no problems in this respect.

Thickening and Setting Times

Thickening time and setting time of Chemical Seal Ring are controlled by adding a catalyst to the slurry during mixing. Thickening time is that time required for the slurry to reach a viscosity equivalent to 100 poise as measured in a standard cement thickening time tester. This is also the working time because at higher viscosities the slurry cannot be easily moved or placed. The amount of catalyst, then, is based on the working time required and the temperature. Setting time is defined as that time after mixing which is required for the slurry to reach a viscosity of 10,000 poises. Cement grout, concrete and stemming sand can all be placed on top of the Chemical Seal Ring when its viscosity has reached 10,000 poises. Setting time is also directly related to the amount of catalyst used.

Typical thickening and setting time curves are shown in Figures 6 and 7.

Slurries with a temperature of 40°F to 120°F are routinely used with predictable thickening and setting times. Laboratory tests are conducted to determine the required amount of catalyst and thickening and setting times in those cases where the slurry temperatures will fall outside this range.

Seal Height vs. Pressure Drop

One of the many series of tests conducted to define and understand Chemical Seal Ring properties, involved the determination of pressure drop per foot of Chemical Seal Ring height. Various sizes of pipes were filled with 20 feet of Chemical Seal Ring slurry. Pressure gauges were installed every two feet. Water pressure was applied to the confined Chemical Seal Ring for short-term and intermediate-term tests. These data, using a typical Chemical Seal Ring formulation, are presented in Figure 8. It shows the length of Chemical Seal Ring required for the pressure to drop to 0 psi.

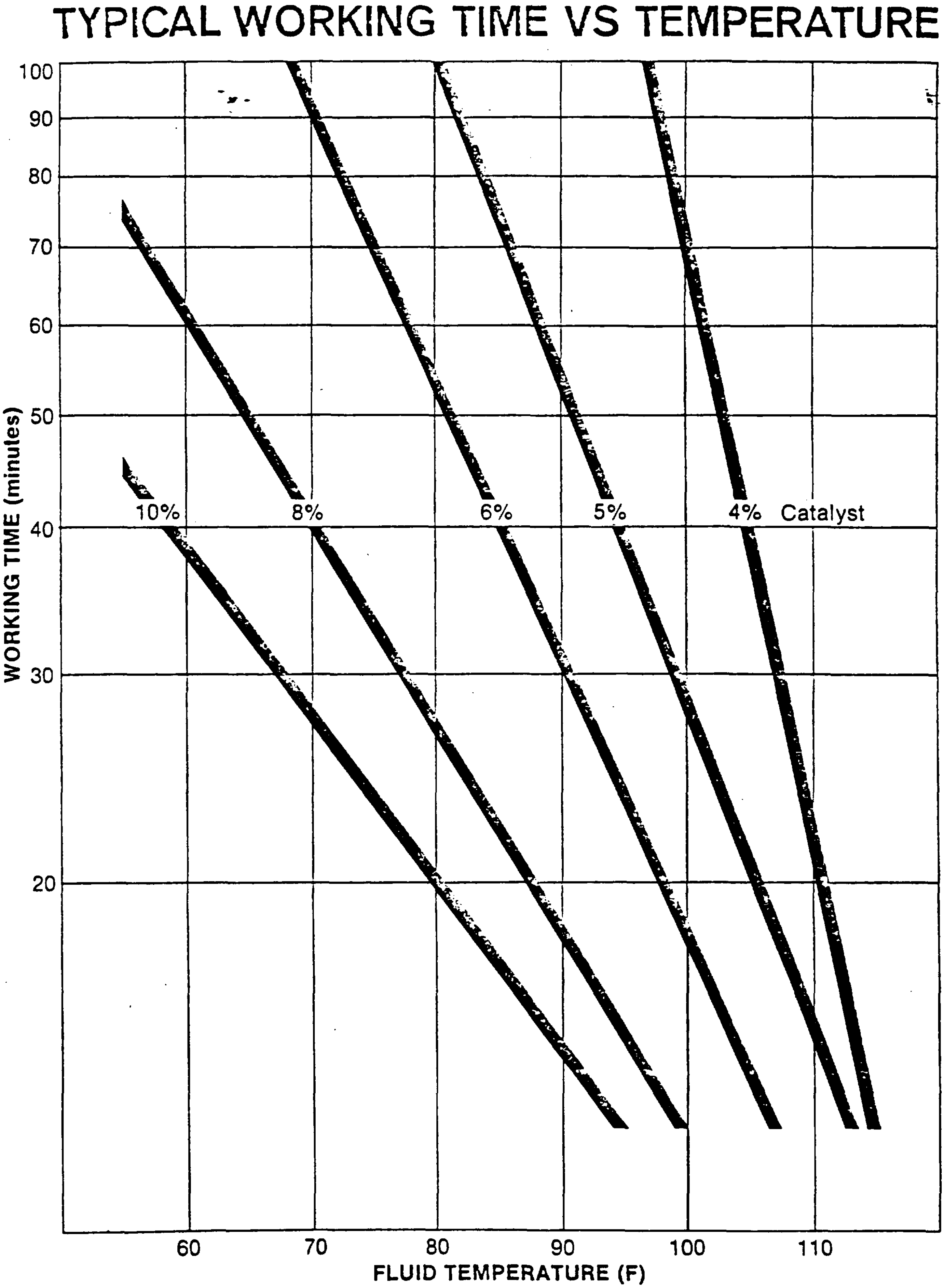

Figure 6. Typical thickening time curves for Dowell Chemical Seal Ring.

TYPICAL SETTING TIME VS TEMPERATURE

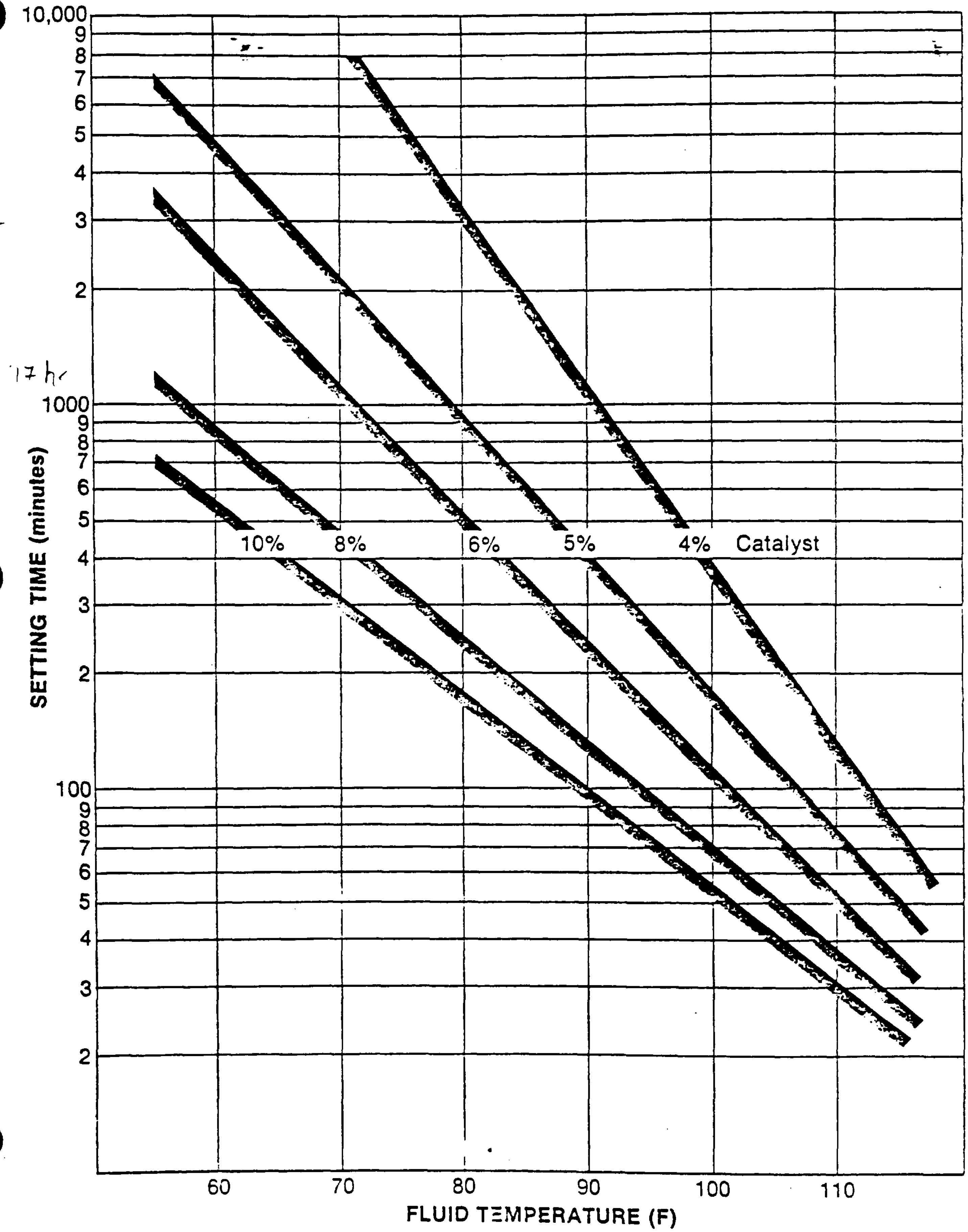

Figure 7. Typical setting time curves for Dowell Chemical Seal Ring.

LENGTH CHEMICAL SEAL RING REQUIRED

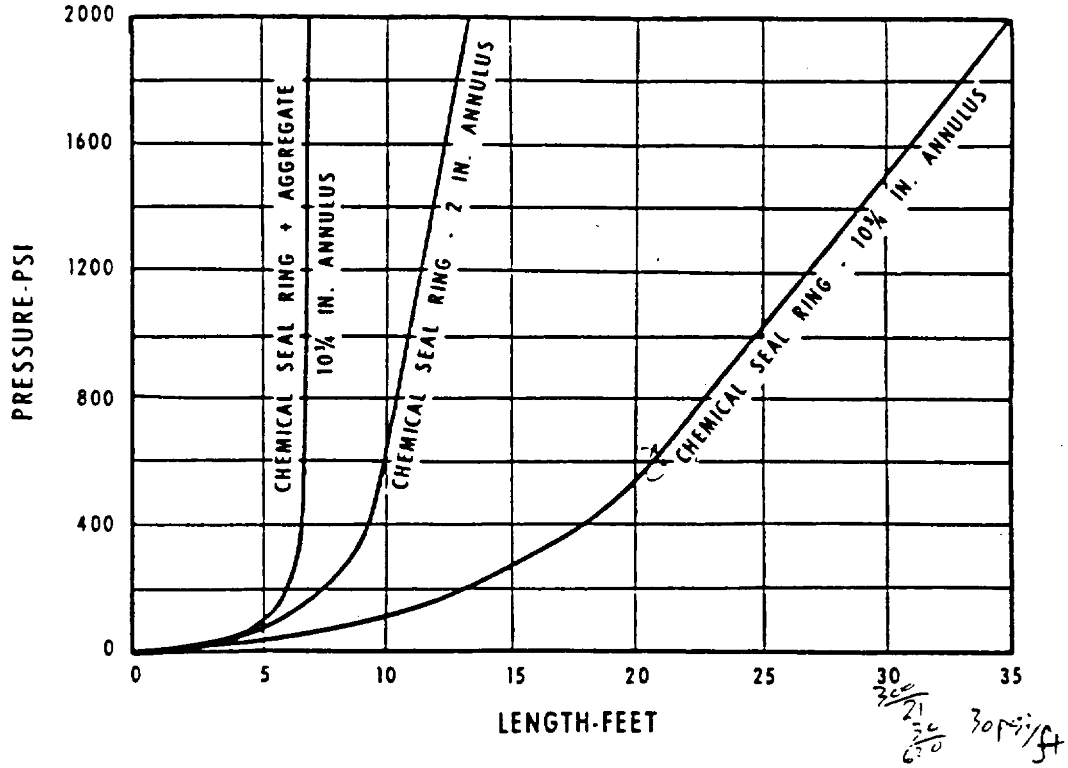

Figure 8. Graph showing the length of Dowell Chemical Seal Ring required for the pressure to drop to 0 psi.

Effect of Aggregate on Seal Ring Height vs. Pressure Drop

The previously discussed pressure-drop tests indicate that the pressure is dissipated over a shorter interval in smaller pipe. This finding was as expected. Tests were conducted to determine if incorporating coarse aggregate would produce the same effect as reducing the cross-sectional area of Chemical Seal Ring.

The addition of two parts of 3/4-inch to 1-1/2-inch aggregate to one part Chemical Seal Ring was tested. Test data indicate that height of aggregate-Chemical Seal Ring need be approximately one-third that of Chemical Seal Ring alone to dissipate a given input pressure.

The use of aggregate offers two advantages. The prime advantage is that the volume of Chemical Seal Ring, hence cost, is substantially reduced. The second advantage is in placing a seal opposite frozen formations, such as those encountered when freeze-sinking through the Blairmore in Saskatchewan. A heated

aggregate, dumped into the poured Chemical Seal Ring, will reduce the setting time and reduce down-time for the shaft sinker.

Resistance to Extrusion

A series of tests were conducted to determine the pressures required to extrude Chemical Seal Ring. The test procedure was purposely severe. Two-inch-long slots were machined in a steel plate. This test apparatus produces a cutting action as compared to long slots formed by rough surface walls, such as formation and concrete. The pressures required to extrude the Chemical Seal Ring through two-inch-long slots of various widths were:

Slot Width (inches)	Pressure (psi)
1/64	600
1/32	500
1/16	400

Extrusion can be prevented by using inert bridging materials in the slurry or using shims with gaskets.

Typical Sunken-Shaft Seal Assembly

Figure 9 is a schematic of a seal assembly in a sunken shaft. The Chemical Seal Ring pressure is maintained some 200 ± psi greater than the fluid pressure it is sealing off. Constant seal pressure can be maintained manually or through the use of automatic equipment.

The seal assembly is, in essence, an impermeable, hydraulic seal pressured in slight excess of aquifer pressures.

Is this what you have in mind for mining technology-based seals? lower

IV. Safety

Large samples of Chemical Seal Ring formulations have been decomposed without toxic products resulting. Although the material is relatively new, these tests indicate that it can be heated to 500°F and remain safe from the standpoint of toxic products.

Both the liquids and polymer powder used in Chemical Seal Ring formulations can be handled safely. Eyes and skin should be protected.

Unset Dowell Chemical Seal Ring slurry will burn with a self-propagating flame. The flame is low and spreads very slowly. Once set, however, Chemical Seal Ring is self-extinguishing.

SEAL ASSEMBLY
USING
CHEMICAL SEAL RING WITH AGGREGATE

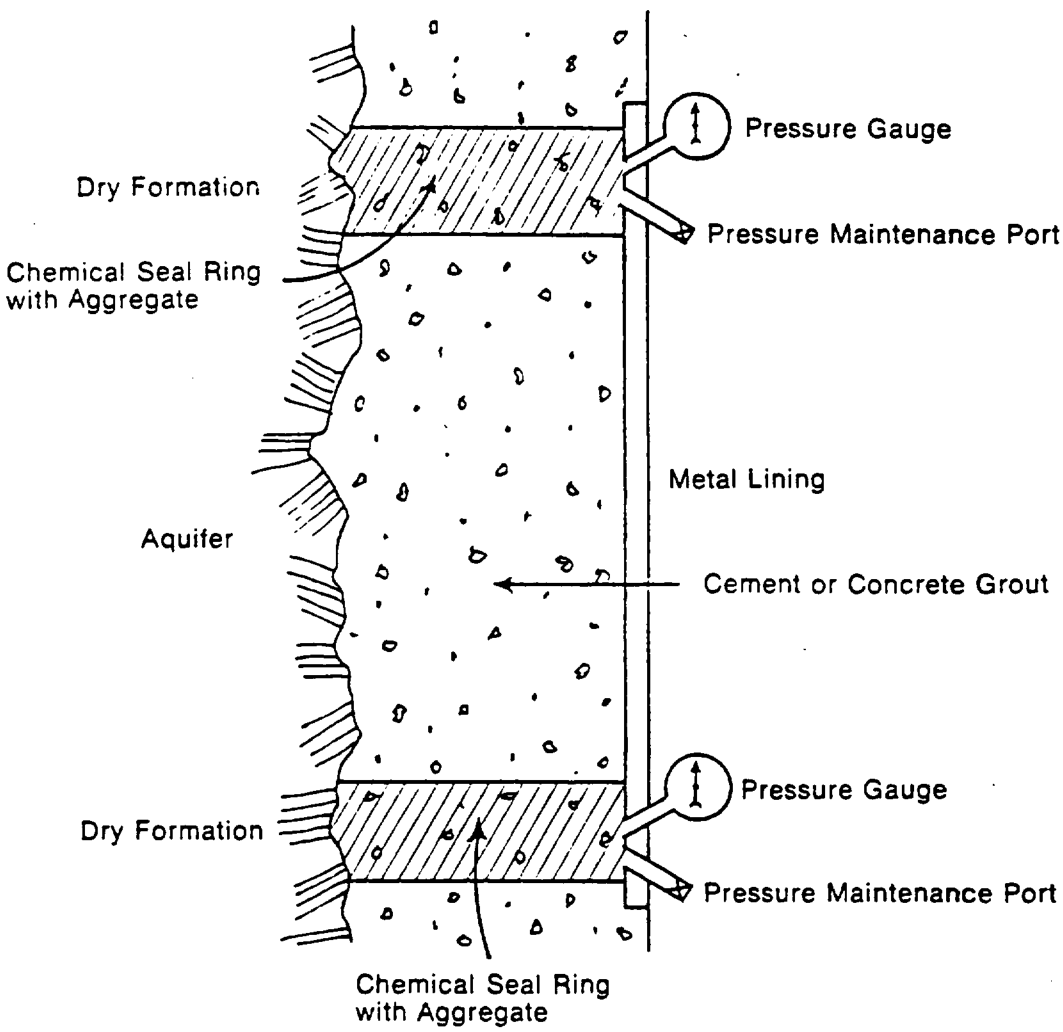

Figure 9. Schematic drawing of a seal assembly in a sunken shaft.

used to keep swelling pressure below design strength
resistance potential offered by metal lining.

V. Case Histories

Dowell Chemical Seal Ring has proved highly successful in a wide variety of sealing uses. These include stemming underground nuclear tests to prevent escape of radioactive gases; annular seals and water stops in Canadian potash mine shafts; and seals in anhydrous ammonia storage caverns, LPG storage caverns, salt mines and reservoir gas storage wells.

One of the early uses of Chemical Seal Ring was to seal large-diameter pipe in competent salt stock at the Tatum Salt Dome near Hattiesburg, Mississippi. Many overlying aquifers and a fractured caprock had made it impossible to obtain a dry shaft in the salt. Many remedial squeeze jobs with cement also failed to obtain a dry shaft. Chemical Seal Ring, placed as shown in Figure 10,

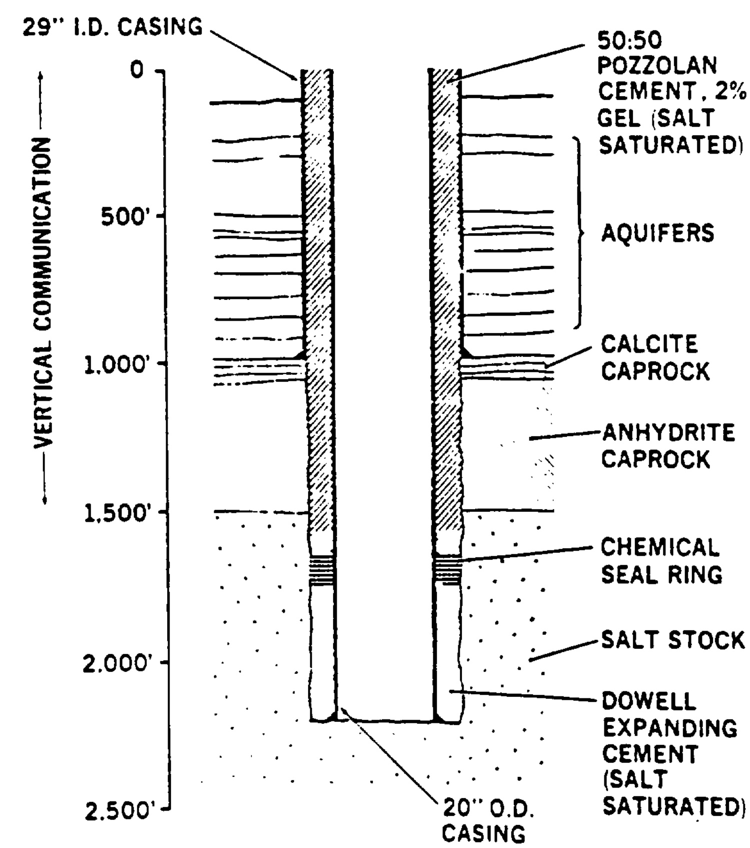

Figure 10. Drawing of placement technique for Dowell Chemical Seal Ring used to seal large-diameter pipe at the Tatum Salt Dome.

resulted in a completely dry shaft. A nuclear device was detonated in the salt about four months later and the shaft still remained dry. During an extensive testing period following the detonation, many tools and devices were run in the shaft. This resulted in a hole in the casing opposite the Chemical Seal Ring. A steel liner was run and cemented to cover the hole. Subsequently, a second nuclear device was detonated in the cavity created by the first shot. The shaft still remained dry and is dry at the present time, nearly four years later.

A more recent use of Dowell Chemical Seal Ring has been in a Canadian potash mine shaft in Saskatchewan. This shaft was sunk to a depth of 3300 feet by the freeze method. The seal was placed to insure that no water bypassed a water-collecting ring placed opposite a salt formation. The seals successfully prevented water migration in the annulus of this shaft.

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