Drips or Blasts—Chemical Seal Ring Stops Water or Gas

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ABSTRACT

A unique polymer sealant, placed as a pumpable slurry with ordinary well-cementing equipment, is described. The patented composition sets into a firm insoluble elastomer which forms gas and water-tight seals between shaft walls and shaft linings. Because the sealant swells when contacted by formation waters, it is able to protect potable water zones from gas stored in mined caverns while at the same time preventing migration of water into the cavern. It has also been used as a stemming material in nuclear device emplacement holes where it is the key material preventing escape of radioactive gases to the atmosphere. The material is also available in the form of prefabricated gaskets which can be compounded and molded to serve a wide range of applications.

The forerunner of this family of sealants was invented to stop water from entering a nuclear test hole in Mississippi. That successful job sparked a series of more and more difficult applications by imaginative engineers, and the products used today evolved to meet their requirements.

INTRODUCTION

During the completion of a hole drilled into the Tatum Salt Dome water, from many overlying aquifers, continued to "dribble" through the fractures in the caprock and made it impossible to obtain a dry shaft in the salt. Remedial work with cement had not solved the problem and, since the salt below had to be air drilled in order to provide a dry emplacement for a nuclear device, the success of "Project Dribble" was at stake.

The solution to this critical problem was a pumpable slurry which set up into a water-swellable elastomer and formed a self-sealing ring in the annulus between the formation and the steel casing. This so-called Chemical Seal Ring not only completely isolated the aquifers, but has withstood the shock of two nuclear detonations without failing.

Since then Chemical Seal Ring has successfully prevented the escape of radioactive gases through the tamped column above many nuclear devices tested underground. It has also efficiently kept water out of mined caverns used to store natural gas and liquified ammonia. A major use was in confining high-pressure aquifers so that mine shafts could be dug into the rich potash deposits of Saskatchewan.

Prefabricated gaskets of Chemical Seal Ring promise to make construction of water-tight steel tunnel and mine-shaft linings easier and less expensive.

The materials for Chemical Seal Ring are mixed and placed, batchwise or continuously, with regular oil-well cementing trucks. The resulting slurry, after a controlled thickening or working time, sets, at a predictable time, into a rubber-like solid. When the proper cross-linking additives are used, Chemical Seal Ring has the unique property of swelling, by imbibing water, but not dissolving. Thus, when properly confined, Chemical Seal Ring forms a permanent self-actuating seal.

Prefabricated gaskets are made by adding suitable fillers and curing the slurry, in molds, under controlled conditions. Joints, and bolted flanges for tunnel and mine-shaft linings have been sealed with Chemical Seal Ring gaskets and have withstood 1400 psi water pressure during long-term tests. Specially designed seals have withstood cyclic tests where the maximum water pressure was 4500 psi.

PROPERTIES OF CHEMICAL SEAL RING

In general there are two types of Chemical Seal Ring placeable as a pumpable slurry: (1) a composition intended primarily for sealing gas, and (2) a composition intended for sealing water as well as gas. Each can be modified to control loss of fluids to formations by including an inert material such as silica flour.

The solid component is a linear polyacrylamide. The mixing fluid consists of polyhydric alcohols and water. When a Chemical Seal Ring must permanently seal off water, a cross-linking agent is dissolved in the water.

Slurries have an initial viscosity of about 5 to 15 poise, depending on the temperature, when mixed. The compositions are varied, with the mixing temperature, to provide a working time of about 30 minutes. The setting time, arbitrarily 10,000 poise, or the time other operations may be resumed, varies between 2 and 4 hours depending on the temperature where the slurry has been placed.

Prefabricated gaskets are made by curing a composition that is augmented with polymer, filler and cross-linker under controlled conditions. The gaskets produced can be molded in any desired shape or stock can be cut and ground, like rubber, for custom fitting.

After setting, both the slurry and gasket compositions will swell several hundred percent if immersed unconfined in water (Fig. 1). This occurs at high water pressures as well as at ordinary pressures. Uncross-linked compositions will, of course, eventually go into complete solution; however, Chemical Seal Ring slurries and gaskets contain a cross-linking system. Thus, the cross-linked Chemical Seal Ring will swell only until tensile and swelling forces are equal and will not dissolve. The behavior is similar to a sponge.

Table 1 gives some of the physical properties of a typical gasket composition (CSRG-201) and a typical slurry composition (CSR-300) after aging 30 days at ambient temperature.

Life expectancy of Chemical Seal Ring is of interest. Since the material is relatively new, by time standards, and since normal placement will be almost completely confined, there is no method of test for determining how long it will last. Accelerated tests in various environments have not resulted in failure of the sealant, except in strong acid and strong alkali. In the range of pH between 2 and 12 the sealant only swells as if it were in water. In fact, formulations having acceptable properties have been made using 10% sulfuric acid instead of water as part of the mixing fluid.

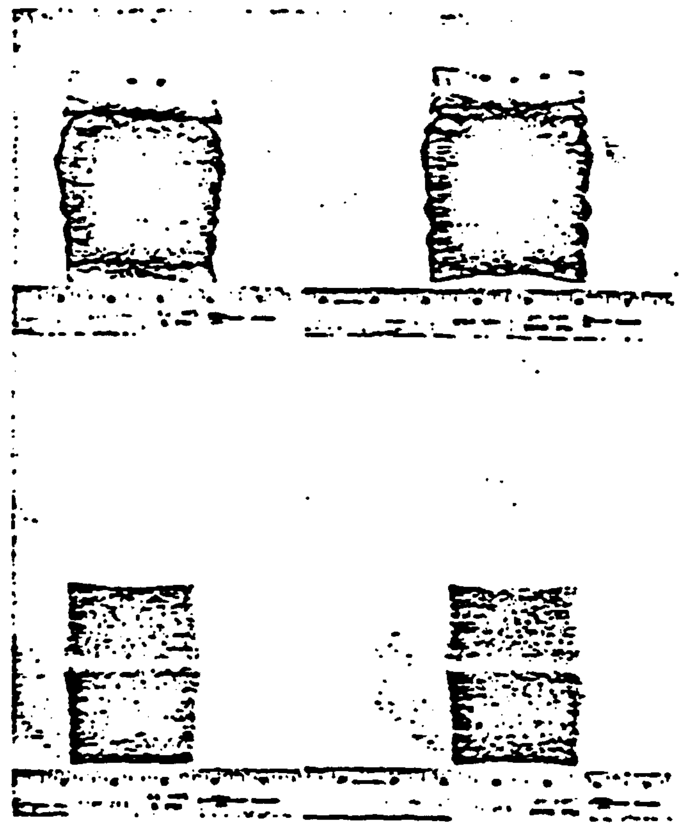

Figure 1. Swelling of Chemical Seal Ring after 40 hours at zero and 1000 psi: Top, CSR-300 Bottom, CSRG-201.

Several important features of Chemical Seal Ring stem from the nature of the chemicals used in its manufacture. A corrosion inhibitor prevents rust wherever the sealant is in contact with iron. This is extremely important in mine shafts.

Gaskets in the warehouse need only be protected from rain—normal humidity does not result in noticeable dimension increase. In tropical storage, however, dimensional changes may occur; but, the pliability and compressibility allows gaskets to be used with no more trouble than that given by any other prefabricated sealing material.

With regard to possible fire hazard, the polyhydric alcohols used apparently become an integral part of the cured polymer, because no fluid can be squeezed out by any mechanical pressure. Furthermore, a standard method of flame

Table 1. Properties of Chemical Seal Ring Formulations.

Property	Specimen Thickness (inches)	ASTM Method	CSRG–201 Gasket System	CSR–300 Slurry System
Tensile Strength, psi	1/8	D412-66	61	60
Tensile Strength, psi	1/4	D412-66	80	56
Elongation, %	1/8	D412-66	118	330
Elongation, %	1/4	D412-66	137	335
Secant Modulus, 2% Elongation, psi	1/4	D638-64T	151	33
Shear Strength, psi	1/2	D732-46	192	58
Tear Resistance, lb/in	1/8	D1004-66	13.1	7.8
Tear Resistance, lb/in	1/2	D1004-66	14.7	7.1
Hardness, Shore A	1/2	D2240-64	30	10
Thermal Conductivity, BTU-in/hr °F Ft²	1	Dow Heat Meter	3.3	2.0
Compressive Strength, psi at:				
5% deformation	1	D695-63	7.3	1.3
10% deformation	1	D695-63	15.0	2.7
25% deformation	1	D695-63	44.0	8.0
Compressive Modulus, psi	1	D695-63	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

testing (ASTM D1692-59T) has shown that the gasket is self-extinguishing. "Samples tend to burn only on the exterior and would not flame-propagate after removal of the flame source."

Setting of Chemical Seal Ring does not release any measurable heat. Thus, large pours are no problem in this respect. Thickening time control methods have been developed which allow slurries to be placed at ambient temperatures from 40°F to 120°F.

Each application of Chemical Seal Ring slurry as an annular seal in, for example, a mine shaft will require application of good engineering design. As a guide, some tests (on the CSR-300 type of cross-linked material) have been made to assist in such designs. For instance, tests were conducted to determine how much sealant is required in various size annuli to support various water pressures. These results are shown in Figure 2. This chart

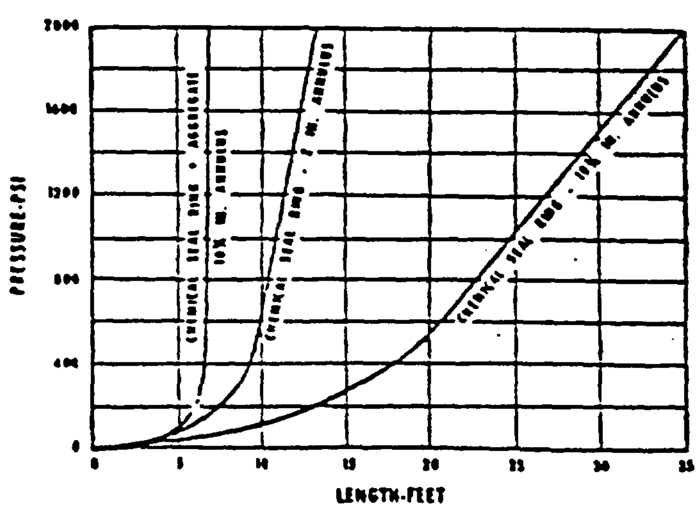

Figure 2. Length of Chemical Seal Ring required for the pressure to drop to zero psi.

data & test procedures

shows the length of sealant required to reduce pressure to zero for various input pressures up to 2000 psi in 2" and 10" I.D. pipe. The major guide indicated is that addition of aggregate will reduce the amount of sealant needed.

Another test of interest was extrusion resistance. Tests were made on slots, simulating sharp-edged openings, that were 2-inch long. Slots which were 1/64", 1/32" and 1/16" wide required 600, 500 and 400 psi to cause the Chemical Seal Ring to extrude.

CASE HISTORIES

The following case histories have been selected to give a historical as well as technical introduction to Chemical Seal Ring applications:

Project dribble.

One of the early uses of Chemical Seal Ring was in cementing 20-inch casing in a 28-inch hole in competent salt stock at the Tatum Salt Dome near Hattiesburg, Mississippi (Dillinger and Boughton, 1965). Many overlying aquifers and a fractured caprock had made it impossible to obtain a dry shaft in the salt. Since the rest of the hole was to be air drilled to provide a dry emplacement for detonating a nuclear device, the success of the entire project was at stake. Many remedial squeeze jobs with cement and other sealants had failed to obtain a dry shaft. The Dowell Division of Dow Chemical Company, however, quickly developed a solution to the problem.

A new sealant (Eilers and Parks, 1967), placed as shown in Figure 3, resulted in a completely dry shaft.

A nuclear device was detonated in the salt and the shaft still was dry. Later operations in the shaft wore a hole through the casing opposite the sealant, but no leak occurred. After a steel liner was set and cemented to cover the hole, a second device was detonated in the cavity formed by the first shot. The shaft remained dry and is dry at the present time, almost five years later.

Project long shot.

Another special Chemical Seal Ring composition was developed to prevent radioactive gases from venting through the stemming column above an 80 kiloton nuclear device fired on Amchitka Island in 1965.

The composition previously used in Project Dribble was impractical for use in cold climates; therefore, different materials had to be used. Enough materials to make 500 gallons on the job

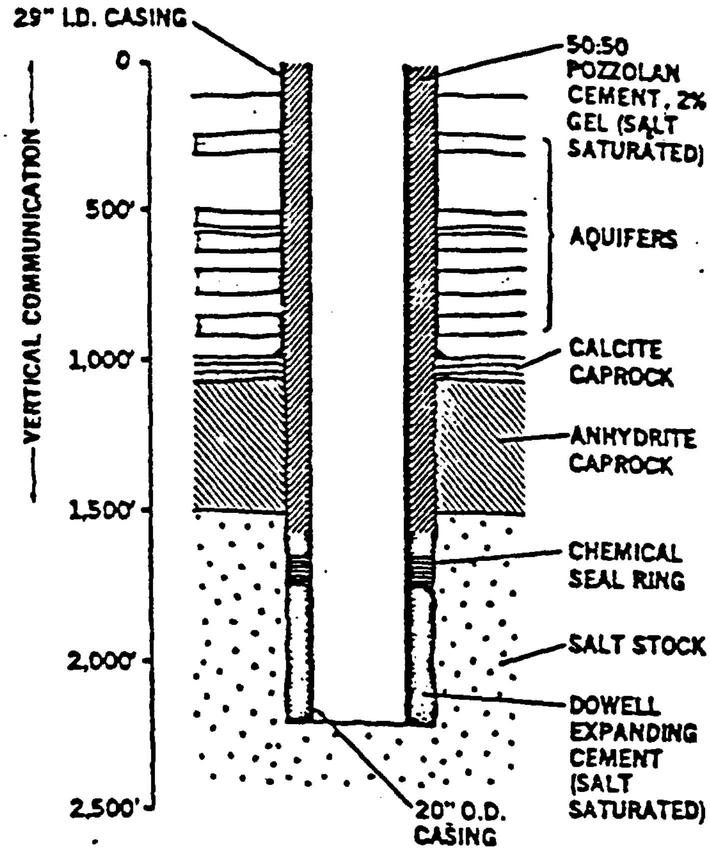

Figure 3. Drawing of placement of Chemical Seal Ring at the Tatum Salt Dome.

were flown from Tulsa, Oklahoma to the island and a Dowell chemist supervised the mixing and placing of the sealant in the hole—four days before the detonation. The device was at a depth of 2,300 feet in a 32 inch casing. The stemming column consisted of layers of sand and cement topped off with a 10 foot "cork" of chemical sealant which worked perfectly.

Nevada test site applications.

Since the successful use of Chemical Seal Ring at Amchitka Island, many jobs using continuously improved compositions, have been done for the Atomic Energy Commission at the Nevada Test Site. Probably the largest of these jobs was done in February, 1966. A total of 17,000 gallons was successfully used to seal a 12-ft diameter hole. In this test, no leak developed even when the entire system dropped 100 feet to form a huge crater after the device had detonated.

Natural gas storage cavern.

The first non-atomic application of Chemical Seal Ring was done in the 10 foot diameter access hole to a cavern mined for storing natural gas. The job was done in November, 1965, in northern Illinois. The customer had completed the first stage of cement in the annulus between 30 inch casing and the 10 foot diameter hole through which the cavern had been mined. Sheet iron was used to form 8 inch thick × 3 foot deep molds around the 30 inch casing and on the periphery of the hole. A total of 750 gallons of Chemical Seal Ring slurry was mixed and pumped, with an ordinary oil well cementing truck, to fill these molds. After the slurry was set, the balance of the hole was filled with concrete.

The two doughnut-shaped seals in this shaft serve to keep gas from seeping up the annulus to a water zone which furnished potable water to the areas nearby. At the same time, of course, the sealant also prevents migration of the water down into the cavern.

Liquid ammonia storage cavern.

In 1966 the vent and access shafts at DuPont's Repauno Plant in Gibbstown, N.J., were sealed with a Chemical Seal Ring composition designed to withstand liquid ammonia at -28°F (Better Living, 1968).

The access hole contains about 340 feet of 42" casing. The Chemical Seal Ring was placed in the annulus, through 2 inch grout lines, and confined above and below with portland cements. The 1,174 gallons of Chemical Seal Ring used formed a 25 foot long seal which has the dual job of keeping water from seeping down and keeping ammonia gas from leaking upward through the annulus.

Chemical Seal Ring in potash mining.

In February of 1967, 3,420 gallons of a new type of Chemical Seal Ring (S.A. Pence, U.S. Patent, 1968) were poured into the annulus between an 18 foot I.D. mine shaft lining and a salt formation about 2,870 feet below the surface as shown in Figure 4. After the lining had been built up to 1,882 feet, another 1,125 gallons of Chemical Seal Ring was placed as shown in Figure 5. Although some repair grouting was necessary, it was felt that the use of Chemical Seal Ring contributed greatly towards the successful driving of a dry shaft (Storck, 1968). This mine produced its first ton of potash in October of 1968.

SUMMARY

A unique polymer sealant, placed as a pumpable slurry with ordinary well-cementing equipment, is described. The patented composition sets into a

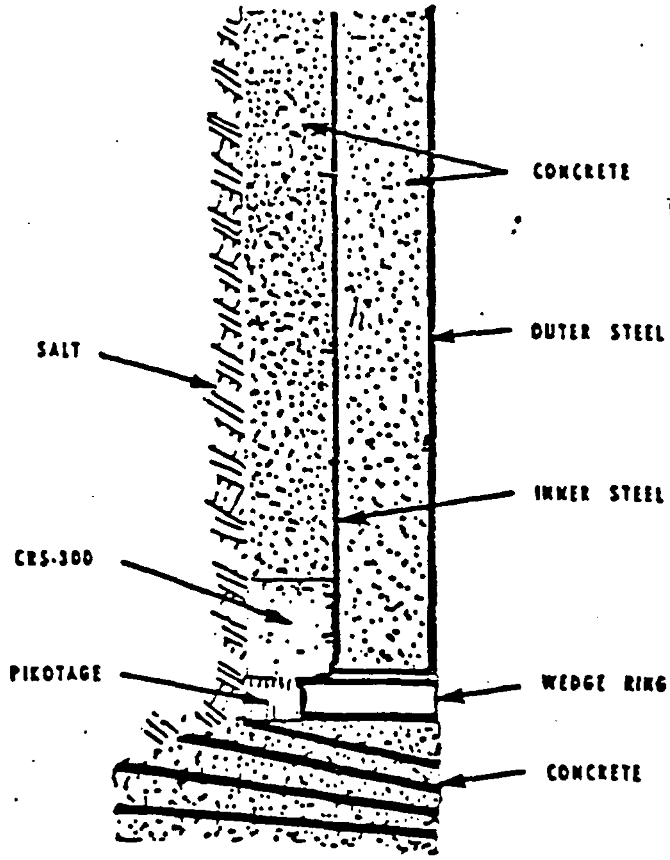

Figure 4. Installation of Chemical Seal Ring in a potash mine at 2870 feet.

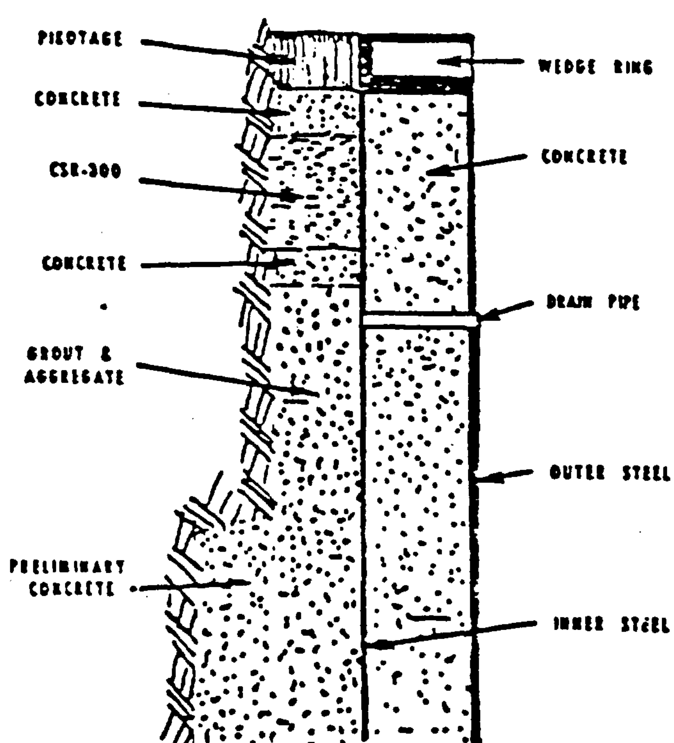

Figure 5. Installation of Chemical Seal Ring in a potash mine at 1832 feet.

firm insoluble elastomer which forms gas and water-tight seals between shaft walls and shaft linings. Because the sealant swells when contacted by formation waters, it is able to protect potable water zones from gas stored in mined caverns while at the same time preventing migration of water into the cavern. It has also been used as a stemming material in nuclear device emplacement holes where it is the key material preventing escape of radioactive gases to the atmosphere. The material is also available in the form of prefabricated gaskets which can be compounded and molded to serve a wide range of applications.

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