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Cement Technology for Borehole Plugging: An Interim Report on Permeability Measurements of Cementitious Solids

Earl W. McDaniel

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PERMEABILITY MEASUREMENTS OF CEMENTITIOUS SOLIDS

Earl W. McDaniel

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CEMENT TECHNOLOGY FOR BOREHOLE PLUGGING: AN INTERIM REPORT ON
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ABSTRACT

The permeability of borehole plug solids and plug-wall rock junctions is a property of major interest in the Borehole Plugging Program. This report describes the equipment and techniques used to determine the permeabilities of possible borehole plugging materials and presents results from tests on various cementitious solids and plug-rock combinations. The cementitious solids were made from mixtures of cement, sand, salt, fly ash, and water. Three different types of cement and four different fly ashes were used. Permeabilities ranged from a high value of 3×10^{-4} darcy for a neat cement paste to a low of 5×10^{-8} darcy for a saltcrete containing 30 wt % sodium chloride.

Miniature boreholes were made in the following four different types of rock: Westerly granite, Dresser basalt, Sioux quartzite, and St. Cloud granodiorite. These small holes were plugged with a mix consisting of 23 wt % Type I Portland cement, 20 wt % bituminous fly ash, 43.2 wt % sand, and 13.8 wt % water. After curing for 91 days at ambient temperature, the permeability of the plug-wall rock junctions ranged from 3×10^{-5} to $<1 \times 10^{-8}$ darcy. Three of the four miniature plugged boreholes exhibited permeabilities of <10 microdarcys.

1. INTRODUCTION

Boreholes in the vicinity of a site selected as a geological repository for radioactive wastes must be plugged to ensure the integrity of the general area. These plugs must form leak-proof bonds with the host wall and have lifetimes comparable with the surrounding formation. An evaluation of the materials and techniques that could be used indicated that one of the more promising solutions involved the use of cementitious materials.¹

The Cement Technology for Borehole Plugging Program was established at the Oak Ridge National Laboratory to assist the Office of Waste

Isolation and later the Office of Nuclear Waste Isolation in devising and testing cementitious mixtures suitable for plugging drill holes that range in size from small exploratory holes to mine shafts. The initial emphasis of this program has been on the development of suitable and reliable methods for measuring the physical and chemical properties of plug-solid candidates. This report covers the measurement of the permeability of solids prepared from mixtures of cement, sand, fly ash, and/or salt. In addition, results from the initial tests made on various plug-wall rock junctions are presented.

To provide the sensitivity required for the permeability measurements relating to borehole plugging, techniques had to be developed that would be reliable for values on the order of 1 microdarcy. The use of geological formations for gas storage extended the range of permeability measurements to these lower values.^{2,3} However, most techniques used today are apropos in the millidarcy range. For example, the American Petroleum Institute has specified a standard system for measuring the permeabilities of materials to water or gas.⁴ The majority of formation permeabilities of interest are in the 0.1- or 0.01-millidarcy range, and this has been the limit of all oil-well-related permeability measurements.

Workers developing concrete mixes to be used in surface structures such as dams, roadways, and navigation locks generally use the procedure described in CRD-C-98-75, "Method of Test for Water Permeability of Concrete,"⁵ to test their product. This test consists of subjecting specially prepared specimens to a water pressure of 200 psi for several days and computing the permeability from the flow rate. Mixes having values ≤ 1 millidarcy are considered to be impermeable.

2. THEORY

Permeability is a measure of the ease with which a fluid may be made to flow through a material by an applied pressure gradient. In principle, the determination of permeability involves only the measurement of the rate of flow of a fluid of known viscosity through a sample of known cross-sectional area under a measured pressure differential. Permeability is, in essence, the fluid conductivity of the porous material.

Fluid conductivity of a porous material was first characterized by Darcy⁶ in 1856. Darcy's law of permeability was developed empirically by measuring the flow of water through a sand bed, but it applies to any fluid, provided that steady flow is maintained. The law is expressed as:

$$K = \frac{\eta QL}{\Delta P \cdot A} \quad , \quad (1)$$

where,

K = permeability, darcy;

η = viscosity of the working fluid, cP;

Q = flow rate, cm³/sec;

L = length of the sample, cm;

ΔP = pressure gradient ($P_1 - P_2$), atm;

A = cross section of the sample, cm².

The unit most widely employed for permeability is the darcy. This unit is defined as the permeability that results in a flow rate of 1 cm³ per second of fluid with a viscosity of 1 cP through a cube having sides 1 cm in length at a pressure differential of 1 atm.

Thus,

$$1 \text{ darcy} = \frac{1 \text{ (cm}^3\text{/sec)} \cdot 1 \text{ (cP)}}{1 \text{ (cm}^2\text{)} \cdot 1 \text{ (atm/cm)}} \quad .$$

Determination of the liquid permeability is complicated by the fact that the liquid being used can alter the internal structure of the solid under examination. The permeability can be either increased or decreased by corrosion, swelling, or the leaching of materials from the solids. To eliminate such problems, many workers have used an inert gas such as nitrogen to determine flow rates since Darcy's law is valid for any fluid as long as steady-state flow is maintained. However, several modifications must be made when a gas is used.

$$K_a = \frac{\eta \bar{Q} L}{\Delta P \cdot A},$$

where

$$\bar{Q} = \frac{Q}{\bar{P}}$$

and

$$\bar{P} = (P_1 + P_2)/2.$$

In this case, the apparent permeability (K_a) is determined at $\bar{Q}$, the flow rate of the gas at the mean pressure. This pressure occurs within the sample as the gas (which is compressed on the high side of the sample) expands and flows through the sample. With this procedure, ideal gas behavior is assumed, and the volume of the gas that has passed through the sample is corrected to the volume it would have occupied at the mean pressure.⁷

In working with gas, it is erroneous to assume that as long as Darcy's law is obeyed (i.e., as long as the flow rate is proportional to the pressure gradient), the permeability is a property of the medium and is independent of the fluid used in its determination, as would be the case with most noncorrosive liquids. Klinkenberg⁸ showed that the apparent permeability of a solid to a gas is a function of the mean free path of the gas molecules; thus, the permeability depends on factors that influence the mean free path such as pressure, temperature, and the nature of the gas. In addition, he demonstrated that values obtained in gas measurements may be used to determine the permeability of a material to a liquid. To apply this Klinkenberg correction, apparent gas permeability measurements are made as a function of pressure. The log of the apparent permeability (K_a) is plotted as a function of the reciprocal of the pressure differential, and the linear relation is then extrapolated to infinite pressure. At this intercept, Klinkenberg found that $K_a = K$, which is the permeability of the solid to any fluid.

3. EQUIPMENT

The gas permeability apparatus used in the current work at the Oak Ridge National Laboratory is a modification of a device designed by Strachan.⁹ The device consists of a sample holder, a means of applying a pressure gradient across the sample, and provision for measuring the gas flow rate. The sample holder, commonly called a Hassler cell, consists of a flexible sleeve to contain the sample to which sealing pressure is applied with a hydraulic pump (Fig. 1). Compressed nitrogen, supplied by a cylinder and reducing valve, is used as the working fluid. The flow rate is determined by displacement of water by the gas. Working pressures up to 100 psi and sealing pressures up to 1000 psi may be used with this system.

Liquid permeabilities were determined with a similar device. The sample holder was a high-pressure Hassler cell. Liquid pressure was applied to the specimen from a reservoir to which pressure was applied by a piston and compressed nitrogen, as shown in Fig. 2. Accurate liquid flow rates were determined by collecting and weighing the permeated liquid.

4. TECHNIQUE

4.1 Sample Preparation

Right circular cylinders 2.54 cm in diameter by 2.54 cm long were used in all measurements. In studies of the permeability of plug-wall rock junctions, 1.59-cm-diam holes were drilled in the same-size rock specimens. These specimens were then filled with the concrete mix under investigation. The cementitious materials were mixed according to ASTM-C-305-70¹⁰ and cured autogenously for 91 days at room temperature. Specimens used in gas-permeability screening tests were then dried to constant weight at a temperature of 100°C and a pressure of 50 microns. The most critical step for these specimens was the drying procedure. Preliminary results showed that the gas permeability of a cementitious solid could vary by as much as three orders of magnitude, depending on the drying technique used with the specimen. The permeability values for specimens containing 57.0 wt % Marquette Type I Portland cement, 10.0 wt % Kingston

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Fig. 1. Schematic of the test apparatus used for measuring gas permeability.

ORNL DWG 79-1448A

Fig. 2. Schematic of the test apparatus used for measuring liquid permeability.

fly ash, and 33.0 wt % water and cured 28 days in saturated limewater ranged from 8.0×10^{-8} darcy after simple blot drying to 1.3×10^{-5} darcy after 24-hr vacuum drying. Other workers have shown that any air-drying of a cementitious solid would result in the loss of water hydration, with possible collapse of gel structure and microcracking.¹¹ For broad screening purposes, however, a drying technique was used to improve reproducibility.

A number of drying methods were examined; from these, a method was selected that produced specimens with minimum microfracturing and yielded reproducible permeability data. The specimens were dried in a vacuum oven at 100°C and a pressure of 50 microns until there was $\leq 0.1\%$ weight variation over 24 hr. An example of the permeability measurements obtained with duplicate specimens of saltcrete dried in this manner is shown in Fig. 3.

In the course of the drying studies, it was observed that microfractures which were not apparent visually were easily detected during the gas permeability measurements. In applying the Klinkenberg correction to gas permeability data, specimens having microfractures showed an increase, rather than a decrease, in permeability at higher pressures (Fig. 4). Since such an effect would not be observed in a liquid measurement, this technique may be used to ensure that a specimen is crack-free prior to making a liquid determination rather than the routine microscopic examination.

4.2 Flow Rate

Before an acceptable steady-state flow rate is obtained, moisture must be expelled from the sample and the sample must be completely saturated with the working fluid. In these measurements, the flow was assumed to be at a steady rate when three duplicate readings were achieved at a differential pressure of 100 psi. Steady-state gas flow is usually achieved in 15-20 min, even for samples with very low permeability, whereas steady-state conditions for liquid flow ranged from 1 to 3 days. The liquid-flow equilibrium time may be reduced if very high pressures are used.¹²

Fig. 3. Comparison of the permeabilities of duplicate saltcrete samples dried to constant weight.

ORNL DWG 79-228R

Fig. 4. Permeability vs reciprocal pressure of a sample having microfractures.

4.3 Measurement of Permeability

After the sample was dried and inserted in the sample holder, an appropriate pressure gradient was applied across the sample, and the steady flow rate was determined. Data were obtained at several pressures and used to determine the fluid permeability by applying the Klinkenberg correction.

5. EXPERIMENTAL RESULTS AND DISCUSSION

Permeability measurements were made on cementitious solids prepared with ASTM Type I Portland cement and API Class C and API Class H cement with and without sand, salt, and/or fly ash. Each type of solid will be described in detail in the following sections.

5.1 Standard Neat Cement Pastes and Mortars

Neat cement pastes and mortars were made with Type I and Class C and Class H cements. Type I cement is ordinary Portland cement. Class C is an oil-well cement that has a high early strength and corresponds to a Type III Portland cement. Class H cement is a coarsely ground oil-well cement that is usually used with an expansive agent. There was very little difference observed in the permeabilities of 91-day-cured pastes made from these cements. The solids contained 62.5 wt % cement and 37.5 wt % water. Nitrogen was used to determine the permeabilities that are presented in Table 1.

Table 1. Permeability of hardened neat cement pastes^a

Cement type	Permeability (darcy)
I	2.3×10^{-4}
C	3.1×10^{-4}
H	8.8×10^{-5}

^aSamples contained 62.5 wt % cement and 37.5 wt % water. Specimens were cured at ambient temperature for 91 days prior to the measurement.

In the case of mortars that were made from the three types of cements, the permeability increased in the order Type I < Class C < Class H. The mortar prepared from Class H was 40 times more permeable than the specimen made from Type I Portland cement. This is just the opposite from values obtained with the neat cement pastes. Since the Class H is a more coarsely ground material, it was expected to have a higher permeability than the solid made from the Type I or Class C. Additional measurements are needed to determine why the lower permeability was found in the neat cement paste. The very low value obtained with the Type I specimen could be due in part to a different drying technique. This specimen was measured before vacuum drying was put into routine operation. Drying to a constant weight at atmospheric pressure could result in more water remaining in the specimen and, thus, a lower permeability. The permeability of the three types of mortar is presented in Table 2.

Table 2. Nitrogen permeability of mortar specimens^a

Cement type	Permeability (darcy)
I	4.0×10^{-6}
C	7.6×10^{-5}
H	1.6×10^{-4}

^aSamples contained 23.0 wt % cement, 63.2 wt % sand, and 13.8 wt % water. The mortar prepared from Type I cement was dried to a constant weight in an atmospheric oven, whereas the other two were dried under 50-micron pressure.

5.2 The Effect of Fly Ash on the Permeability of Mortars

Fly ash is a pozzolanic material used to react with the lime that is released during the hydration of Portland cement. Such pozzolanic materials often have little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide to form a cementitious solid. In this investigation, two classes of fly ash were investigated: (1) ASTM Class F, which is produced from bituminous coal, and (2) ASTM Class C, which is produced from lignite or subbituminous coal. The latter class usually has some

cementitious properties¹³ because of the presence of lime in the fly ash. The analyses of the fly ash samples used in these studies are listed in Table 3.

Table 3. Chemical analysis of fly ash samples

Compound	Composition (wt %)				
	Class C samples			Class F samples	
	P-8	P-17	P-20	P-15	P-16
SiO ₂	39.7	31.3	40.99	48.57	44.3
CaO	24.78	40.3	26.7	1.32	7.36
Fe ₂ O ₃	5.4	4.36	4.97	9.0	19.60
Na ₂ O	1.64	0.76	1.27	0.33	0.25
P ₂ O ₅	1.85	0.90	1.39	0.99	0.58
TiO ₂		0.88	1.33		
MgO	3.95	2.67	3.24	1.31	0.38
Al ₂ O ₃	19.4	11.8	17.3	28.5	16.9
SO ₃	0.27	2.28	1.57	0.37	3.08
K ₂ O	0.48	0.44	0.76	3.14	2.22
C	0.84	0.29	0.22	2.70	2.19
LOI ^a	0.81	0.94	1.23	2.84	5.49
Moisture	0.019	0.03	0.05	0.09	0.46

^a LOI = Loss On Ignition.

A locally generated Class F fly ash (P-15) was used in initial experiments designed to optimize the amount of fly ash that would be later used in more detailed studies involving the effect of such pozzolans on the permeabilities of mortars containing fly ash. The three classes of cement were used to make standard mortars in which 10, 20, and 30 wt % of the sand was replaced with fly ash. The permeabilities of the solids to nitrogen were determined after curing for 91 days. The mix composition of 20 wt % fly ash, 43.2 wt % sand, 23.0 wt % cement, and 13.8 wt % water was selected for use in future studies. The permeabilities were $\leq 10 \mu$ darcys, and the mixing properties were amenable to the preparation of specimens (Table 4).

Table 4. The effect of fly ash content on the permeability of mortars

Composition (wt %) ^a		Cement		
Fly ash	Sand	Type I permeability (darcy)	Class H permeability (darcy)	Class C permeability (darcy)
10	53.2	1.9×10^{-5}	1.1×10^{-5}	6.8×10^{-5}
20	43.2	2.5×10^{-5}	8.5×10^{-6}	3.0×10^{-5}
30	33.2	2.3×10^{-5}	1.2×10^{-5}	too thick for good mix

^aAlso contained 23.0 wt % cement and 13.8 wt % water. Samples were cured for 91 days at ambient temperature.

The permeability of mortars containing fly ash was found to be slightly dependent on the lime content of the fly ash as well as the cement used to prepare the mortar. As the lime content increased, the permeability increased slightly (Table 5). These mortars were made with 20 wt % fly ash that contained from 1.3 to 40.3 wt % calcium hydroxide. The maximum permeability observed was 1.3×10^{-4} darcy for the specimen made from Class C cement and a fly ash containing 40.3 wt % lime. This fly ash would not be recommended for borehole plugs.

Table 5. The effect of fly-ash lime content on the permeability of mortars containing fly ash^a

Fly ash No.	Calcium hydroxide (wt %)	Cement		
		Type I permeability (darcy)	Class C permeability (darcy)	Class H permeability (darcy)
P-15	1.3	2.5×10^{-5}	3.0×10^{-5}	8.5×10^{-6}
P-16	7.4	3.5×10^{-5}	2.8×10^{-5}	3.2×10^{-5}
P-8	24.8	3.0×10^{-5}	4.6×10^{-5}	4.0×10^{-5}
P-17	40.3	6.0×10^{-5}	1.3×10^{-4}	5.6×10^{-5}

^aSample composition: 23.0 wt % cement, 20.0 wt % fly ash, 43.2 wt % sand, and 13.8 wt % water. Samples were cured at ambient temperature for 91 days.

5.3 The Effect of Salt on the Permeability of Mortars and Mortars Containing Fly Ash

The presence of 10 to 30 wt % salt in a standard mortar decreased the permeability of the resulting solids with respect to mortars (Table 6). Salt has been used for many years in oil-well cement slurries to bond the set cement to salt sections and shales encountered in various geologic media.¹⁴ Such mixes are called saltcretes. Since similar geologic media will be encountered in plugging holes in the vicinity of a repository, studies were necessary to determine the effect of salt on the permeability of cementitious solids.

Table 6. The effect of salt on the permeability of mortars

Composition (wt %) ^a		Permeability (darcy)
Sand	Salt	
63.2	0	6.3×10^{-7b}
53.2	10	2.4×10^{-7}
33.2	30	4.8×10^{-8}

^aAlso contained 23.0 wt % Type I Portland cement and 13.8 wt % water. The samples were cured for 91 days.

^bDried at atmospheric pressure and 100°C.

The substitution of fly ash for the sand in a saltcrete increased the permeability by almost three orders of magnitude, depending on the type and amount of fly ash (Table 7). The permeability increased as the concentration of bituminous fly ash was increased but decreased with increasing lignite concentration. Additional studies should be made with other combinations to determine the full extent of these effects.

Table 7. The effect of fly ash on the permeability of saltcretes

Composition (wt %) ^a		Permeability (darcy)	
		Bituminous (P-15) fly ash	Lignite (P-8) fly ash
Fly ash	Sand		
0	33.2	4.8×10^{-8}	4.8×10^{-8}
10	23.2	1.2×10^{-6}	3.6×10^{-5}
20	13.2	6.8×10^{-6}	1.1×10^{-5}
30	3.2	1.0×10^{-5}	5.2×10^{-6}

^aAlso contained 23.0 wt % Type I Portland cement, 13.8 wt % water, and 30.0 wt % sodium chloride and was cured at room temperature for 91 days.

5.4 Comparison of Liquid and Gas Permeability Measurements

Gas permeability measurements on various mortars using the Klinkenberg correction technique were quite comparable to those obtained by measuring water permeability directly (Table 8). Mortar specimens containing various amounts of sand were dried to a constant weight under vacuum and used in the nitrogen permeability measurements. The specimens were then placed in distilled water, and a vacuum was applied to saturate the solids with water prior to the water permeability determinations. The maximum variation observed between the liquid and the corrected value from the gas determinations was a factor of 5. Although this variation was somewhat high, it indicated that the values obtained in the gas determinations were reasonably close to the liquid permeability of the solid.

Table 8. Comparison of liquid and gas permeability of mortars

Composition (wt %) ^a		Permeability (darcy)	
		Liquid	Gas
Cement	Sand		
60.0	7.0	1.2×10^{-5}	1.2×10^{-5}
54.0	13.0	3.6×10^{-5}	1.8×10^{-4}
47.0	20.0	2.7×10^{-5}	6.1×10^{-5}
40.0	27.0	5.0×10^{-5}	4.8×10^{-5}

^aAlso contained 33.0 wt % water. The specimens were cured for 28 days.

5.5 Permeability of Plug-Wall Rock Junctions

Preliminary data indicate that satisfactory plugs for crystalline rock formations can probably be made from mortars containing fly ash. Studies were made in which miniature boreholes in Westerly granite, Dresser basalt, Sioux quartzite, and St. Cloud granodiorite were plugged with a mortar containing 23 wt % Type I Portland cement, 20 wt % bituminous fly ash, 43.2 wt % sand, and 13.8 wt % water. With the exception of the Sioux quartzite, the water permeabilities of the plug-wall rock junctions were $\leq 6 \times 10^{-6}$ darcy after curing for 91 days at ambient temperature and pressure (Table 9).

Table 9. Permeability of wall rocks and plug-wall rock junctions^a

Wall rock	Permeability (darcy)		
	Corrected nitrogen	Plug-wall rock junction	
		Corrected nitrogen	Distilled water
Westerly granite	2.6×10^{-7}	3.3×10^{-5}	2.2×10^{-6}
Dresser basalt	$<1.0 \times 10^{-8}$	9.0×10^{-8}	$<1.0 \times 10^{-8}$
Sioux quartzite	7.0×10^{-7}	1.6×10^{-7}	3.0×10^{-5}
St. Cloud granodiorite	1.0×10^{-8}	5.4×10^{-5}	5.9×10^{-6}

^aThe plug mix contained 23 wt % Type I Portland cement, 20 wt % bituminous fly ash, 43.2 wt % sand, and 13.8 wt % water. The plug was cured for 91 days prior to the permeability measurements. After drying to constant weight, the plug solid had a corrected nitrogen permeability of 2.5×10^{-5} darcy and a water permeability of $<1 \times 10^{-7}$ darcy.

It was necessary to use thin samples (0.6 cm) in order to measure the permeability of the host rocks. When working with thin samples under pressure, there is a good possibility of altering the internal structure.⁷ Alterations such as gel-pore collapse can result in incorrect data. In addition, the plug-wall rock specimens were not dried to a constant weight prior to the gas measurements. The drying tended to cause cracking at the junction, resulting in extremely high permeability values. The 2.54-cm-diam rocks containing the miniature boreholes were difficult to handle. It is recommended that larger specimens (on the order of 5 cm in diam) be used in future tests.

A major discrepancy appears in the values obtained for the Sioux quartzite. Measured water permeabilities were usually less than the liquid permeabilities obtained by the Klinkenberg correction of the gas values. The higher water result suggests that a crack occurred in the specimen, although a visual examination did not reveal any flaws. Unfortunately, the program was discontinued before additional measurements could be made.

6. CONCLUSIONS

The techniques and equipment described in this report were found to give satisfactory and reproducible measurements of the nitrogen and distilled water permeability for a wide variety of cementitious materials. Measurements ranged from 10^{-4} to 10^{-8} darcy. The Klinkenberg correction allows the calculation of liquid permeabilities from gas measurements and is useful in detecting specimen fractures that would go unnoticed and result in abnormally high liquid values.

Mortars and saltcretes with and without fly ash exhibit microdarcy permeability. Mortars containing Type I Portland cement and a bituminous fly ash showed promise as plugging material for holes in crystalline rocks.

The major problem in permeability measurements is sample preparation. Our work has shown that if a sample has not been dried to constant weight prior to a gas determination, the result can vary by as much as three orders of magnitude. It is recommended that slightly larger specimens (5.0 cm in diam) be used in future experiments.

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