MINIMIZING THE EFFECTS OF CEMENT SLURRY BLEED-WATER ON WATER QUALITY SAMPLES

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Abstract

Some groundwater monitor wells produce water quality samples with anomalously high pH measurements. In some of these wells it is obvious that these water quality samples are affected by the bleed-water from the cement used to seal the annuli. To gain an understanding as to why cement bleed-water occurs and how it can be controlled, literature from both the cement and petroleum industries are reviewed.

Cement is a very alkaline material. When too much water is used to prepare the slurry, alkaline bleed-water can drain through or along the cement sheath surrounding the casing. This results in an increase in the pH measurements of groundwater samples. This bleed-water can separate from the cement in three ways: it can move into the formation during cementing, it can accumulate within the cement forming pockets and channels behind the casing, and it can remain within the interconnected capillaries that exist throughout the cement sheath.

The drainage of alkaline bleed-water from the cement can be greatly reduced by controlling the amount of water used in the preparation of the slurry. The amount of water added can be monitored during well construction by measuring the slurry density. By implementing this quality control procedure during well construction along with specifying the correct amount of mix-water for the slurry, the elevated pH levels in groundwater samples should be greatly reduced if not completely eliminated.

Introduction

Groundwater monitor wells are being installed in response to the many new federal and state groundwater quality protection programs. These wells provide the water samples required to evaluate the impacts of our society's past and current waste disposal practices on the underlying aquifers. The water samples collected from these wells are required to be representative of the aquifers' water quality and should not be affected by well construction materials.

In a well were the borehole diameter is larger than the casing's, cement can be used to seal the annular space above the gravel pack. Unfortunately, some of these wells produce water samples with anomalously high pH measurements (above 10.0) that can be attributed to the alkaline bleed-water from the cement. This effect can be particularly striking when it occurs in an area where groundwater has a pH range that is approximately 7.5. In some cases these alkaline wells can not be used for the collection of water quality samples. This can be very costly especially with deep monitor wells. For example, the cost of replacing a rotary drilled well in the Southwest where depth to water can easily be 350 feet would be between $20,000.00 to $25,000.00 (Cady, 1987).

Groundwater professionals have noted that cement "grouts" can cause interference with water quality samples (Barcelona et al., 1983 and Nukamoto, 1986). But, a description of the fundamental processes of how a cement slurry can increase the pH of water quality samples in monitor wells does not appear to be well documented in the groundwater industry literature. In an attempt to understand the fundamental processes occurring downhole after the slurry has been pumped into place, both the cement and the petroleum industries literature are reviewed.

Chemical Composition of Cement

The cement used in well construction is a chemically complex material composed of various oxides. These oxides can be divided into major and minor components. The major components consist of tricalcium silicate ($3CaO.SiO_2$), dicalcium silicate ($2CaO.SiO_2$), tricalcium aluminate ($3CaO.Al_2O_3$) and tetracalcium aluminoferrite ($4CaO.Al_2O_3.Fe_2O_3$). The minor components, which represent less than six percent of the total weight of the cement, consist of MgO, TiO_2, Mn_2O_3, K_2O and Na_2O. In addition, a small amount of unreacted free lime is present as a residue from the cement's manufacturing process.

This cement is referred to as a hydraulic cement since it must be mixed with water to produce a slurry that will develop strength and harden. Since contact with water is required for this reaction to occur, a slurry can hydrate and set while under water (Neville, 1981).

Physical Structure of a Cement Slurry

The size of an individual cement particle is not measured directly. Cement is so finely ground during the manufacturing process that the degree of fineness is measured by the Wagner turbidity meter. The greater the measured turbidity, than the finer the grind. A finer ground cement provides more surface area for the water to react with. This turbidity measurement relates the amount of surface area to the weight of the sample. The unit of measurement is in centimeters squared per gram (cm^2/g). For a typical cement used in well construction, the Wagner fineness measurement is 1,800 cm^2/g.

When water is mixed with cement, a slurry, or paste, is formed. A simplified cement-paste model was described by Powers in 1958 that illustrates the physical structure on a colloidal level. This model is presented in Figure 1. There are three features in the model of interest. They are: gel particles which are represented by the solid dots, gel pores which are the interstitial spaces between the gel particles, and the capillary pores which are labeled with a "c".

A gel particle is formed as a cement particle begins to hydrate with the free water. A gel is formed on the particle surface. As the particle continues to hydrate with the water, the surface area begins to increase greatly. These gel particles will begin to interlock as the chemical reactions proceed and crystal growth begins.

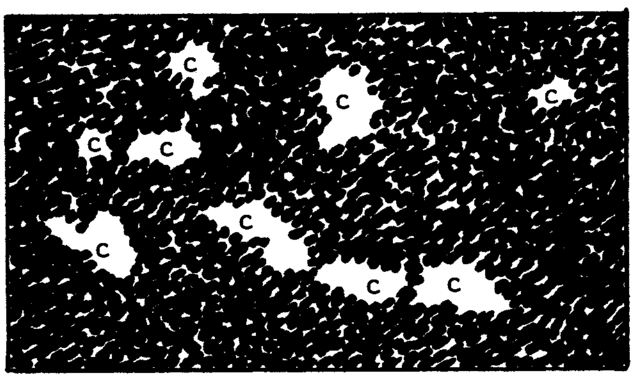

Figure 1. Simplified Model of Paste Structure (Modified after Powers, 1958)

Small spaces exist between the gel particles. As the gel particles hydrate and grow, free water molecules can get trapped within these spaces permanently. These spaces, referred to as gel pores, may be as small as 15 Å in diameter. Since this is only one order of magnitude larger than a water molecule, any water trapped within these spaces cannot drain out and is considered as part of the solid cement mass.

The last feature, and the most significant to well construction, are the capillary pores. A majority of the water exists here prior to reacting with the cement. As the cement continues to hydrate and age, these capillaries began to segment as they are blocked by expanding gel particles. But these capillaries will not be blocked off if too much water has been added to the slurry. This highly alkaline free water can remain in the cement that has been used to seal a monitor well annulus since there is no opportunity for it to evaporate. This free water, commonly referred to as bleed-water, can affect water quality samples if it can drain downward and enter the filter pack.

The potential for increases in the pH measurements of water quality samples should increase as the amount of mix water in the slurry increases past the amount required by the cement to properly hydrate. There are two reasons for this. First, as the amount of excess bleed-water is increased, the source of alkaline water that could impact water quality samples by draining down the cement column is increased. Secondly, this increase in excess mix water produces a final set cement with a higher permeability. Therefore, any unreacted water within the cement could more easily drain down through the cement and enter the filter pack.

Studies have been conducted which define the ratio of water to cement by weight at which capillaries become segmented (Powers, et al., 1959). This data is presented in Table 1.

Water/Cement Ratio by Weight	Time Required
0.40	3 days
0.45	7 days
0.50	14 days
0.60	6 months
0.70	1 year
over 0.70	impossible

Table 1. Approximate Age Required to Produce Maturity at which Capillaries Become Segmented (Powers, et al., 1959)

Problems Identified by the Petroleum Industry with Excess Water to Cement Ratios

As early as 1940, Colman and Corrigan conducted bench tests to determine the effects of various water to cement ratios. The results provide insight for those designing slurries for monitor wells. They found that the water "that does not adhere to or react with the cement particles tend to move upward in the cement,...". They cited invesitgations that showed that when molds as high as 6 to 12 feet were used, the excess water did not always migrate to the top of the cement column. It was concluded that "there would be no large quantity of water above the top of the set cement (within the well) and that most of the excess water would be trapped in pockets or channels at various points in the column of the set cement."

Colman and Corrigan determined that "there is a range of water to cement ratios for any cement so that the cement will set without producing water pockets or channels." It was also determined that this ratio is directly related to the fineness of the grind of the cement if the chemical composition remained constant. The finer the grind, the higher the acceptable range of water to cement ratios.

The range of acceptable water to cement ratios has been defined. They are referred to as the maximum and minimum water ratios for a particular cement. The maximum amount is defined as the amount of mix water that can be added to the slurry which would not exceed the amount required to keep the cement particles in suspension, thus preventing the formation of water pockets and channels. The minimum amount would be defined as the least amount of mix water required to provide an easily pumpable slurry (Saunders and Nussbaumer, 1952).

One of the major causes of cementing failures in oil wells could be attributed to slurries with excessive cement to water ratios. Within the cement column, it is possible to have alternating zones of weak, bridged, or settled cement separated by water pockets or channels. It is obvious that in an oil well these weakened and defective seals could not prevent the migration of high pressure fliuds behind the casing resulting in operational and cross-contamination problems (Willis and Wynne, 1959).

The filtration properties of cement slurries should also be considered. Fluid can be lost into a permeable formation prior to the setting of the cement. The extrapolated 30-minute American Petroleum Institute filtration test of a properly designed and mixed slurry can be 600 cubic centimeters under a pressure of 100 pounds per inch squared (Morgan and Dumbauld, 1953). The potential exists for alkaline water leaving the cement and affecting the water quality around the borehole. But since monitor wells with correctly designed slurries do not result in alkaline wells, this effect is probably not significant. However, if the well has a slurry with excess mix water, the fluid lost to the formation may contribute to the problem.

In monitor well construction any excess bleed-water would tend to drain down through the cement column or leak into the formation and drain down around the borehole. Excess amounts of bleed-water, which would occur when the maximum amount of mix water is exceeded for the cement being used, would result in alkaline water contaminating the filter pack and/or the aquifer immediately around the borehole. Contamination of the aquifer immediately opposite a well's screened interval could explain why some wells produce water quality samples with elevated pH measurements even after purging.

Appropriate Water to Cement Ratios for Monitor Wells

Very little data are available to review to determine the appropriate mix water requirements for monitor well construction. There are no standardized quality control procedures that require hydrogeologists to monitor and verify the amount of water used to prepare the slurry. A water to cement ratio of 0.46 (5.2 gallons/94 pound sack) appears to be the maximum amount for an ASTM Type I or II when these cements are compared to the API Class A and B. (API Class A and B cements are similar in composition and grind to an ASTM Type I and II respectively.)

It has been noted that a well constructed with a water to cement ratio over 0.71 (over 8.0 gallons/94 pound sack) has experienced elevated pH levels (~10.0) which are over ambient pH level (~7.0). This well has continued to produce water samples (collected after the well was purged) with elevated pH levels for over one year.

Conclusion

By reviewing both the construction and petroleum literature, a conceptual description can be developed as to how elevated pH measurements are caused by bleed-water from the cement slurries used to seal monitor well annuli. Alkaline bleed-water can separate from cement in three ways: it can move into the formation during cementing, it can accumulate within the cement forming pockets and channels behind the casing, and it can remain within the interconnected capillaries that exist throughout the cement. Unfortunately, studies have not been conducted to quantify bleed-water effects on groundwater samples from monitor wells. But by designing slurries with a 0.46 water to cement ratio (for ASTM Type I and II), elevated pH measurements should be reduced if not completely eliminated when caused by alkaline bleed-water from cement.

Disclaimer

The views expressed in this paper are those of the author and do not necessarily reflect those of the Arizona Department of Health Services.

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Biographical Sketch

Lauren Evans received her B.S. in Geology from Northern Arizona University in 1979. From 1980 through 1983, she worked for the Arizona Department of Water Resources as a hydrologist participating in hydrogeologic investigations of alluvial basins in the Southwest. Since 1984, she has been with the Arizona Department of Health Services (2005 N. Central Ave., Phoenix, Arizona 85004). Currently, she manages a hydrology unit which provides the hydrogeologic support to the Department's hazardous waste and underground stroage tank programs.