

## 8. STATIC BARRIER EVALUATION

The construction of the barrier shown in Figure 5.3 permitted the sampling of water and measurement of pH at points along the entire length of each unit. Data on the variation of pH and other water quality parameters along the length of the barrier are presented in Appendix "C". The deterioration of the units due to inhibitory coatings on the limestone could be identified by monitoring the performance of the barriers from the time of start up.

For each sampling and pH measurement, the load factor was computed by Eq. 4.18 using the weight of limestone upstream of the sampling point, the stone size and the flow rate of AMD. A theoretical pH value was computed at points along the length of the barrier for comparison with the observed value using the influent pH and the computed load factor.

**Significance of Reactivity Coefficient:** pH values were calculated with limestone reactivity coefficient values of 1.0, 0.2 and 0.05. A value of 1.0 applies to the exposure of limestone to metal-free mineral acid under laboratory conditions such that no inhibitory coatings form. A reactivity coefficient of 1.0 may therefore be expected to describe the performance of freshly started barriers when limestone surfaces are uncontaminated by deposits of sediment or metal oxyhydrates.

Under field conditions the surface of crushed limestone can be expected to become coated with sediment or metals even if the water being treated appears clear and contains concentrations of metals that are considered low (say 0.1 to 1.0 mg/l). This occurs because neutralization in the barrier reduces the solubility of clays and metals usually to solubilities below their initial concentration in the water. Consequently, clays and metals are precipitated by the neutralization process, as demonstrated by the generally decreasing concentrations of clay forming aluminum and silica, and of oxyhydrate forming iron, along the length of each barrier (see Appendix "C"). Coatings that form on the surface of crushed limestone in this manner reduce the reactivity of a fresh limestone by approximately 5 times. Therefore, a reactivity coefficient of 0.2 accounts for the effect of surface coatings on the neutralization process.

**Scouring Criteria:** Provided hydraulic conditions in a barrier are sufficiently aggressive, both solids that precipitate on the stone surfaces and limestone fines dislodged from the surfaces, are continuously swept from a barrier. However, if these solids are not removed but instead settle in the barrier, they will clog the barrier pores. This accumulation blankets the contact between the limestone and acid water, and creates a further reduction of the reactivity coefficient. A value of 0.05 of the reactivity coefficient is considered indicative of partial clogging of barrier pores by sediment, metal oxyhydrates, or settled limestone fines.

To identify the hydraulic conditions for an effective flushing of precipitated solids, the Quakake barriers were constructed on grades ranging from 1% to 30%, and with limestone in the size ranges of 5 mm (1/4") to 20 mm (3/4"). Steep grades and large stone size are conducive to flushing because an increase in either of these two factors increases the velocity of flow through the stone. The vertical component of flow velocity is suggested as the criterion of flushing effectiveness as it determines the particle size which can be transported. Vertical velocity is the product of barrier slope and superficial flow velocity, the latter being computed from barrier gradient and stone size by the Carman Kozeny equation. Other factors affecting superficial

velocity are stone porosity, stone shape factor and water temperature. An objective of the Quakake demonstration study was to identify hydraulic conditions (i.e. vertical flow velocity) at which sediment would not accumulate in the barrier pores, so that the reactivity coefficient would remain indefinitely above about 0.2.

**Observed and Computed pH Profiles:** A summary of observed pH change along barrier length (pH profiles) and the variation of pH with load factor for selected runs are presented in Figures 8.1 thru 8.6. Complete test and field data are presented in Appendix "C". Also shown are computed profiles for reactivity coefficients of 1.0, 0.2 and 0.05.

Figures 8.1 and 8.2 summarize the results for barriers 2 and 4 which used 5 mm (1/4") stone at different loading rates. Startup in the fresh condition (Figure 8.1) resulted in satisfactory performance with a reactivity coefficient exceeding 1.0 over most of the length of the barrier (The significance of an apparent reactivity coefficient in excess of 1.0 is discussed later). A considerable reduction in pH values was observed after 240 hours of operation at the first two sampling points where the barrier reactivity coefficient fell below 0.05. Subsequently, a further reduction in pH and reactivity took place with time. This reduced neutralization activity continued downstream until after 744 hours of operation 60% of the barrier (6 bins) had become fouled and the water ran over the bed tops rather than through the limestone. It can be expected that ultimately this deterioration would penetrate the entire length of a barrier.

The steep barrier, using 5 mm (1/4") stone (Barrier 6 - Run No. 1), succeeded in sustaining a higher effluent pH at lower load factors. Nevertheless, this barrier was also subjected to the same progressive fouling as shown in Figure 8.3 Vertical fluid velocities through the barriers containing 5 mm stone ranged from .0001 fps (feet per second) in Barrier 2 and 4, to 0.0028 fps in Barrier 6. The better performance seen in Barrier 6 indicates that while higher velocities are beneficial, velocities in this range are not adequate to prevent the progressive fouling seen in all the barriers.

The stone interstices in all barriers using the 5 mm (1/4") stone were clogged with precipitates to the extent that the AMD ultimately flowed over the surface of the bed. In this condition, only the surface layer of the limestone was effectively exposed. Figure 8.4(a) shows observed pH profiles compared with theoretical profiles assuming all the stone in the barrier is reactive. The observed profiles in Figure 8.4(b) are compared with theoretical profiles which assume that only the surface layer of stone (one stone thick) is reactive. Initially, process performance is well described on the basis that all the stone is reactive. But there is a progressive deterioration of the process so that ultimately only the surface stone is effective and a final reactivity coefficient of 0.2 is reached.

Figure 8.5 shows that the reactivity of Barrier 1 which contained 20 mm (3/4") limestone, degraded to a value of 0.2 in approximately 144 hours. The reactivity eventually dropped to a value of approximately 0.05. The vertical fluid velocity within the barrier was approximately 0.004 fps at the design flow of 0.5 cfs. Figure 8.6 shows that by drying and flushing, a barrier can be restored to its original reactivity coefficient of 1.0. However, the decline of reactivity coefficient is much faster than that occurring during fresh startup, using new clean stone. It is of interest to note that sediment in Barrier 1 could be flushed from the barrier when the flow was increased to 1 cfs (corresponding to a vertical fluid velocity of 0.014 fps).

Figures 8.7 and 8.8 show the performance of Barrier 5 and 6 when they were filled with 13 mm (1/2") stone which represents the best sustained treatment achieved by the static barriers. By increasing the vertical velocity to 0.053 fps in the steep barrier, deterioration was effectively controlled as shown in Figure 8.8. The barrier achieved steady operation with a reactivity coefficient above 0.2 for eight days.

Several factors affect evaluation of the barrier performance. In a few cases,  $r$  values greater than 1.0 are shown and can be attributed to the fresh limestone containing 1 to 3 percent fines. Although the barriers were flushed for several hours prior to the first sampling, not all the fines were removed, particularly in the 5 mm stone. In addition, the theoretical curves were developed assuming no loss of CO<sub>2</sub> during the process. Therefore, if some CO<sub>2</sub> was exsolved during the neutralization process, the resulting pH values would have been somewhat higher than those predicted. Fluid velocities mentioned in this section are generally for the first neutralization bin in the series and would not be applicable to successive bins or to other units. The rate of fouling varied considerably from bin to bin, as can be interpreted from examination of Figures 8.1 through 8.8.

**Scouring Effectiveness:** Barrier clogging can be minimized by establishing increasingly aggressive hydraulic conditions. From observations, depicted in Figure 8.9, it can be seen how vertical velocities control the progress of siltation. This is reflected by the change in hydraulic gradients that were developed in a barrier following a fresh startup. At the lowest vertical velocity of 0.0001 ft./sec., siltation progressed until the barrier pores were entirely clogged and water ran over the surface of the barrier.

Figure 8.10 shows the size distribution of sediment from a clogged barrier. At the highest vertical velocity (Barrier 6, Run No. 3) the hydraulic gradient actually decreased during the run, apparently due to the washout of fines which initially adhered to the limestone and maintained an open stone void system by effective scouring.

Sediment traps were provided ahead of each unit so that sediment from outside sources was not introduced into the system. However, silt and sand size particles of limestone were produced during the reaction between the acid and the stone. Apparently the acid attacks minute joints or other planes of weakness in the larger stone particles. This causes sand sized chips to form and subsequently flake off. Depending on the velocity of flow through the stone voids, these dislodged particles are either transported through the system or clog the voids between the larger stone sizes. Samples of the finer material were completely coated with metal precipitates. The settled fines from the upper bins of Barrier 1 were coated with a deep brown precipitate; whereas, samples from the lower bins had a grayish white precipitate. This suggests that the iron complexes precipitate on the stone prior to the aluminium complexes.

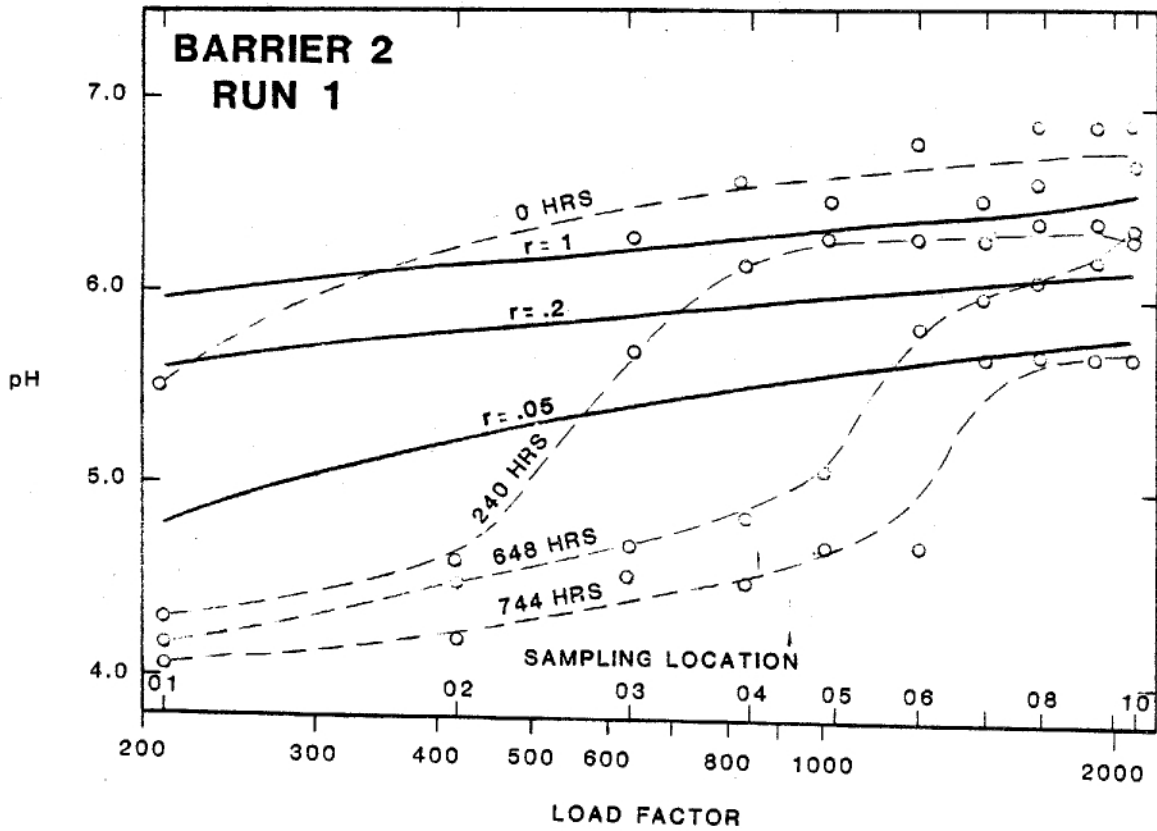
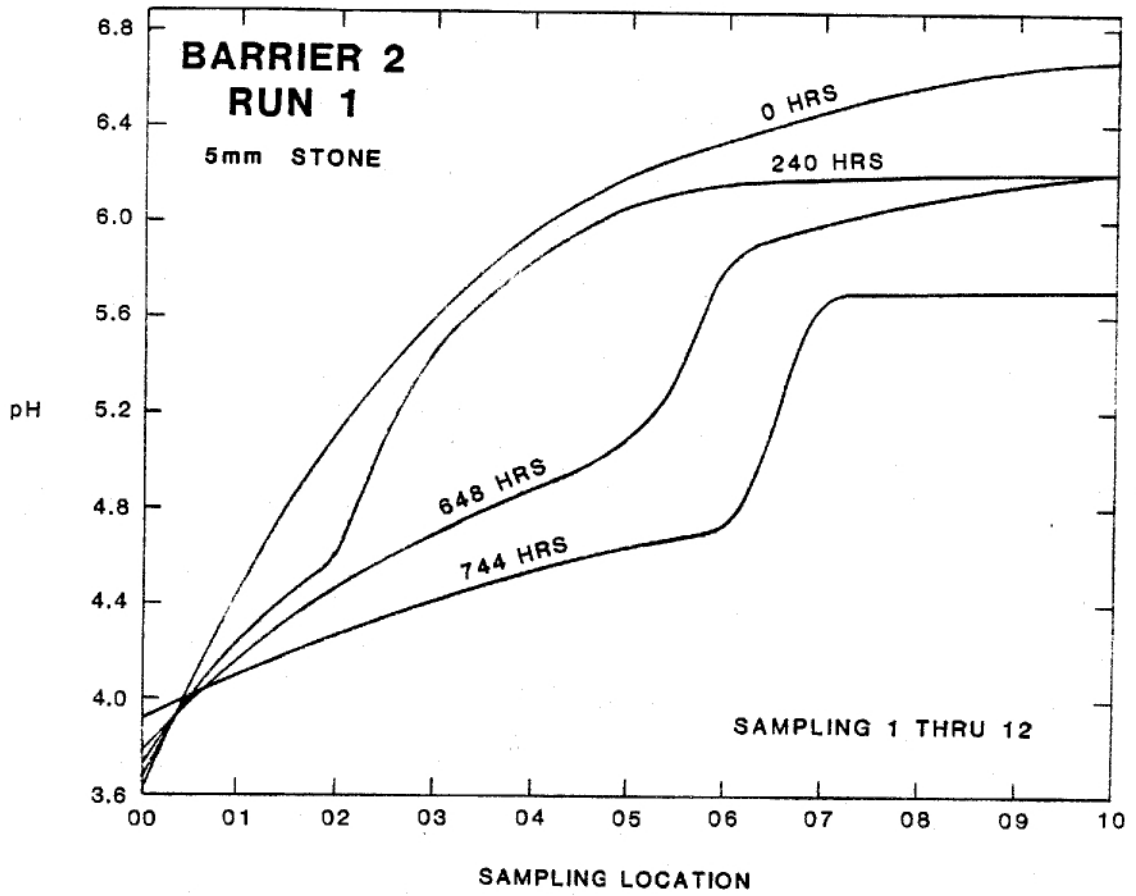


Figure 8.1 Typical Prototype Results - Barrier 2, Run 1

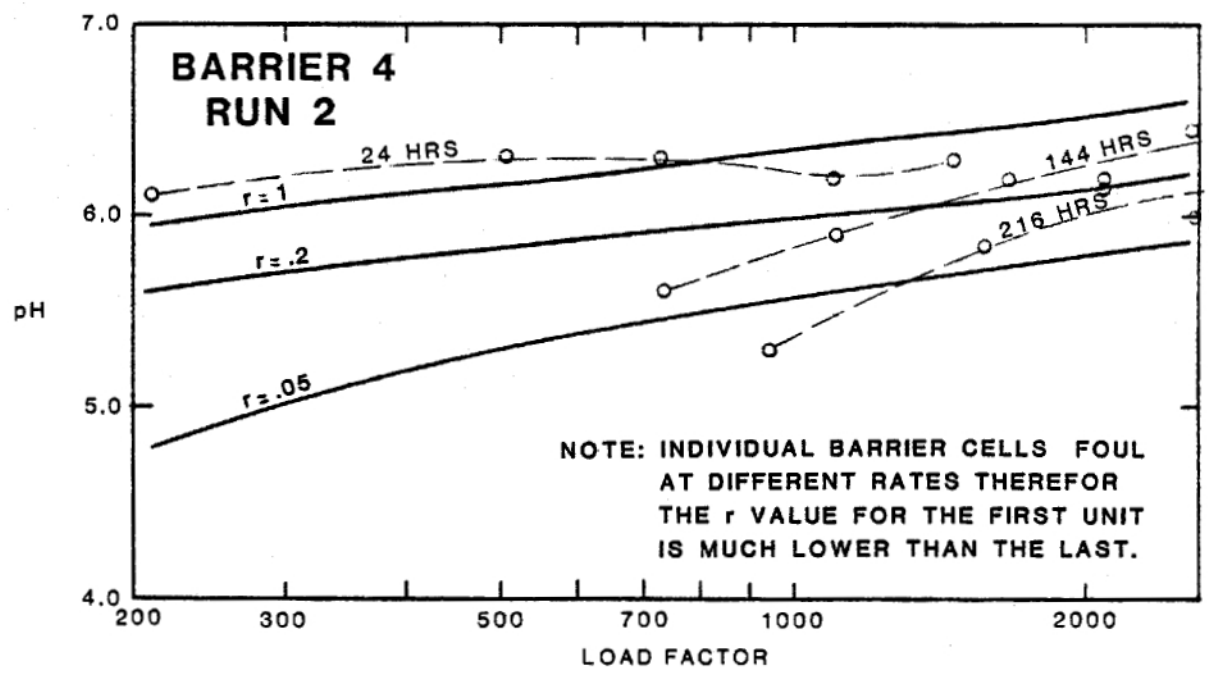
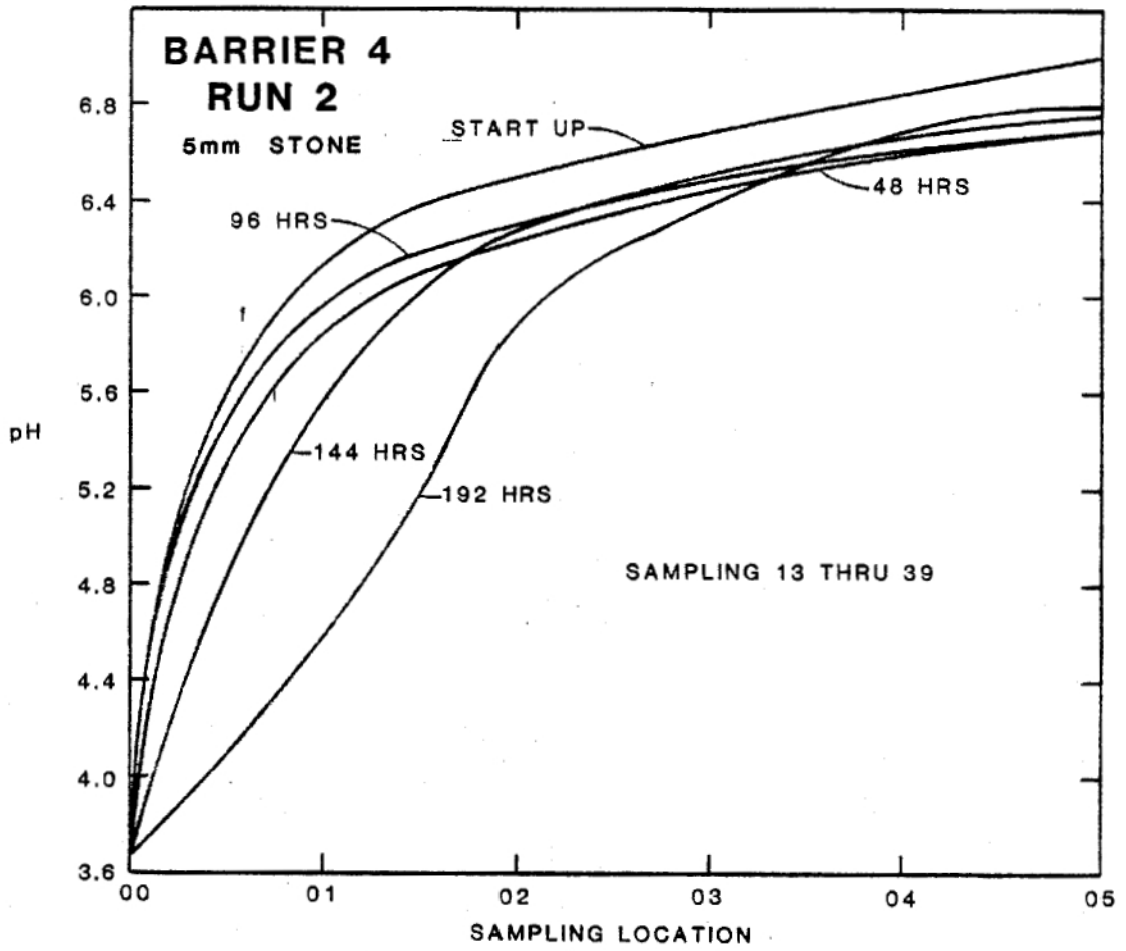


Figure 8.2 Typical Prototype Results - Barrier 4, Run 2

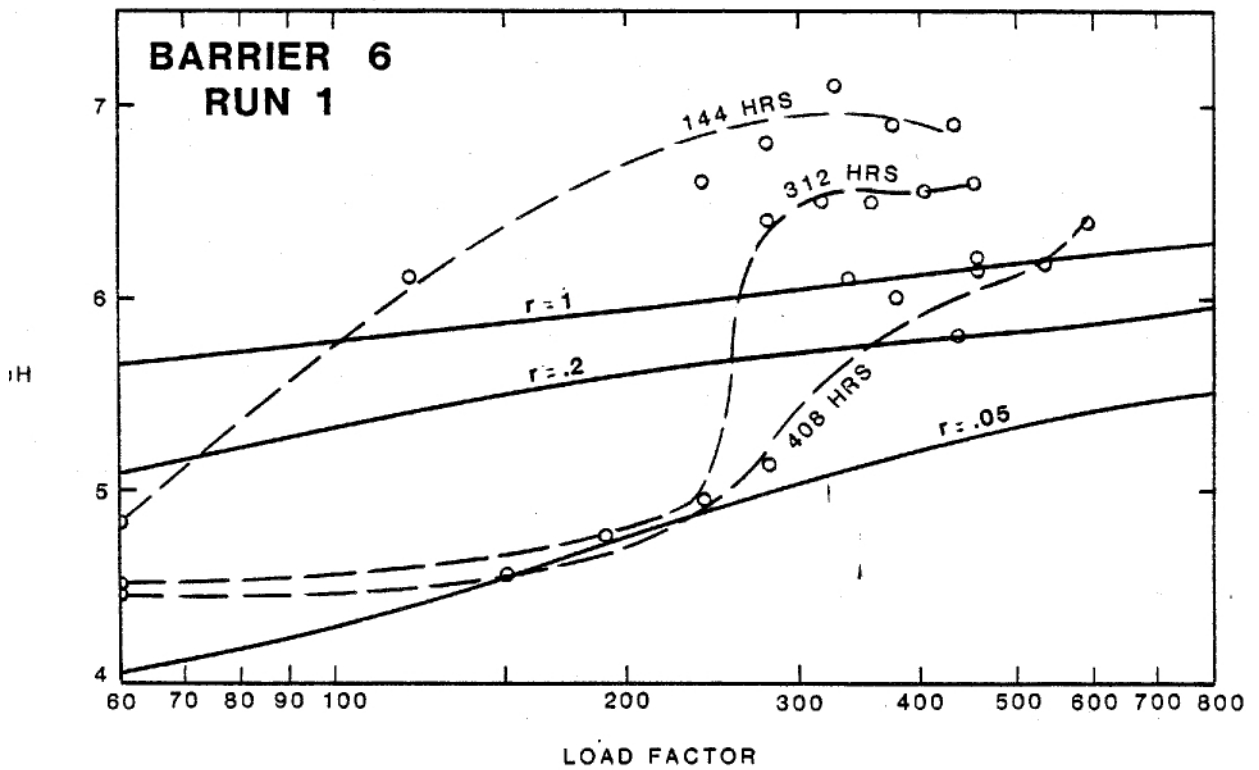
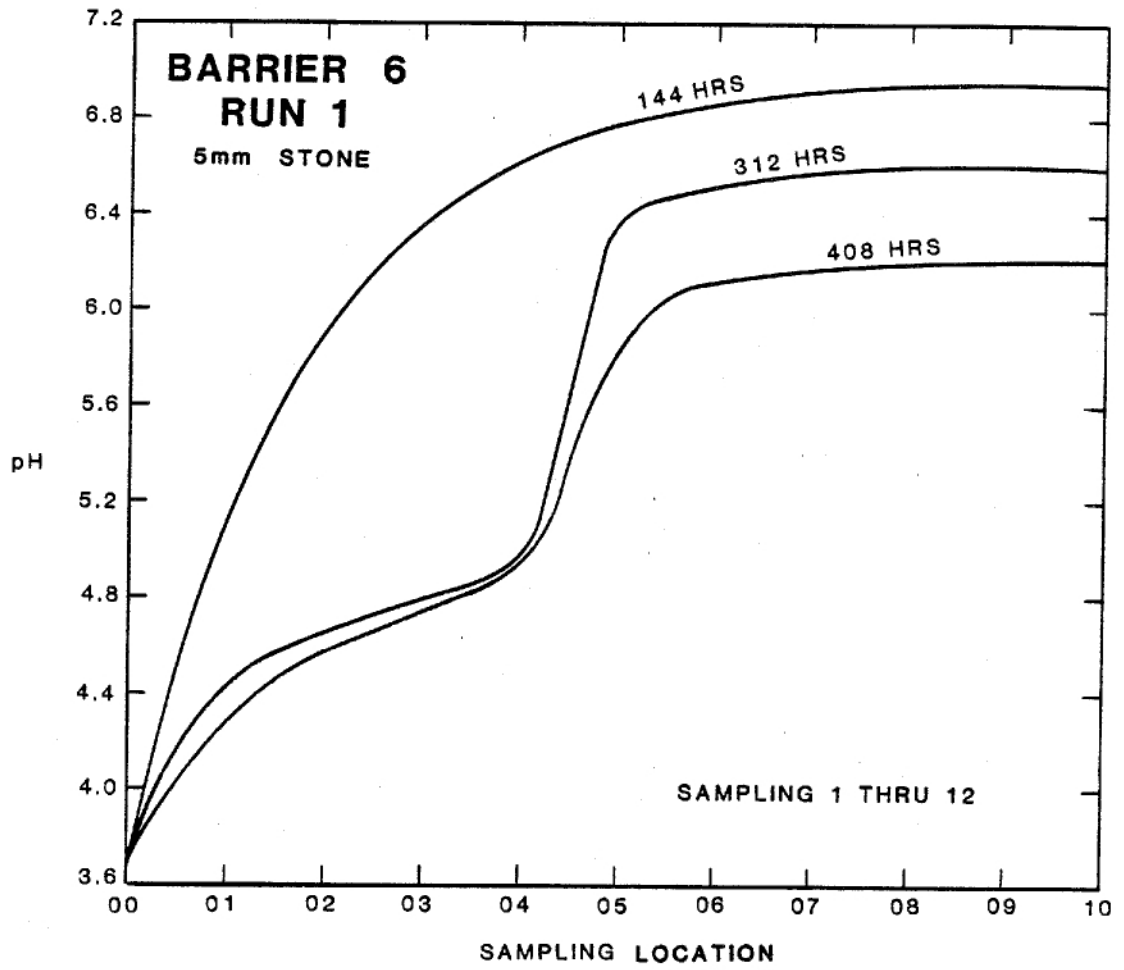


Figure 8.3 Typical Prototype Results - Barrier 6, Run 1

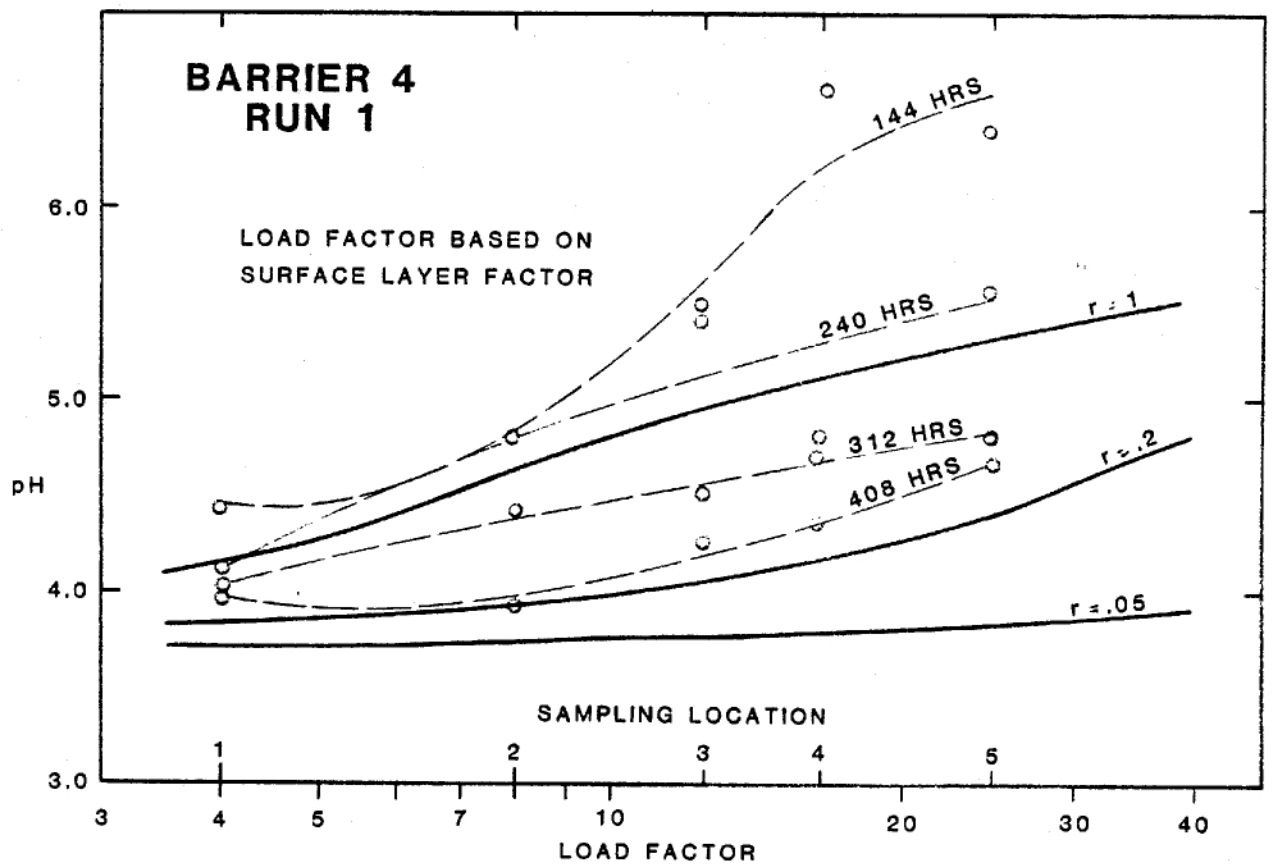
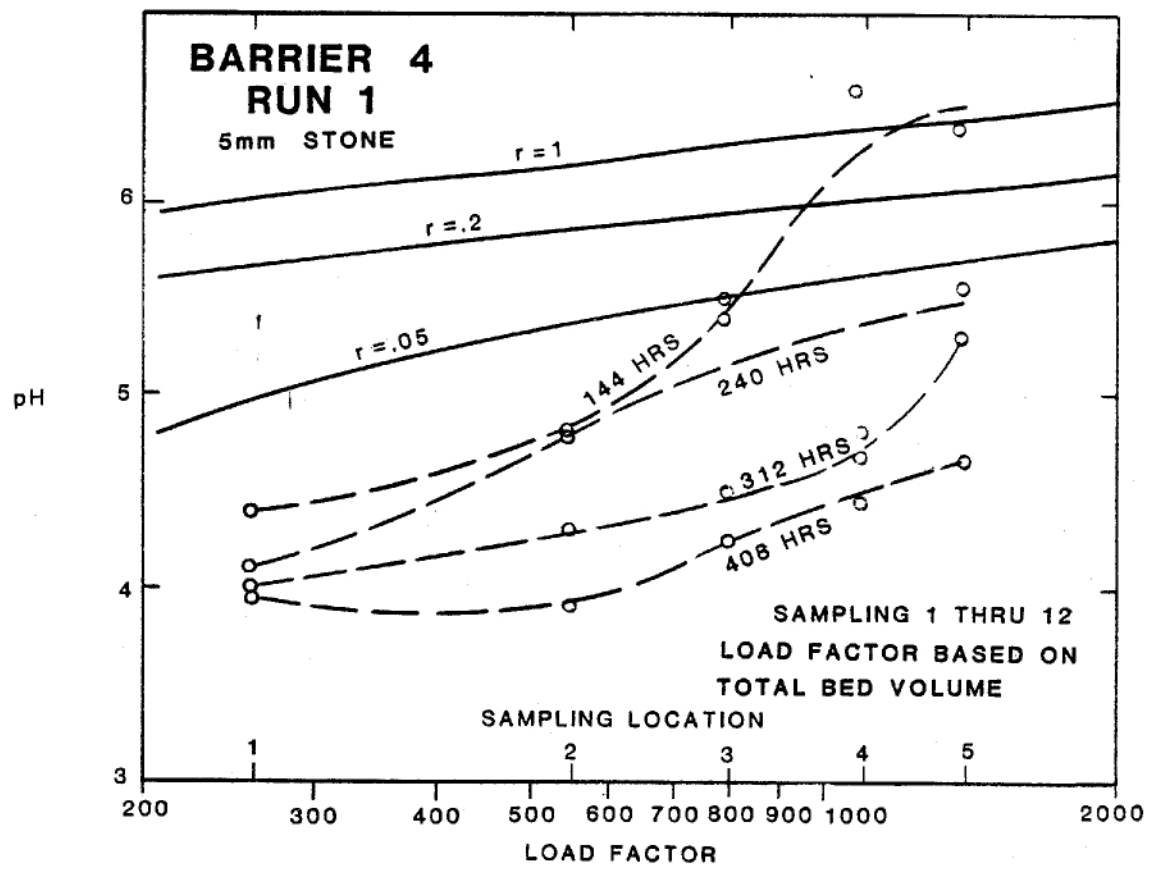


Figure 8.4 Typical Prototype Results - Barrier 4, Run 1

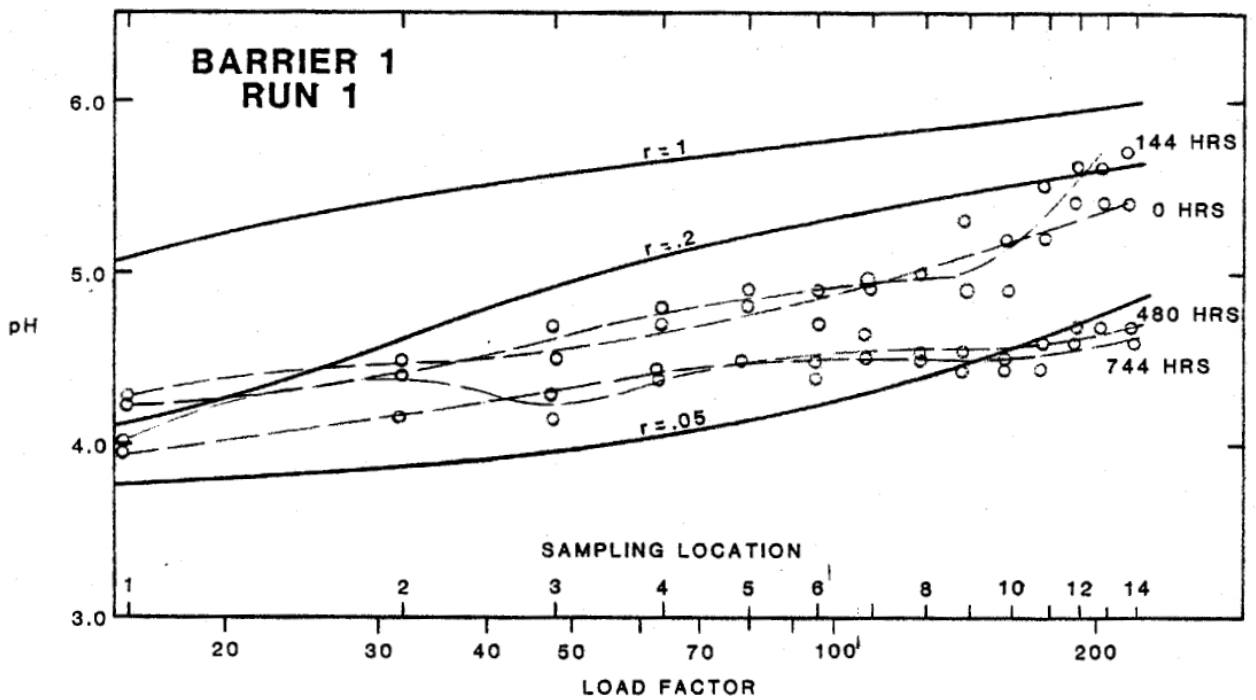
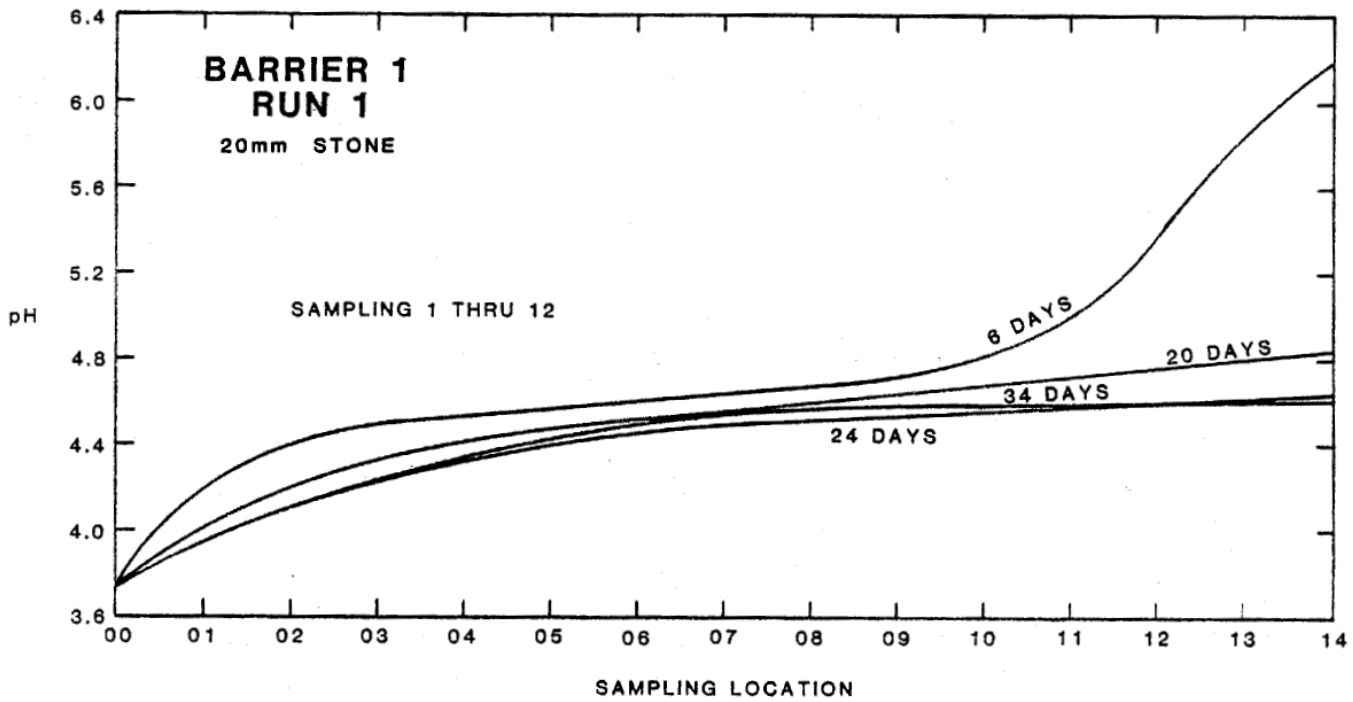


Figure 8.5 Typical Prototype Results - Barrier 1, Run 1



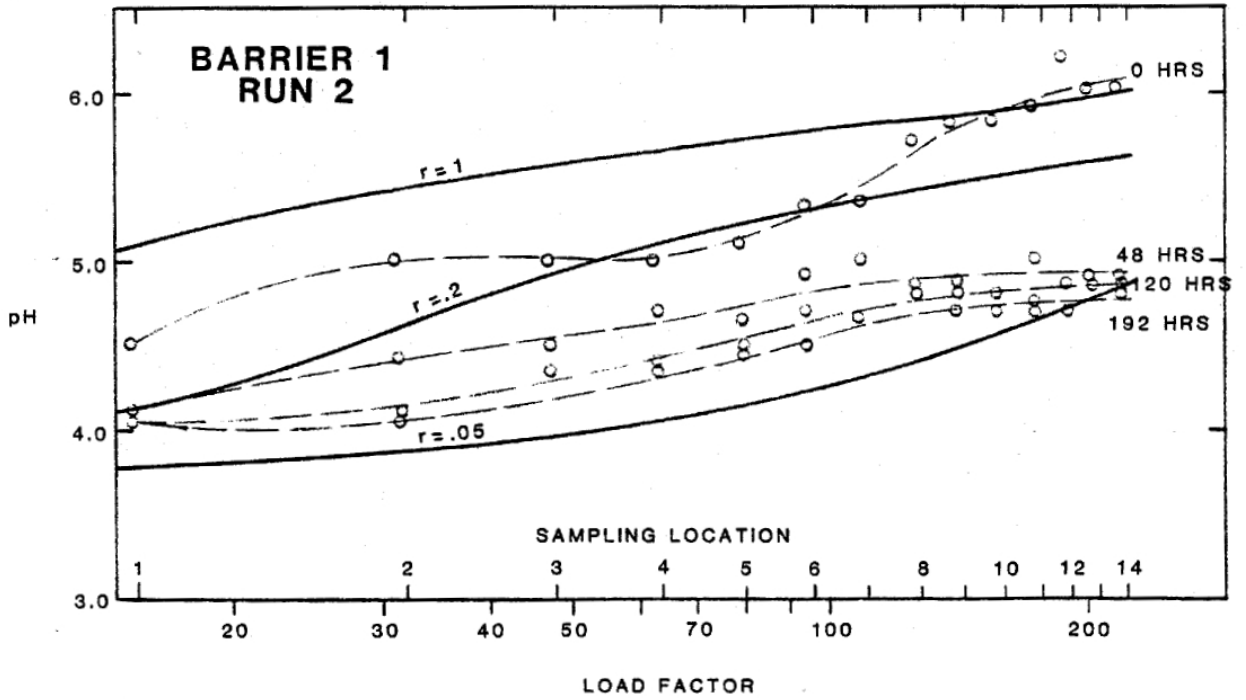
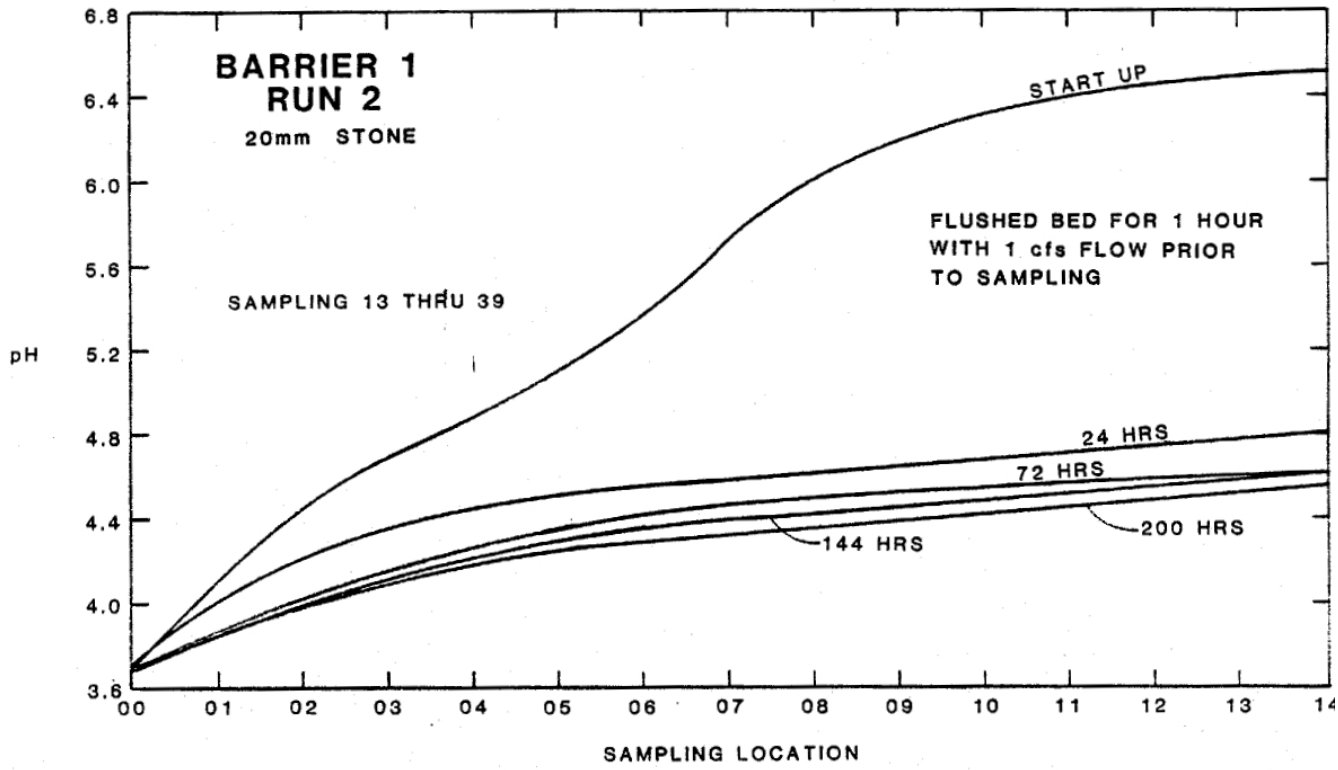


Figure 8.6 Typical Prototype Results - Barrier 2, Run 2

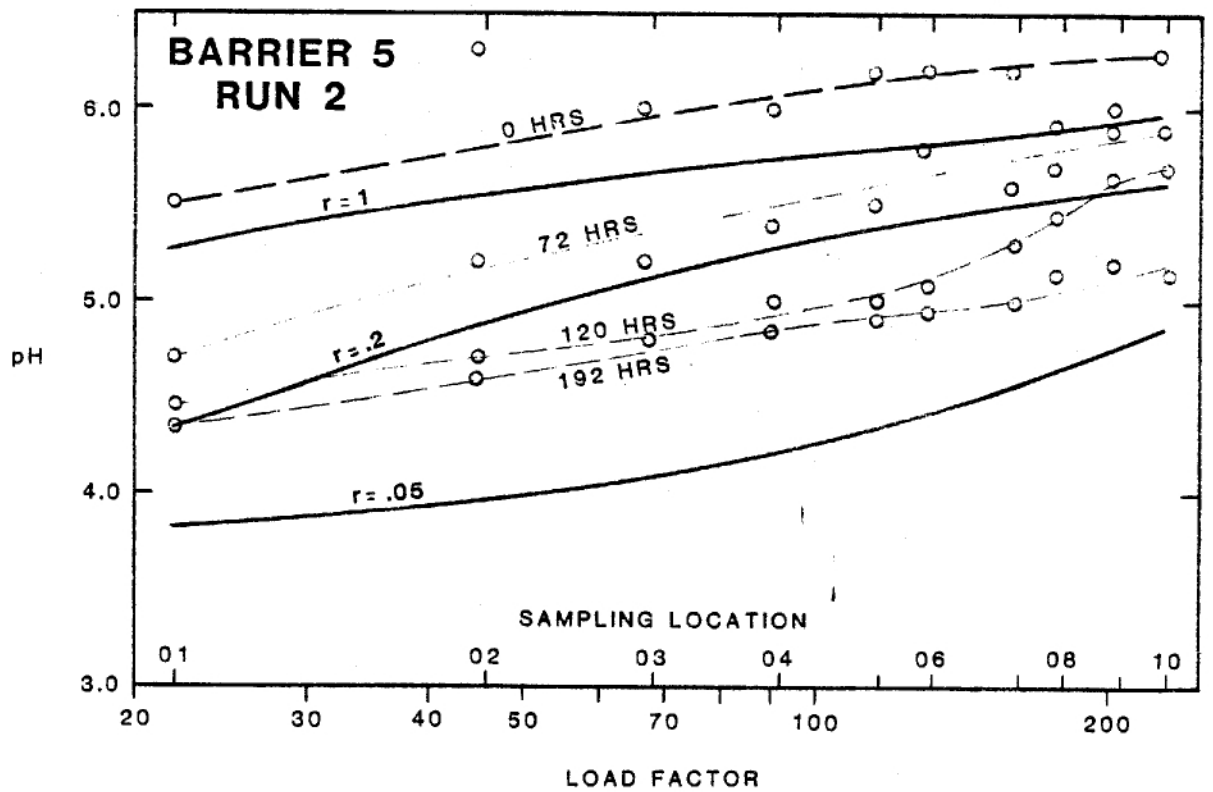
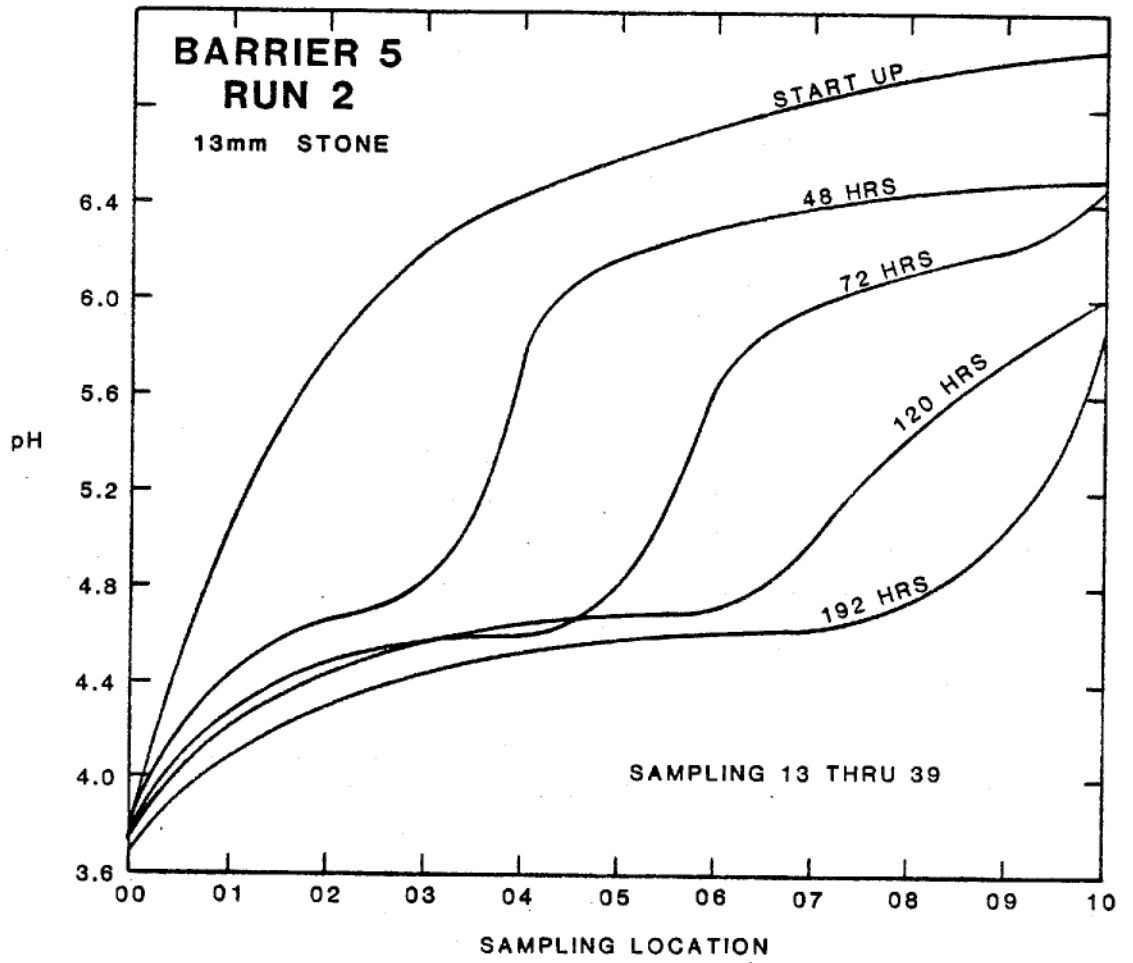


Figure 8.7 Typical Prototype Results - Barrier 5, Run 2

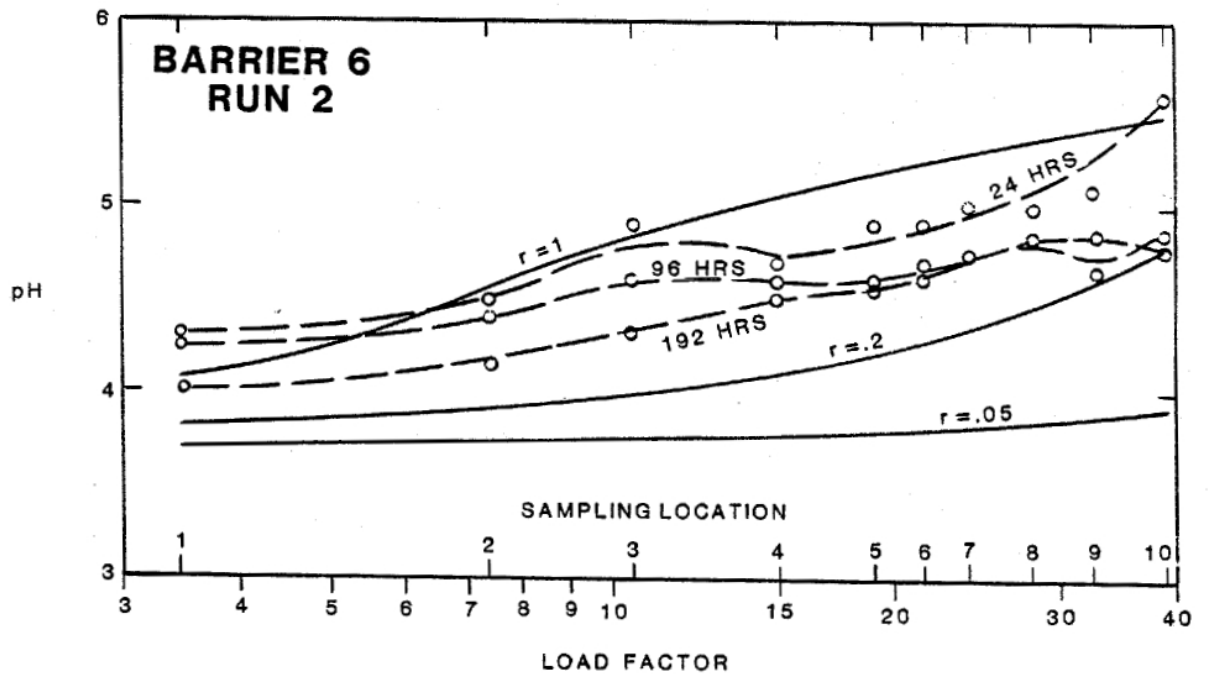
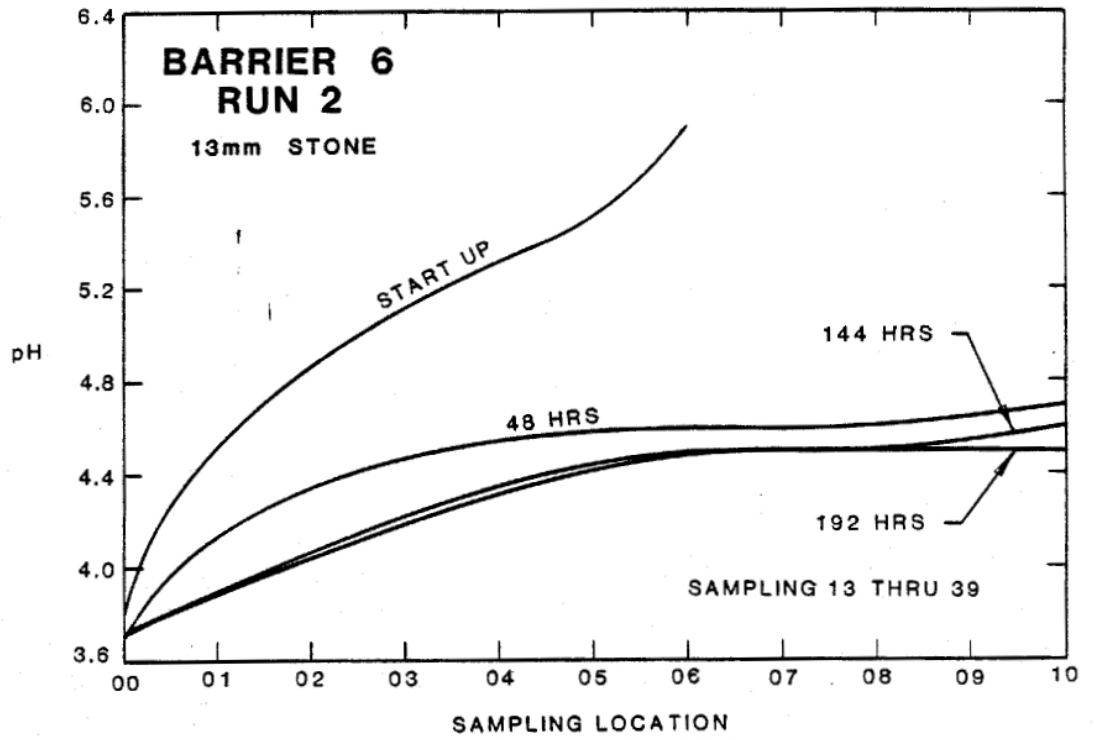


Figure 8.8 Typical Prototype Results - Barrier 6, Run 2

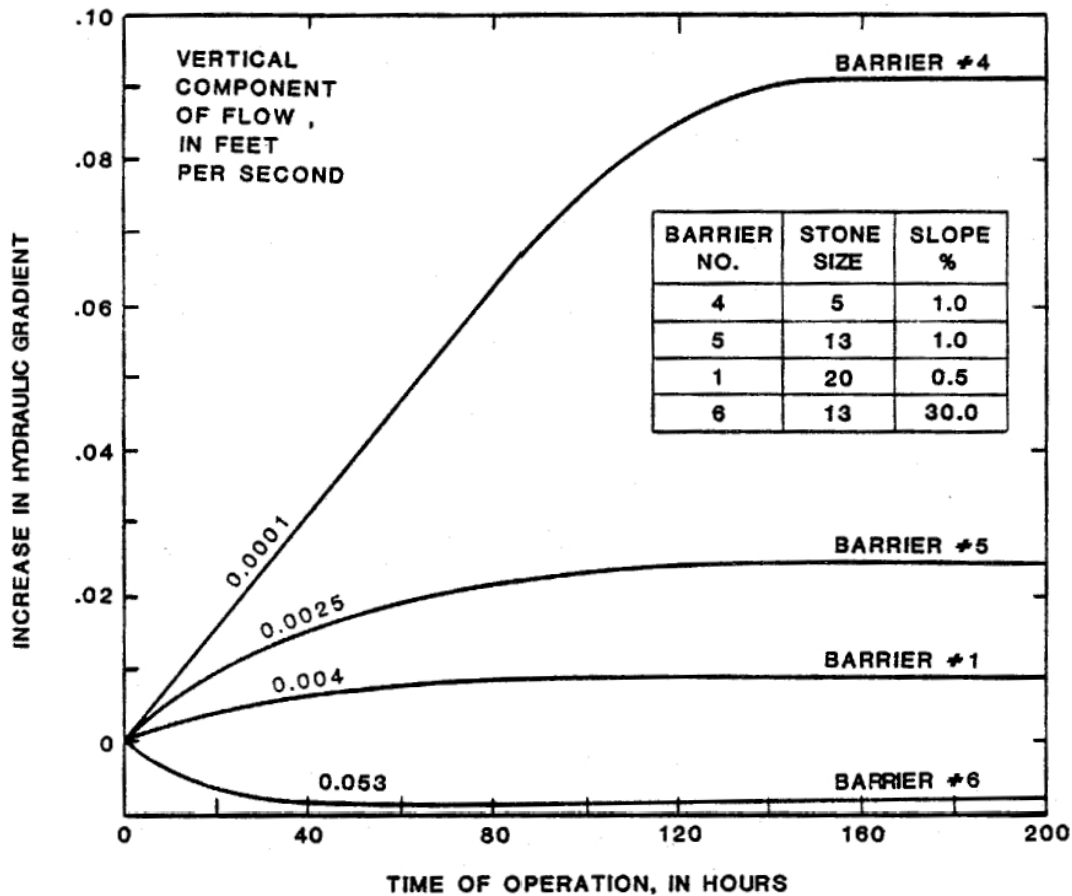


Figure 8.9 Increase in Barrier Hydraulic Gradient With Time

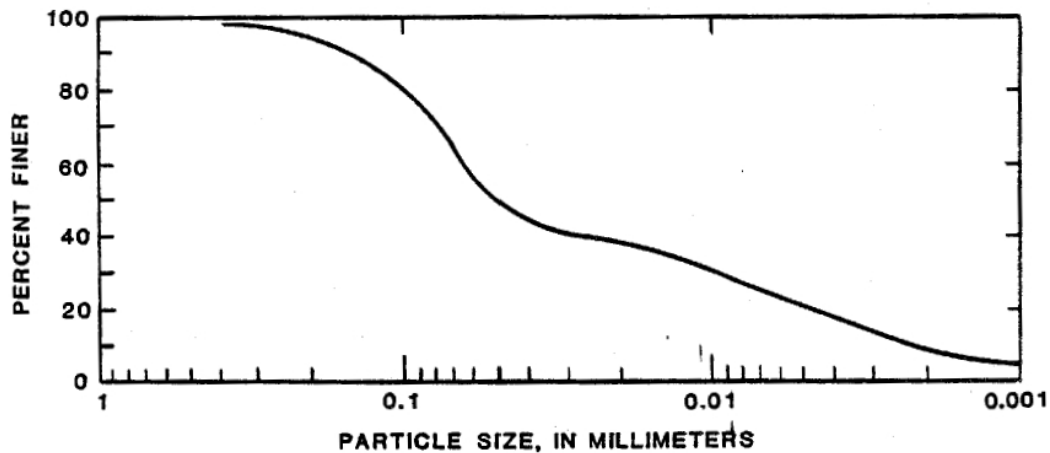


Figure 8.10 Particle Size Distribution of Barrier Sediments