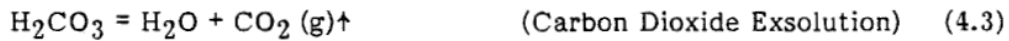
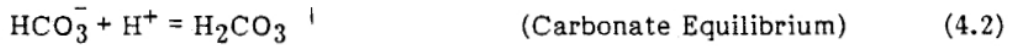
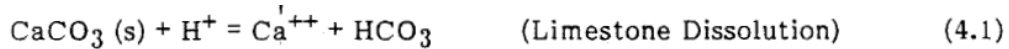


ZURBUCH'S OTTER CREEK TUMBLING DRUM INSTALLATION

4. PRINCIPLES OF AMD NEUTRALIZATION BY CRUSHED LIMESTONE

The following outlines of the chemical principles involved in the neutralization process are presented to facilitate an understanding of conventions used to evaluate the data obtained at the Quakake Tunnel.

Chemical Reactions: The neutralization of acidity by crushed limestone is controlled by the following chemical reactions:



Where H_2CO_3 = Dissolved Carbon Dioxide

HCO_3^- = Bicarbonate

Because the first reaction upsets the equilibrium between the bicarbonate and dissolved carbon dioxide, part of the bicarbonate formed reacts with hydrogen ions to form dissolved carbon dioxide. The formation of dissolved carbon dioxide by the second reaction in turn upsets the natural equilibrium between dissolved carbon dioxide and the level of carbon dioxide in the atmosphere. As a result, there is a chemical driving force for dissolved carbon dioxide to transfer from water to air, as represented by the third reaction.

Reaction Rates: Reactions involving only one phase (solid, liquid or gas) are usually faster than multi-phase reactions that are limited by rates of transfer of materials across the surface separating the phases. Thus, the reactions of Eq. 4.1 and Eq. 4.3 which occur across the liquid-solid limestone surface and across the liquid-gas water surface respectively, are much slower than the rate of Eq. 4.2 that occurs in the liquid phase and is instantaneous for all practical purposes.

The rates of Eqs. 4.1 and 4.3 depend on the rate constant and order of each reaction, the limestone surface area per unit flow for Eq. 4.1 and the water surface area per unit flow for Eq. 4.3. The reaction rates are influenced by temperature, ionic strength and the intensity of turbulence, but the range of their effects is minor and invariant. Consequently values for average conditions can be assumed for practical design procedures. Equations 4.1 and 4.3 have been found experimentally to be first order with respect to the concentrations of reactants (14). This means the reaction rate in Eq. 4.1 is directly proportional to the concentration of mineral acidity (hydrogen ions) in the AMD. Similarly the reaction rate in Eq. 4.3 varies directly with the concentration of dissolved carbon dioxide. Equations 4.4 and 4.5 define the change of mineral acidity and carbonic acidity with respect to the limestone surface area and the free water surface:

$$- \frac{d[\text{H}^+]}{d\alpha} = k_1[\text{H}^+] \quad (4.4)$$

$$- \frac{d[\text{H}_2\text{CO}_3]}{d\beta} = k_3[\text{H}_2\text{CO}_3] \quad (4.5)$$

in which:

- [] = Concentration - moles
- α = Surface area of crushed limestone per unit flow of AMD, sec-m^{-1} ;
- β = Free water surface area per unit flow, sec-m^{-1} ;
- k_1 = Proton effective diffusion rate constant
- k_3 = Carbon dioxide diffusion rate constant

$$* (\text{area in m}^2)/(\text{Flow in m}^3/\text{sec}) = \text{sec-m}^{-1}$$

Pilot scale investigations (16) under laboratory conditions have shown that the rates of Eqs. 4.1 and 4.3 under standardized conditions of no turbulence, 10°C temperature and an ionic strength of 0.001 kg mole-m^{-3} are:

$$\begin{aligned} k_1 &= 0.0055 \text{ m-sec}^{-1} \\ k_3 &= 0.00058 \text{ m-sec}^{-1} \end{aligned}$$

Acidity and Alkalinity: The alkalinity of a water is the capacity of that water to accept protons (e.g. hydrogen ions -- $[\text{H}^+]$). Conversely the acidity of a water is the capacity of that water to donate protons. Alkalinity and acidity are measured by the procedures specified in "Standard Methods" (22). Acidity is measured by titrating the water to a pH of 8.3 where the concentrations of acid, base and carbonate are equal. The proton condition of a pure carbonate solution at the pH = 8.3 end point is:



At low pH values the solution contains strong acids such as H_2SO_4 . In this case the solution is said to contain mineral acidity or free acidity. The concentration of mineral acidity is commonly measured by titrating the solution to the methyl orange acidity end point of pH = 4.5. The proton condition of a pure solution at this end point is:



When the initial pH of a solution is greater than 4.5 the solution is titrated with a strong acid to the methyl orange end point. The concentration of acid required to accomplish the titration is termed alkalinity.

Alkalinity and acidity are formulated as follows:

$$[\text{Alk}] = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+] \quad (4.8)$$

$$[\text{Acy}] = [\text{H}_2\text{CO}_3] - [\text{CO}_3^{2-}] - [\text{OH}^-] + [\text{H}^+]$$

in which:

$$[\text{Alk}] = \text{alkalinity in kg mole-m}^{-3}$$

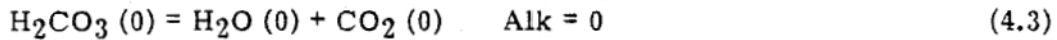
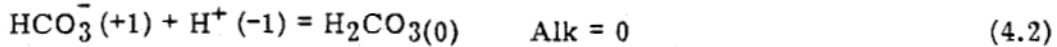
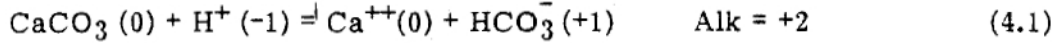
$$[\text{Acy}] = \text{acidity in kg mole-m}^{-3}$$

$$[\text{H}^+] = \text{is interpreted to include protons released by hydrolysis of metals and by dissociation of non-carbonic weak acids, as well as from mineral acidity}$$

Alkalinity Change as a Measure of Neutralization: The change in alkalinity is a measure of

proton consumption as the reaction proceeds. The value of alkalinity as described by eq. 4.8 can be computed for the controlling chemical reactions; Eq. 4.1, 4.2 and 4.3.

The first reaction removes one proton from solution thereby increasing the alkalinity by one unit. It also adds a bi-carbonate ion resulting in a net alkalinity increase of 2 units. The remaining two reactions do not affect the alkalinity concentration as shown below:



(\pm) = Positive or negative alkalinity unit

Equating the incremental decrease in proton concentration by Eq. 4.1 to the incremental increase in alkalinity:

$$d[\text{H}^+] = 0.5 d[\text{Alk}] \quad (4.10)$$

Eq. 4.4 can then be transformed to reflect the alkalinity change throughout the neutralization process:

$$0.5 \frac{d[\text{Alk}]}{d\alpha} = k_1[\text{H}^+] \quad (4.11)$$

The value of [Alk] is dependent on the concentration of carbonate and protons in the solution as described by Eq. 4.8. The total concentration of carbonate in solution is described by:

$$C_t = \text{H}_2\text{CO}_3 + \text{HCO}_3^- + \text{CO}_3^{--} \quad (4.12)$$

and if Eqs. 4.8 and 4.9 are combined, we find:

$$C_t = [\text{Alk}] + [\text{Acyl}]$$

Where C_t = the total concentration of carbonate, kg-mole-m^{-3}

Alkalinity can be formulated in terms of C_T and H^+ as follows:

$$[\text{Alk}] = \frac{C_t}{1 + [\text{H}^+]/K_1} - [\text{H}^+] \quad (4.13)$$

Where K_1 is the first dissociation constant for carbonic acid.

Eq. 4.13 disregards the $[\text{OH}^-]$ and $[\text{CO}_3^-]$ concentrations as they are very small in the pH range of interest. Table 7.1 presents a complete description of the carbonate equilibrium system.

A numerically soluble expression describing the neutralization process can be obtained by calculating the derivative of Eq. 4.13 with respect to $[H^+]$;

$$\frac{d[H^+]}{d\alpha} = \frac{2k_1[H^+]}{(1 + K_1 C_t / (K_1 + [H^+]^2))} \quad (4.14)$$

Roughly translated, Eq. 4.14 states that the change in proton concentration with respect to the neutralization opportunity (i.e., stone surface area, AMD volume, contact time) is a function of the concentrations of protolized ions (e.g. H^+ , Al^{++} , Fe^{+++}) and the inorganic carbon (i.e., Acidity + Alkalinity).

Inorganic Carbon Balance: The solution of Eq. 4.14 is complicated by changes in concentration of inorganic carbon concentration during the neutralization process. During neutralization, the carbonate concentration is increased in the AMD at a rate equal to the rate of dissolution of limestone, according to Eq. 4.1. This increase in inorganic carbon concentration is offset by a decrease due to the expulsion of carbon dioxide from solution. The rate of carbon dioxide exsolution is proportional to the concentration of carbon dioxide present in solution, as Eq. 4.5 shows. The total incremental change in concentration of inorganic carbon is expressed by the differential:

$$dC_t = K_1 [H^+] d\alpha - k_3 \cdot \frac{C_t}{1+K_1/[H^+]} d\beta \quad (4.15)$$

which may be written:

$$\frac{dC_t}{d\alpha} = k_1[H^+] - k_3 \frac{C_t}{1+K_1/[H^+]} \frac{d\beta}{d\alpha} \quad (4.16)$$

The linked differential Equations 4.13 and 4.16 can be solved by numerical methods. The solution mathematically models the neutralization process for given initial concentrations of protons and CT and for given treatment conditions. The treatment conditions being the limestone and free water surfaces provided per unit flow.

Limestone Characteristics: The neutralization characteristics of crushed limestone depend on both the physical and chemical properties of the stone. Particle size and shape control both the hydraulics of flow through the crushed stone and the surface area of $CaCO_3$ available for reaction with the acid water. Hardness of the stone determines the rate of abrasion and chemical dissolution of the stone, which is related to the Magnesium Carbonate ($MgCO_3$) content of the stone.

The hardness of the limestone was measured by the Los Angeles Abrasion Test (ASTM C-131) which consists of rotating an aggregate sample in a 28-inch diameter drum at a speed of 30 to 33 RPM for 500 revolutions. The fine material ground from the original sample is discarded and the difference between the original weight and the final weight, expressed as a percentage, is reported as the percent L.A. Abrasion wear. Zurbuch (20) found that this abrasion test method correlated well with observed limestone use rates in revolving drums.

The rate of dissolution of limestone is dependent on its magnesium carbonate content. It appears that the rate of dissolution of a limestone is inversely proportional to its $MgCO_3$ percentage. Pearson (16) derived this relationship from data presented by Hoak, Lewis and Hodge (8).

Shape Factor: The shape factor of the crushed limestone particles is required to determine for the surface area per volume of stone and computations of flow through the beds of crushed limestone. The shape factor is defined as:

$$\frac{V}{A} = \frac{SD}{6} \quad (4.17)$$

where:

- S = Shape factor
- D = Nominal particle diameter, equal to the diameter of a sphere of the same volume
- V = Volume of the particle
- A = Surface area of the particle

This equation defines the shape factor as the ratio of the surface area of a sphere with the same volume as the particle, to the surface area of the particle. Previous investigators (23) estimated the shape factor-surface area relationship by individual measurements on more than one ton of crushed limestone. For 1,218 stones, the mean shape factor was 0.76 with a standard deviation of 0.04 and a range of 0.59 to 0.89. Accordingly, a shape factor of 0.76 was used for design of the prototypes and evaluation of the operating data.

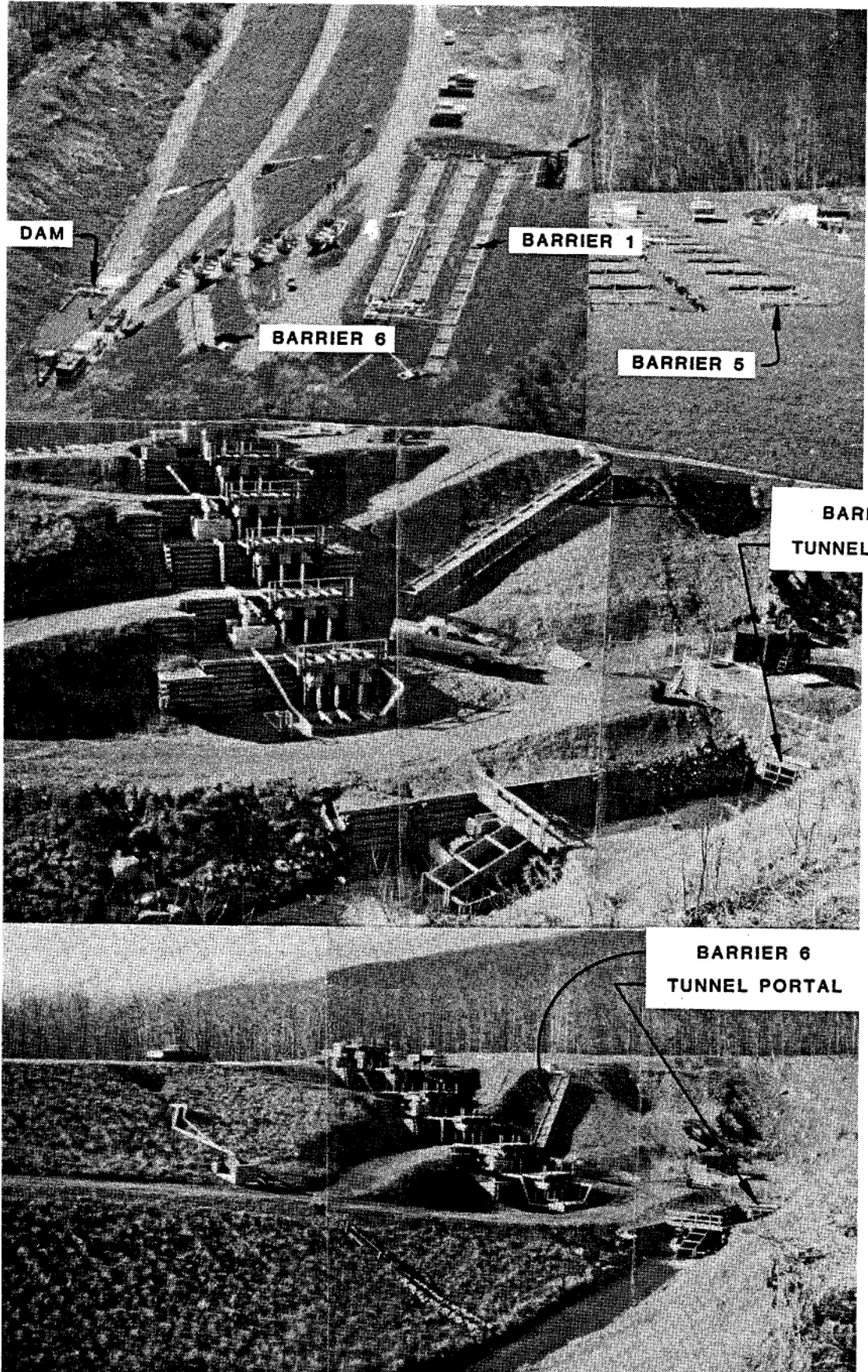
Reactivity Coefficient: The rate constant for the dissolution of limestone by AMD was determined experimentally for clean limestone in the laboratory. But, it has been observed that limestone placed in natural streams carrying AMD develops a surface coating of sediment, aquatic organisms and/or heavy metal oxyhydrates, depending on the chemical make up of the AMD. Comparisons between observed and predicted performances of four limestone barriers in the Trough Creek Watershed, Pennsylvania (17), indicate that both sediment/biological coatings, and the heavy metal oxyhydrate coatings reduced the reactivity of the limestone. At Trough Creek, the reactivity of the limestone was found to be 20 percent of the reactivity obtained for clean limestone under laboratory conditions. This factor of 20 percent has been termed the reactivity coefficient, and describes the effect of the thin film that forms on the stone surface which inhibits the neutralization process. It does not account for those surfaces of the limestone which are unsubmerged in AMD or blanketed by sediment, nor does the factor account for the deposit of metal oxyhydrates in the pores between the stones.

Load Factor: For design purposes, it is convenient to express the ratio of reactive limestone surfaces to AMD volume (a in Eq. 4.4) in terms of commonly used stone and flow measurements. Therefore a (in $\text{sec}^{-1}\text{m}^{-1}$) is converted to Load Factor (LF) in terms of tons of limestone per cfs of AMD per inch of stone size.

$$LF = \frac{Wr \text{ (TONS)}}{pSQD(\text{in})(\text{cfs})} \quad (4.18)$$

in which:

- W = mass of crushed limestone, tons;
- D = diameter of crushed limestone, inches;
- Q = AMD flow, $\text{ft}^3 \text{ sec}^{-1}$;
- S = stone shape factor
- r = limestone reactivity coefficient; and
- p = percentage magnesium carbonate in limestone (1.0 for limestone containing 1% MgCO_3 , or less)



OVERVIEWS OF THE QUAKAKE DEMONSTRATION PROJECT

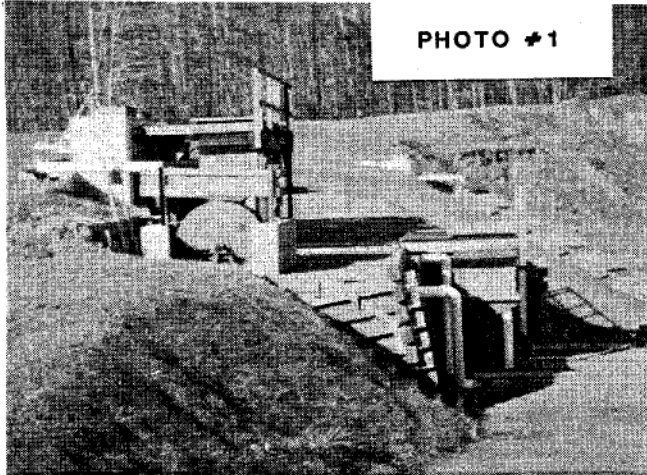


PHOTO #1

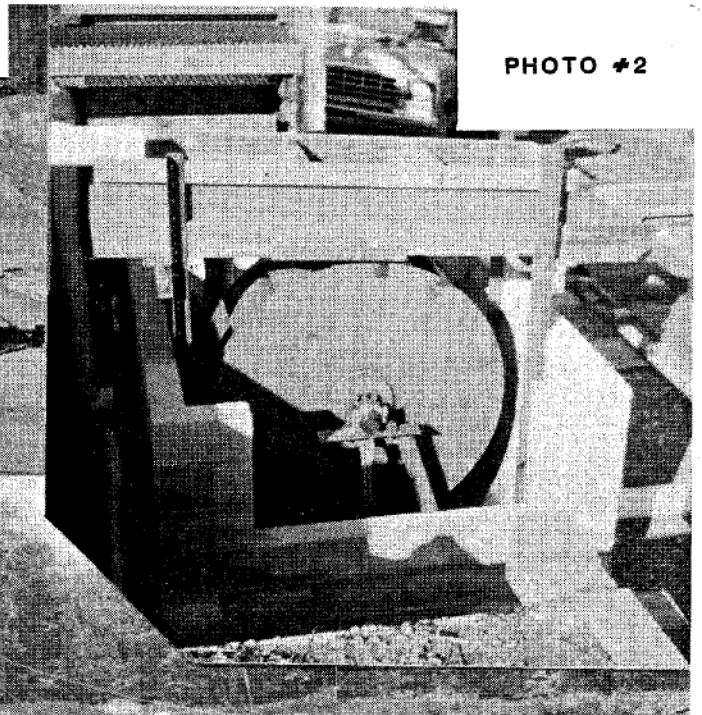


PHOTO #2

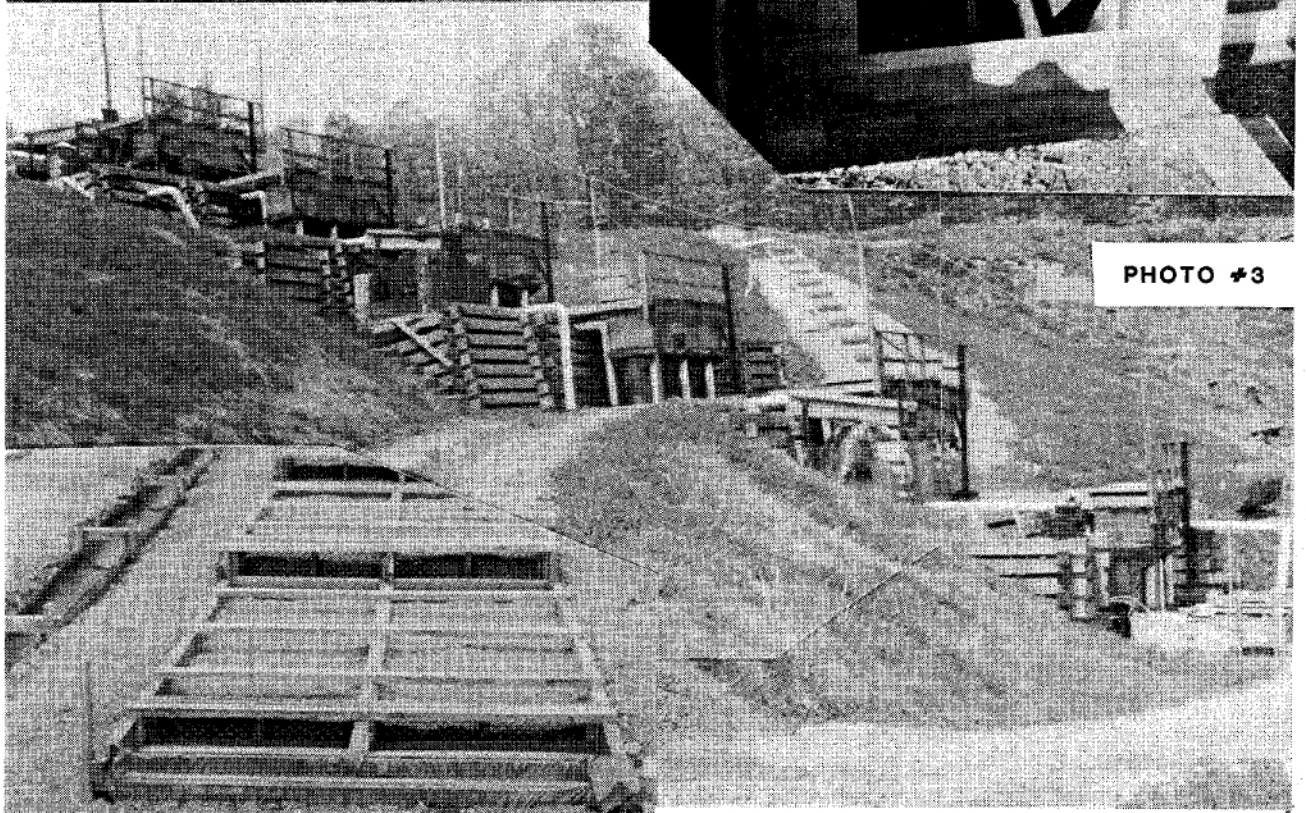


PHOTO #3

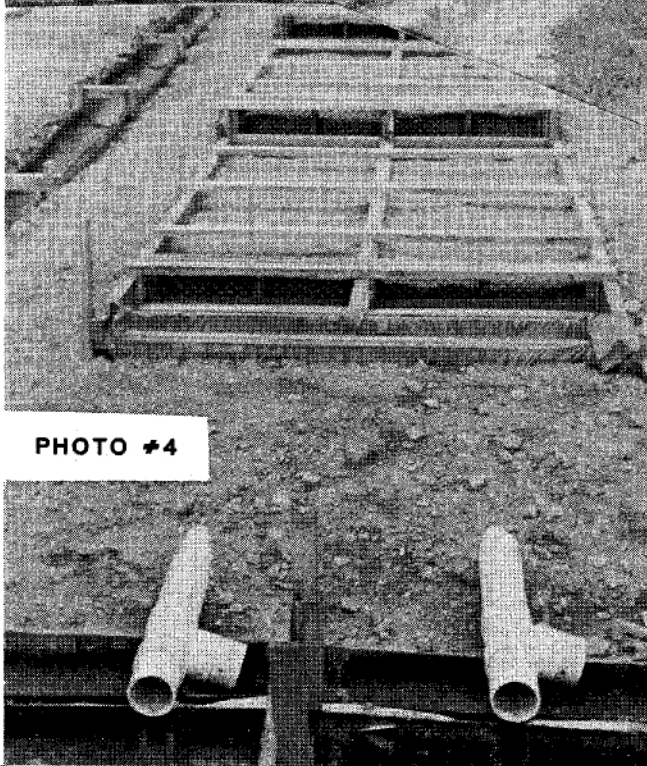


PHOTO #4



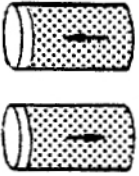
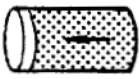
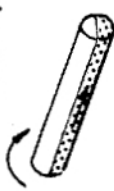

PHOTO #1 UPFLOW/DOWNFLOW UNITS 1 & 2
AND DRUM #2

PHOTO #2 DRUM #2

PHOTO #3 UPFLOW/DOWNFLOW UNITS
DRUMS 2,3 & 4

PHOTO #4 END OF BARRIERS 4 & 5

TABLE 5.1 PROTOTYPE PROCESS CHARACTERISTICS

PROCESS TYPE	SCHEMATIC CONFIGURATION	NO. OF UNITS AT QUAKAKE	STONE SIZE (mm)	DESIGN FLOW (RANGE, cfs)	NEUTRILIZATION PROCESS MECHANISM
STATIC BARRIER		6	5, 13, 20	1/2	LIMESTONE DISSOLVES IN AMD. EXCESS TREATMENT CAPACITY PROVIDED TO OFFSET SEDIMENT AND CHEMICAL COATING.
DOWNFLOW BED		6	5	1/4 TO 3/8	LIMESTONE DISSOLVES IN AMD. STONE CLEANED BY PERIODIC MANUAL BACKWASH.
ALTERNATING FLOW BED		6	5	1/4 TO 3/8	LIMESTONE DISSOLVES IN AMD. MINOR ABRASIONS OF FINES. STONE CLEANED BY FREQUENT AUTOMATIC BACKWASH.
UPFLOW FLUIDIZED BED		6	5	1/4 TO 3/8	LIMESTONE DISSOLVES IN AMD. FINES ABRADED BY FLUIDIZED OPERATION SELF CLEANING.
AUTOGENOUS MILL	 0.01 rpm	1	5	1/4 TO 1/2	LIMESTONE DISSOLVES IN AMD. BED CLEANED BY PERIODIC REVOLUTION OF DRUM.
TUMBLING DRUM	 6 rpm	5	20	1/2 TO 1	CONTINUOUS ABRASION OF LIMESTONE. AMD NEUTRILIZED BY FINES PRODUCED.

FILTER TYPE UNITS