ACID WASTE NEUTRALIZATION
USING LIMESTONE BEARING SAND

by
G.E. Ho¹ and B. Nguyen-Cong²

¹ Senior Lecturer in Environmental Engineering, Murdoch University, Murdoch, W.A. 6153
² Postgraduate student, School of Environmental & Life Sciences, Murdoch University, Murdoch, W.A. 6153

ABSTRACT

The disposal of acidic wastewaters has been a problem facing mining and processing industries. One way of neutralising the acid is by percolating it through limestone bearing sand, such as practised at Australind, W.A. The disposal of acid effluent from a process of converting ilmenite to titania pigment is effected in soakage lagoons located on calcareous sand dunes.

Laboratory sand column experiments have been conducted to obtain a better understanding of the processes involved in the neutralisation of sulphuric acid waste using beach sand. The flow of effluent through sand and the quality of the neutralised effluent are dependent on the deposition of calcium sulfate, the evolution of carbon dioxide gas, and the carbonate equilibrium.

A simple mathematical model has been developed to describe the neutralisation process. It can be used to aid in the management of disposal, or the design of engineered systems. It is based on one-dimensional saturated flow in a porous bed, and neutralisation kinetics using a shrinking-sphere approximation for the limestone grains.
1. INTRODUCTION

1.1 The present study has been motivated by the disposal of acidic wastewater from a titania plant in Bunbury, Western Australia. The plant converts ilmenite, a beach sand containing 55% of $\text{TiO}_2$ and 35% Fe, into titanium dioxide, a white pigment widely used in industry, by a sulphate process (Ref.1). In this process, sulphuric acid is used for digestion, and the resulting wastewater is strongly acidic with a high iron content. It is estimated that the plant discharges 4000 to 8000 cubic metres of wastewater per day, and its composition is (Refs. 2 and 3):

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>1</td>
</tr>
<tr>
<td>Fe</td>
<td>4.5 kg/m³</td>
</tr>
<tr>
<td>Acidity (as $\text{H}_2\text{SO}_4$)</td>
<td>17.1 kg/m³</td>
</tr>
<tr>
<td>Free</td>
<td>26.5 kg/m³</td>
</tr>
<tr>
<td>Total</td>
<td>26 kg/m³</td>
</tr>
<tr>
<td>$\text{SO}_4$</td>
<td>1.3 kg/m³</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.03</td>
</tr>
</tbody>
</table>

The daily discharge of acid is estimated at 95 tonnes/day as $\text{H}_2\text{SO}_4$.

1.2 The commonly used methods to date for the disposal of acid wastes are: barging wastes to sea, deep well disposal, neutralisation using lime followed by disposal on lagoons, and acid recovery (recycling), Ref. 4.

The method employed at Bunbury is unique, utilising naturally occurring limestone in sand dunes to neutralise the acid in situ. The effluent is discharged to unlined lagoons located in depressions in the dunes. Figure 1 shows the geography of the disposal area (Leschenault Peninsula).

1.3 Geology of disposal area

The neutralisation taking place as the waste percolates through the sand is governed by the properties of the geological formations below the disposal lagoons. Figure 2 shows a typical cross-section of the sand dune at Leschenault Peninsula (Refs. 2 and 3). The elevation of the dune reaches up to 45 m. Down to just below sea level, the dune consists of fine to medium grains of quartz and calcium carbonate (calcareous sand). Locally, cementation of the quartz grains by calcium carbonate exists. A strong manifestation of this phenomenon is the existence of beds of compact kankar (calcrete) at an elevation of about 2 m above sea level. Minor layers of soil (rondinas) are present in the sand dune due to buried old plant and vegetation surfaces in the dynamic formation of the dune system. The calcium carbonate content of the sand dune varies locally from 1% to 30%, with an average of around 15%.

The dune sand is underlain by a layer of estuarine mud, containing grey, black quartz mud and estuarine shell fragments. Its thickness varies from 0.1 m to 7 m from the ocean side towards the Leschenault Inlet.
The estuarine sand overlies a 7 to 9 m thick sandy limestone, which is essentially grey, lime-rich calcarenite. Its limestone content reaches 79%, but averages 35%. The platform of the dune system is mesozoic sediments of clay, clayey sand and quartz sand.

1.4 Neutralization of acid waste in dunes

As the acid waste percolates down the sand the sulphuric acid is neutralised by limestone in the dune, according to an overall reaction:

\[ \text{H}_2\text{SO}_4 + \text{CaCO}_3 \rightarrow \text{CaSO}_4 + \text{H}_2\text{O} + \text{CO}_2 \]

Assuming an average limestone content of 15% by weight, the amount of acid as \( \text{H}_2\text{SO}_4 \) that can be neutralised per cu.m. of sand is 0.25 tonnes. The area of a typical soakage lagoon (e.g. no. 7 at Leschenault) is about 12,000 m². Its depth to the undisturbed water table is about 12 m. The amount of sand available under the lagoon is 144,000 m³, capable of neutralising 36,000 tonnes of acid or over one year of waste production.

As the neutralized effluent is heavier than the water, that is originally contained in the aquifer, its movement is generally downward. As the formations below the water table are richer in limestone, more than one year of acid flow can be neutralised by the formations under a typical lagoon.

The downward flow of effluent is interrupted by the existence of relatively impermeable layers (rendzina soils, calcrete), causing horizontal movement along these layers until breaks are encountered to allow further downward movement.

One product of neutralisation is \( \text{CaSO}_4 \), which has a limited solubility (2.0 g/l at 30°C). Calculations show that with soil consisting of 100 percent limestone grains, an acid concentration of 0.015 mol/l (cf. effluent from titanium plant has 0.13 mol/l) produces the saturation concentration. If the acid concentration is above 0.015 mol/l, \( \text{CaSO}_4 \) particles are formed which may deposit and surface coat the limestone grains, preventing access of the limestone to the acid. In an actual situation, where the limestone grains are distributed amongst silica grains, and liquid movement takes place, the acid concentration causing particle coating and eventual flow blockage should be higher for two reasons: liquid motion distributes the \( \text{CaSO}_4 \) formed, and deposition of \( \text{CaSO}_4 \) particles occurs far downstream from the reaction zone.

In laboratory column experiments using an acid concentration of 0.13 mol/l, blockage of flow occurred at the top of the sand with a limestone content of 38%, whereas no blockage was observed with a limestone content of 8%. Particles of \( \text{CaSO}_4 \) were, however, observed in the effluent leaving the column. In the real world situation these particles will be deposited further down by a mechanism similar to sand-filtration, and eventual blockage may occur. A compensating factor is dilution of the waste by the original freshwater in the aquifer, and by rainwater re-dissolving some of the \( \text{CaSO}_4 \) particles. The degree of dilution is thought to be small, as mixing between the waste and the

1.5 Objective

The objective of our research is to simulate the neutralisation process, and to develop a model that can be used to assist in the management of current disposal, and also in the design of an engineered system using beds of limestone bearing sand.

The present paper is confined to the simulation and modelling of neutralisation in the dune sand above the water table. As mentioned in 1.4 above, this zone has a considerable capacity for acid neutralisation.

The pressure in this region is near atmospheric, because the pressure in the unsaturated sand surrounding the downward flow of
effluent is atmospheric. The downward flow of liquid has been assumed to be one-dimensional to maintain the simplicity of the working model.

2. KINETICS OF ACID NEUTRALISATION BY LIMESTONE

2.1 Works of the treatment of acidic wastewater by lime and limestone were reported back in the 1940's (Refs. 5 and 6). Most of these works dealt with the operational problems of the neutralisation reactor which had been designed on a trial-and-error basis with the emphasis on the maximum loading concentration of sulphuric acid to prevent the precipitation of gypsum which might coat the bed grains, and reduce the removal efficiency of the bed. Acidic wastewaters mentioned in most of the articles published so far are mainly from acid mine drainage, steel pickling liquors, and chemical plating industries. Most of the investigations were confined into mixing chamber design (Ref. 7), with the neutralizing agent (lime or limestone) added in excess without any kinetic consideration. Design was based on more or less empirical approach.

Mariani (Ref. 8), however, reported an attempt to treat wastewater from a titania plant, but most of his effort was concentrated on in-plant waste reduction and by-product recovery rather than treatment of the waste itself.

During the last four decades of the use of lime/limestone to neutralise acid waste, only the last 10 years have seen some attempt to improve design by taking neutralisation kinetics into account.

By considering the overall equation:

\[
CaCO_3(s) + 2H^+ = Ca^{2+} + H_2O + CO_2
\]  

(1)

Wentzler et al (Ref. 9) inferred from their experiment of nitric acid neutralized by rotating limestone discs that the dissolution of limestone in nitric acid solution was acid-transport-controlled.

They proposed a kinetic equation in the form:

\[
dw = kA(c - c_e) 
\]

(2)

where \(dw\) is the dissolution rate, \(k\) is the rate constant, \(A\) is the reacting surface, \(c\) is the bulk concentration, and \(c_e\) is the concentration at the interface of the disc and the acid solution.

A few years later, Pearson et al (Ref. 10) evaluated equation (2) further. By simulating the neutralisation of acid mine drainage streams by barriers of crushed limestones (5 to 10 cm in diameter), they found that a rate mechanism based on hydrogen ion diffusion together with carbonate surface reaction and CO2 exsolution successfully modelled the observed data. However, from their work, it can be seen that the amount of CaCO3 was always present in excess, i.e. CaCO3 was not a limiting factor for the reaction, and the surface available for reaction to take place was regarded as unchanged throughout the neutralisation course.

A more recent work by Barton et al (Ref. 11), combining equation (2) and a consideration for the shrinking of limestone grains due to acid attack, is considered to be more appropriate to the present case. Sulphuric acid was used in their experiments to test the shrinking spherical grain model. The dissolution rate of limestone was correlated with different assumptions on the reaction mechanisms, e.g. zero-order control, CO2− diffusion control, surface-reaction control, and first-order kinetics with respect to hydrogen ions, and they found that the first-order kinetics with respect to \(H^+\) proved to be the most appropriate.

Thus, they suggested that:

\[
dw = kA(c - c_e) 
\]

(3)

where \(c\) is concentration in the bulk phase, and \(c_e\) is the equilibrium concentration after the neutralisation is completed.

2.2 Change in concentration

Consider a bed element of limestone-bearing sand with porosity \(e\), cross-sectional area \(A\) in cm², and thickness \(L\) in cm. This element is regarded as a mixture of quartz sand and pure CaCO3 grains of the same size of radius \(r\) (cm). The volume fraction of CaCO3 portion in the bed is \(f\), which is the ratio of total volume of CaCO3 grains over the volume of the bed element. The number of CaCO3 grains available in one bed element is thus:

\[
N = 5.14E/(4\pi r^3) 
\]

(4)

In the shrinking-sphere model, the number of carbonate grains is seen as a constant, thus \(N\) is also,

\[
N = 5.14E0/(4\pi r_0^3) 
\]

(5)

where \(r_0\) and \(r\) are the initial volume fraction and initial size of carbonate grain, respectively.

The total surface of carbonate grains at time \(t\) is:

\[
A = 4\pi r^2 - 360 \frac{f_0}{f} Saz r^2 
\]

(6)

Substituting the value of \(A\) into (3):

\[
dw = 3k \frac{fo}{f_0} Saz r^2 (c - c_e) 
\]

(7)

Stechiometric consideration from (1) gives:

\[
dw = \frac{1}{2} \frac{dh}{dt} 
\]

(8)

where \(dh/dt\) is the rate of total \(H^+\) reacted in one bed element.

Thus:

\[
dw = kA(c - c_e) 
\]

(9)
On the other hand, dH is the rate of change in concentration times the amount of liquid available in the bed element:

\[
\frac{dc}{dt} = 6000k \frac{c_e}{r_0^3} \frac{1}{e} r^2 (c - c_e) \]  (10)

In equation (10), where \( e \) = bed porosity

\frac{dc}{dt} \text{ is in [mole/L.min], } k \text{ in [Mcm}^2 \text{.min], } r, r_0 \text{ in [cm] and } c, c_e \text{ in [mole/L].}

In finite-difference form, (10) can be rewritten as the change of concentration over time \( \Delta t \) due to reaction:

\[
\Delta C(\text{reaction}) = 6000k \frac{c_e}{r_0^3} \frac{1}{e} r^2 (c - c_e) \Delta t \]  (11)

### 2.3 Change in Grain Size

The amount of \( \text{CaCO}_3 \) dissolved from time \( t \) to \( t + \Delta t \):

\[
\Delta w_1 = \frac{dW}{dt} \Delta t \]  (12)

During that time, \( \text{CaCO}_3 \) grains are reduced in size from \( r \) to \( r_N \), thus the amount of \( \text{CaCO}_3 \) lost due to shrinking:

\[
\Delta w_2 = \frac{(r^3 - r_N^3)}{2} \frac{P}{M} r \Delta t \]  (13)

where \( P \) and \( M \) are the density and molecular weight of \( \text{CaCO}_3 \), respectively.

Mass balance gives:

\[
\Delta w_1 = \Delta w_2 \]

Thus:

\[
r_N^3 = r^3 - \frac{3kM}{P} (c - c_e)r^2 \Delta t \]  (14)

#### 2.4 Limit on AC (reaction) due to the availability of \( \text{CaCO}_3 \)

The above considerations are for the assumption of excess \( \text{CaCO}_3 \) in the system. Suppose that near the end of neutralisation in a particular bed element, during time \( \Delta t \), \( r \) may be reduced to nil, i.e. \( r_N = 0 \), thus the amount of \( \text{CaCO}_3 \) dissolved in that time will be:

\[
\Delta w = \frac{r^3}{2} \frac{P}{M} r \Delta t \]  (15)

And the corresponding change in concentration will be:

\[
\Delta C = 2000 \frac{1}{6} \frac{P}{M} \frac{1}{e} r^2 \]  (16)

(15) and (16) are applicable when:

\[
r^3 < \frac{3kM}{P} (c - c_e) \]  (17)

### 3. MODEL DEVELOPMENT

#### 3.1 Miscible Displacement and Chemical Reaction in Continuous Once-Through Flow System

Consider an acidic liquid flow which contains hydrogen ion as active chemical reactant through a bed of carbonate grains mixed with silica sand. Within a given elementary bed volume, the change in hydrogen ion concentration is due to the hydrodynamic dispersion of the reactant within the flow by itself, and due to the reaction between hydrogen ions and carbonate grains. The change in hydrogen ion concentration due to flow can be described by (Ref. 12).

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} \]  (18)

where \( D \) is the hydrodynamic dispersion coefficient of \( H^+ \) due to flow and \( v \) is the liquid interstitial velocity.

Within the bed element, reaction takes place with a rate of \( \text{R} \) given by equation (10).

Taking reaction into account:

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - \frac{6000k}{r_0^3} \frac{1}{e} r^2 (c - c_e) \]  (19)

#### 3.2 Working Model

Substituting equation (10) into equation (19) gives

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - v \frac{\partial C}{\partial z} - 6000k \frac{c_e}{r_0^3} \frac{1}{e} r^2 (c - c_e) \]  (20)

Equation (14) can also be written in the differential form:

\[
\frac{\partial C}{\partial t} = \frac{kM}{P} (c - c_e) \]  (21)

Equations (20) and (21) are to be solved simultaneously with appropriate initial and boundary conditions, to predict the movement and concentration of the acid effluent and the change of bed composition at any particular time and depth. These equations then mathematically describe the model. A numerical method is required to solve these equations.

#### 3.3 Finite Difference Scheme in Sand Columns of Finite Length

Since bed columns of finite length were used in the experimental work, appropriate initial and boundary conditions for this type of column as suggested by Lai (Ref. 13) and Brenner (Ref. 14) are used in conjunction with equations (22) and (23) for the modeling works. Denoting \( c(z, t) \) and \( r(z, t) \) as functions of depth \( z \) and time \( t \), the initial condition is:

\[
c(z, 0) = c_e \text{ for } 0 < z < L \]  (22)

where \( L \) is the sand column length.
The upper-boundary condition is:
\[ c(o, t) = c_0 \text{ for all } t > o \]

And the lower-boundary condition is:
\[ \frac{dc}{dz} = 0 \text{ at } z = L \text{ for all } t > o \]

It follows from equation (24) that the exit concentration \( c_L \) is given by \( c_L = c(L, t) \).

As described earlier the change of concentration is due to dispersion and reaction. This fact is exploited in the numerical computation method:
\[ \frac{dc}{dt} = \frac{dc}{dt} \text{ (dispersion)} - \frac{dc}{dt} \text{ (reaction)} \]  

Or in finite-difference term:
\[ \Delta c = c(j, i + 1) - c(j, i) - \Delta c\text{(dispersion)} - \Delta c\text{(reaction)} \]  

The explicit centre-in-difference scheme applied for the change of concentration due to dispersion gives:
\[ \Delta c\text{(dispersion)} = \frac{6000k_0}{r_0^2} \frac{1}{N} \Delta t [r(j,i)]^2 (c(j,i) - c_e) \]  

\[ \Delta t < \frac{D}{6000k_0 c_e} \]  

On the other hand, the change in concentration due to reaction is calculated as:
\[ \Delta c\text{(reaction)} = 6000k_0 \frac{r_0}{N} \frac{1}{z} \Delta t [r(j,i)]^2 (c(j,i) - c_e) \]  

\[ \Delta t < \frac{k_0 N}{3k} \frac{1}{r_0^2} \Delta t [r(j,i)]^2 \]  

This is applicable only when:
\[ [r(j,i)]^3 < \frac{3k}{r_0^2} \frac{1}{z} \Delta t [r(j,i)]^2 \]  

otherwise:
\[ \Delta c\text{(reaction)} = 2000k_0 \frac{r_0}{N} \frac{1}{z} \Delta t \frac{1}{r_0^2} \frac{1}{c_e} \]  

\[ \Delta t = -r^3 \]  

Both (29) and (31) are found stable when:
\[ 6000, k \frac{1}{r_0} \frac{1}{z} \Delta t \leq 0.1 \]  

A Fortran program has been written for implementing the numerical computation.

4. EXPERIMENTAL

4.1 Preliminary column experiments using dune sand from the southern part of Leschenault peninsula, containing 7.5% calcium carbonate, and a synthetic waste containing 0.1 M H2SO4, resulted in only about 65% of calcium carbonate in the column having been utilized when acid broke through. The addition of FeS04 to the synthetic waste reduced the calcium carbonate utilization to 35%.

To enable the model proposed in this paper to be tested it was decided to use a rather more dilute acid concentration so that CaSO4 coating would not be a significant factor in reducing the total availability of CaCO3. It is planned to take into account the effect of coating as a parameter dependent on the acid concentration, above a certain critical concentration when coating begins to contribute to the decrease in the total availability of CaCO3.

Sieved dune sand was used to produce a narrow size distribution, so that the dispersion coefficient could be predicted using existing correlations. The effect of carbon dioxide gas evolution on liquid flowrate was determined experimentally.

4.2 Sand selected for the experiment was a mixture of 2 sizes: 0.250 and 0.355 mm in sieve size with an overall carbonate content of 11.6% by weight.

900 g of this mixture was then poured into a 4.4 cm ID perspex tube, 50 cm long. As shown in Fig. 3, the underdrain...
system consisted of one piece of coarse filter cloth on top of two layers of glass beads of graded sizes. A flow meter and a pH electrode were incorporated in the drainage pipe and the electrode was connected to a Philips PM-9414 pH-meter and a Rikadenki chart recorder. The column was flooded firstly with deionized water till full saturation and a constant flow was obtained. The feed pipe was then switched to the acid feed line. Acid solution of 0.03 M H$_2$SO$_4$ was prepared in a feed tank and pumped to the column, a piece of glasswool was also inserted on top of the sand bed to reduce any possible disturbance on the top sand layer.

5. RESULTS AND DISCUSSION

5.1 A plot of the pH of effluent leaving the column versus cumulative flow through the column is shown in Fig. 4. Note that the plot is slightly different from ordinary break-through curves, where concentration is plotted versus cumulative flow. Although the pH of deionized water used in the experiment was always around 7, the pH of water after having passed through the column was high, usually more than 9. This was due to the buffer effect of dissolved bicarbonate and carbonate species leached from the sand into the outflow, which gave higher pH values (Ref. 16). However, as soon as acid solution was fed into the system, effluent pH dropped down very rapidly and remained constant in the range of 5.8 to 5.5 until breakthrough occurred. This is regarded as the range of the equilibrium value of the neutralisation process of the system as is governed by the bicarbonate equilibrium.

5.2 Although performed under identical conditions, a variation in the breakthrough curves was observed, as shown in Fig. 4. This was partly due to possible differences in grain sizes and compositions of the sand between experimental runs, but to a larger extent due to flow variation through the column. During the six runs, the initial flow rate of deionized water was constant at a pore velocity of 12 cm/min (74 cc/min), but as soon as acid was introduced to the column, the flow dropped and varied in the range of 4 to 8 cm/min. The recorded variation in flow pattern was not quite the same for all the runs. This variation was due to the production and release of carbon dioxide gas bubbles and thus increased the bed resistance toward the incoming flow.

The final effluent pH was recorded in the range of 1.5 to 1.8. This is higher than the value of 1.22 expected from a pure 0.03 M H$_2$SO$_4$ solution; this again is due to the buffer effect of dissolved carbon dioxide-carbonic acid system in an acidic medium (Ref. 16).

5.3 A stoichiometric calculation based on equation (1), shows that 900 g of limestone-bearing sand requires 34.8 litres of 0.03 M H$_2$SO$_4$ solution for complete neutralisation. The amounts of acid used to achieve complete neutralisation, as shown in Fig. 5, were slightly higher than the calculated value, leading to a conclusion that complete neutralisation was achieved in all runs.

5.4 In order to test the validity of the infiltration-neutralisation model developed in section 3, values of all model parameters need to be evaluated. Recorded cumulative flows in all runs were averaged over the operating time, and an average pore velocity (v) was derived as 6.99 cm/min. The bed column length (L) was 38 cm.
6. CONCLUSIONS

6.1 The percolation and neutralisation of acidic wastewater in a limestone-bearing sand body can be described by a model containing the infiltration process of liquid in a porous media, the hydrodynamic dispersion of hydrogen ions within the flowing liquid, and the effect of reaction between the hydrogen ions and the feed concentration \( c_0 \) as 0.06 moles H\(^+\)/l, the equilibrium concentration \( c_e \) was taken as 0.18 x 10\(^{-3}\) moles H\(^+\)/l, corresponding to a pH value of 5.74, volume fraction of CaCO\(_3\) \( f_c \) was calculated as 0.07 and the hydrodynamic coefficient as 3 cm\(^3\)/min. The latter was calculated from the empirical correlation in Bear (17). The reaction rate constant was derived from an equation based on the operating temperature as suggested by Barton (Ref. 18) and this was calculated as 1.3 x 10\(^{-3}\) litres/cm\(^2\)/min.

5.5 The computer program was first tested with the case of dispersion only (no chemical reaction) and the results were found to match quite favourably with the numerical results found by Brenner (Ref. 14) with the same value of dispersion coefficient, as shown in Fig. 5. The final program of dispersion and neutralisation was then run to produce computed results to be compared with experimental data as shown in Fig. 6.

5.6 In order to test the sensitivity of the mathematical model, the computer program was run with different values of \( D \) and \( k \); some of the output results are presented in Fig. 7. It can be seen that all the outputs converge at 170 pore volumes for complete neutralisation of 900 g of dune sand used in the experiment but with different shapes in their breakthrough curves. Higher values in either \( D \) or \( k \) lead the curves closer to the piston-flow configuration. For the same value of \( k \), e.g. 13 x 10\(^{-3}\) l/cm\(^3\)/min, different values of \( D \) do not give any difference in the number of pore volumes of acid solution prior to the effluent quality deteriorating. On the other hand, different \( k \) values with the same \( D \) give distinctly different curves in shape as well as in the starting point of deterioration. This leads to the suggestion that the model is more sensitive toward \( k \) values than \( D \). This can be explained, as with dispersion only, the breakthrough process occurs only within less than 2 pore volumes, as shown in Fig. 5, while incorporating chemical reaction, it takes about 20 pore volumes or more to complete the breakthrough process.

5.7 Although the model gives a higher value of required amount of acid solution for neutralisation, the predicted breakthrough curve starts nearly at the same time as experimental curve, which is at about 100 pore volumes. This is important for design purposes, since the operation of a treatment system must be stopped before the treated effluent deteriorates, so that constant effluent quality can be maintained.

The predicted breakthrough curve is more gently inclined than the experimental curve since it is based on a model which does not include the effect of variations in flow rate. The latter may retard and then accelerate the change in effluent pH values at a critical stage, just before the last volume of sand is neutralised.

The percolation and neutralisation of acidic wastewater in a limestone-bearing sand body can be described by a model containing the infiltration process of liquid in a porous media, the hydrodynamic dispersion of hydrogen ions within the flowing liquid, and the effect of reaction between the hydrogen ions and the
Neutralisation process by carbonate grains can be described by a model of hydrogen-ion diffusion coupled with the decrease in reaction surface with time based on the assumption of uniformly shrinking spheres.

Separated finite-difference scheme with centre-in-difference explicit approach can be used to solve numerically the model's system of equations. With the initial and boundary conditions imposed on sand columns of finite length, the scheme is found to be stable when:

\[ \Delta t < \frac{D}{e} \]
\[ \Delta t < \left( \frac{\Delta x}{2D} \right)^2 \]
and

\[ 6000 \frac{k_{10}}{e} \frac{1}{c} \Delta t \leq \frac{1}{10} \]

6.4 For a sand mixture of sizes 0.250 and 0.355 mm with an average carbonate content of 11.6%, the model predicted successfully the termination of the discharge of acid solution of strength 0.03 M before the treated effluent quality deteriorated.

6.5 An improvement of the existing model to include the effects of carbon dioxide generation on infiltration flow rate, of other chemical components such as ferrous ions on reaction rate, and of the precipitation of calcium sulphate, needs to be carried out to obtain a more thorough understanding of the disposal of acid waste as occurring at Australind.

7. ACKNOWLEDGEMENT

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8. REFERENCES

1. LAPORTE AUSTRALIA LTD., "Titanium Oxide", Company's Leaflet, Bunbury, Western Australia.
9. NOTATION

A  surface area of limestone grains
C  concentration of acid in solution
C~  at interface of solid and liquid
C~0  at end of neutralisation
D  hydrodynamic dispersion coefficient
f  volume fraction of limestone in bed
f0  initial fraction
k  reaction rate constant
L  length of sand bed column
M  molecular weight of limestone
N  number of limestone grains per bed volume
r  radius of limestone grains
r0  initial radius
R  rate of reaction per unit volume of solution
S  cross sectional area of sand bed
t  time
V  liquid pore velocity
w  mass of calcium carbonate
z  distance down sand bed
c  porosity of sand bed
p  density of limestone

ABSTRACT

This paper describes investigations into the water quality of Pumicestone Passage which are currently in progress as part of an overall study of future urban development adjacent to the Passage. An outline of the investigation rationale, the planning and execution of associated field programs, and the results of the investigation to date are presented.

The available results confirm that existing water quality in the Passage and tributaries is generally good, with some local degradation in the tributaries reflecting catchment land use and the effects of limited tidal exchange.

A water quality model being developed will be used to predict the likely effects of a number of development modes.