

Modelling of Coal Ash Leaching

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ABSTRACT: The safe disposal of coal ash produced from power stations involves the assessment of rates of production and quality of ash leachate. Laboratory column experiments have been used to obtain data on the ash leachate. The extrapolation of this data to the field conditions requires theoretical modelling of the underlying chemical leaching and transport mechanisms. In the current paper, a model was developed to simulate the leaching of ash which exists in saturated or near-saturated conditions. The model was applied to simulate the experimental results, and good agreement was obtained between the experimental and model results.

1 INTRODUCTION

In the Latrobe Valley region of Victoria Australia, large quantities of brown coal ash are produced annually in the power station complexes which supply the majority of the electricity requirement for Victoria. One of the principal environmental concerns associated with the management of these facilities is the hydrogeological impact of the disposal of coal ash. Currently, all coal ash produced by the power stations is slurried to on-site disposal ponds. Since the capacity of the ash ponds is limited, options for the future management of the ash ponds are considered, and the feasibility of depositing of aged ash in a nearby overburden dump is investigated. In the environmental impact assessments of the ash disposal strategies, assessment of the leaching of some chemicals from the ash is essential. The current paper relates to chemical leaching of coal ash which exists under saturated or near-saturated conditions as would be found in disposal ponds.

There has been considerable research undertaken on Latrobe Valley brown coal ash, and the early research was predominantly concentrated on solving problems in transport pipes such as scaling, or on predicting ash quality based on coal quality. Deed (1981) reported early research on ash leaching on the basis of field experiments, but the interpretation of results was difficult owing to poor experimental design and lack of detailed chemical analyses of ash and leachate. Subsequently, Black (1990a, 1990b) undertook a study comprising a series of column and sequential batch leaching tests under controlled laboratory conditions. This study was targeted to investigate the chemical leachate quality simulating more closely those expected in the ash ponds.

Laboratory experiments using small columns have generated data on leachate quality and production rates in small columns. A basis to extrapolate this data to the field conditions is then required. For example, one may want to assess the quality and production rates of leachate at the base of an ash pond on the basis of experimental findings. For this purpose, Black (1990a) has used the linear transformation of the leaching rates relative to the height of the leaching mass. This approach is elementary and ignores the influence of all the dominant variables involved. In the current paper, a theoretical model for the coal ash leaching is developed, and a numerical scheme to solve the governing equations under given boundary conditions is presented. Numerical simulations were carried out to compare the model and experimental results.

2 THEORETICAL MODEL FOR ASH LEACHING

2.1 *Leaching mechanisms.*

Various mechanisms have been identified, by which chemicals can leach out from solid material. These include bulk diffusion, advection, chemical reactions, and surface transfer phenomena such as matrix dissolution (Côté, 1986a; Côté *et al.*, 1986b). Leaching of chemicals by the way of bulk diffusion and advection are more important for solid wastes such as cement based solidified wastes. Nevertheless, for particulate wastes such as coal ash, these mechanisms will play a significant role in the migration of solutes through the porous medium, once they are leached out from the solids. Chemical reactions and surface phenomena are more important for coal ash, and are described on the basis of kinetic formulations for a particular

species of interest or using mass transfer coefficients. For coal ash, initial wash-off of chemicals is also considered to be a significant mechanism in exchange of chemicals from surface and aqueous solutions.

Recent advances in chemical analysis and speciation techniques have led to the use of geochemical equilibrium models combined with detailed ash speciation and mineral analysis to predict the chemistry of ash leachates (e.g. Eighmy *et al.*, 1995). However, these were for batch tests only and required intensive analysis of the ashes to obtain detailed quantitative mineral data for input into the geochemical model. While this approach is considered in a limited sense in the overall research project, a more simplified approach is adopted to model the ash leaching as would be applicable to ongoing management of ash disposal.

2.2 Theoretical Leaching Model

The model developed for coal ash leaching is based on the work of Straub & Lynch (1982) and subsequently used by others (e.g. Lu, 1996; Demetracopoulos *et al.*, 1984) on landfill leaching. It postulates that the leaching rate for a certain chemical is proportional to the ratio of current soluble mass S (per unit volume) to the initial soluble mass S_0 (per unit volume) in the ash particles as well to a concentration deficit from a maximum value (C_{max}) to the current concentration (C) in the aqueous solution. This can be expressed mathematically as:

$$L_R = \alpha \left(\frac{S}{S_0} \right)^\beta (C_{max} - C) \quad (1)$$

where α is a mass transfer coefficient applicable to a particular chemical species and β is an exponent signifying the effect of decaying chemical mass. C_{max} represents the maximum concentration of a chemical species, for example the concentration at saturation in aqueous solution. At a particular instant, the concentration deficit ($C_{max} - C$) provides the driving force for leaching by surface phenomena. When this deficit is zero, it can be assumed that the system is in equilibrium. The model is considered to entail matrix dissolution of chemicals from the surface to the aqueous phase under reducing chemical mass. The initial wash-off is modelled by defining the initial concentration (C_0) in the aqueous solution. It is interesting to note

that if β is assumed to be unity and $C_{max} - C \approx C_{max}$, the leaching rate given by Equation (1) signifies a situation where the soluble mass decays exponentially with time.

Based on the principle of conservation of mass, the migration of solutes through saturated ash incorporating leaching can be expressed by the advection-dispersion equation (ADE) as:

$$\frac{\partial C}{\partial t} = D_z \frac{\partial^2 C}{\partial z^2} - v_z \frac{\partial C}{\partial z} + L_R \quad (2)$$

where D_z is the longitudinal dispersion/diffusion coefficient, v_z is the linearised advective velocity, and z is the depth measured from top of the ash surface. This equation assumes one-dimensional uniform flow in a non-deforming saturated medium.

The boundary and initial conditions for the problem are expressed as:

$$\begin{aligned} z = 0 & \quad C(0, t) = g(t) \\ z = H & \quad \frac{\partial C}{\partial z} = 0 \quad \text{and,} \\ t = 0 & \quad C(z, 0) = C_0 \end{aligned} \quad (3)$$

where $g(t)$ is the concentration of the influent water, H is the height of the column or the ash deposit, and C_0 is the initial concentration of the of the pore fluid in the ash depicting initial wash-off of the chemicals.

3.0 NUMERICAL SOLUTION

3.1 Finite difference approximation

The equations, subject the boundary and initial conditions given in Section 2, are solved using a block-centred explicit, upwind finite difference scheme (Peaceman, 1977; Zheng & Bennett, 1995) subject to the following stability criteria

$$\Delta t \leq \frac{\Delta z^2}{2D_z + v\Delta z} \quad (4)$$

The change in soluble mass incorporating the leaching rate can be expressed in difference form as:

$$S_{k+1} = S_k - (L_R)_k \Delta t n \quad (5)$$

where k is the time step and n is the porosity.

3.2 Control of numerical dispersion

One of the main difficulties with solving the ADE lies in the fact that the equation has both a parabolic component (dispersion) and a hyperbolic (advection) component to the partial differential equation (PDE). Solution techniques such as finite difference (and other methods), work well for one form of PDE, but not for both combined (Press *et al.*, 1992). Approximating the ADE using finite difference equations gives rise to a phenomenon known as numerical dispersion, which leads to artificial smearing of the advective solute front. Detailed accounts of the source and control of numerical dispersion are given in Zheng & Bennett (1995), Noorishad *et al.* (1992) and Peaceman (1977).

There are two dimensionless parameters which can be used to help minimise the effects of numerical dispersion. They are the Courant number, Cr , (controlling advective flow) and the Peclet number, Pe , (controlling hydrodynamic dispersion). By maintaining low Courant and Peclet numbers, that is, a high spatial and temporal discretization, it is possible to reduce the effects of numerical dispersion. For the one-dimensional case of explicit upwind scheme, the numerical dispersion can be calculated by the following relation (Peaceman, 1977; Zheng & Bennett, 1995).

$$D_{num} = \frac{1}{2} v_z \Delta z (1 - Cr) \quad (6)$$

For advective flow only, where hydrodynamic dispersion (D_z) can be taken as zero, the ADE equation represents predominantly a plug flow with a sharp concentration front, except for the smearing due to numerical dispersion. Nevertheless, if the values of Δz and Δt are chosen so that $Cr = 1$, $D_{num} = 0$ and a step concentration can be modelled exactly without numerical dispersion.

4.0 EXPERIMENTAL RESULTS

As noted previously, Black (1990b) has conducted a series of column leaching tests on a range of ash samples including Hazelwood precipitator ash (HPA) and Hazelwood ash pond sediment (HAPS). He used a 50 mm diameter by 300 mm long perspex columns packed with dry ash for leaching tests. Glass wool was used at the influent and effluent end to introduce uniform flow conditions. Pure water was fed to the top of the columns with a pump at a

constant rate of 0.015 mL/minute, and leachate was collected from the bottom at various intervals and subjected to various chemical analyses. The salient data applicable to column tests are summarised in Table 1. Because of the relatively high flow rate used, it is reasonable to expect that the ash was reasonably well saturated when the leachate was collected. The results of the above tests were used to compare the numerical model against experimental results in the following section.

Table 1. Salient data for column tests by Black (1990b)

Ash Type	Ash Height (mm)	Pore Volume (ml)	Total Volume (ml)	Porosity
HPA	161.3	217.3	316.6	0.69
HAPS	192.5	268.3	377.9	0.71

5.0 NUMERICAL SIMULATIONS

5.1 Parameters and sensitivity analyses

The main parameters needed for the numerical model are the linearised advective velocity (v_z), maximum (saturation) concentration (C_{max}), mass transfer coefficient (α), initial concentration (C_0), hydrodynamic dispersion (D_z) and the initial soluble mass (S_0). Both the linearised velocity and initial mass are derived from the results of Black (1990b). The value for hydrodynamic dispersion was approximated from the general range of values given in Fetter (1993), and was calculated as

$$D_z = \lambda v_z + D^* \quad (7)$$

where λ is longitudinal dispersivity, and D^* is the effective molecular diffusion coefficient. Based on Fetter (1992), λ is taken as $H/10$. However, since the flow system in the columns were dominated by advection, the value of λ was decreased to $H/20$.

Assuming a coefficient of molecular diffusion of D^* of $4.32 \times 10^{-5} \text{ m}^2/\text{day}$, Equation (7) gave D_z of 1.72×10^{-4} and $1.97 \times 10^{-4} \text{ m}^2/\text{day}$ for HPA and HPAS respectively. Numerical simulations indicated that the value of λ chosen in this range does not significantly influence leachate concentration curves. Furthermore, it is not possible to use experimental data to examine the influence of this parameter in detail because only a few data points on the initial leaching phase are available.

The maximum concentration C_{max} was assumed to be the first available leachate concentration from the experiments. Since it is assumed that ash became significantly saturated prior to leaching, the initial concentration C_0 was approximated to be equal to C_{max} . The mass transfer coefficient α was determined by fitting the numerical results to the experimental data. The value of α principally controls the residual concentration values after the initial wash-off, and has a relatively low influence on the initial drop in concentration. The effect of β was also examined, and it was found that β does not have a significant impact primarily because the leaching is dominated by initial wash-off. Hence, the value of unity was adopted for β . In these numerical simulations, the goodness of fit was determined by the eye.

5.2 Comparison with experimental results

Comparisons of simulated and experimental results for SO_4 , Cl, Na and K are shown in Figures 1 and 2 for Hazelwood precipitator ash (HPA) and Hazelwood ash pond sediment (HAPS) respectively. These chemical species were chosen to cover a range of chemical leaching characteristics. Parameters used for these simulations are shown in Table 2. Owing to the high initial concentrations present in the ash, it is difficult to see clearly the residual leaching profiles. Therefore, the model and experimental residual concentrations at about 90 days of leaching are separately compared in Table 3.

5.3 Discussion of results

Good agreement was obtained between the experimental and model results. It can be seen that all the chemical species considered leach out primarily by initial wash-off and subsequent advection dominated flow. The species SO_4 and Na have some residual leaching fuelled by high initial soluble masses. The species Cl and K have not shown significant residual concentrations partly because of relatively small initial soluble masses in the ash. In general, HAPS ash contained lower initial soluble masses because of the slurring process removing some of the chemicals. Impact of this is evident for Cl leaching given in Figure 2(b) where it leaches out at a slower rate than for fresh ash shown in Figure 1(b). This effect is also evident where the significant difference in α values was obtained for Cl for the two types of ashes.

Table 2. Parameters used for numerical simulations

Species	$\alpha \times 10^3$ (day ⁻¹)	C_{max} (mg/L)	S_0 (mg/L)
HPA - SO_4	1.8	94,315	125,063
Cl	0.005	28,636	3,790
Na	1.0	76,570	49,273
K	1.4	74,94	4,737
HAPS - SO_4	2.1	31,690	86,679
Cl ¹	0.08	740	1,032
Na	0.8	27,440	17,464
K	1.0	2,709	2,382

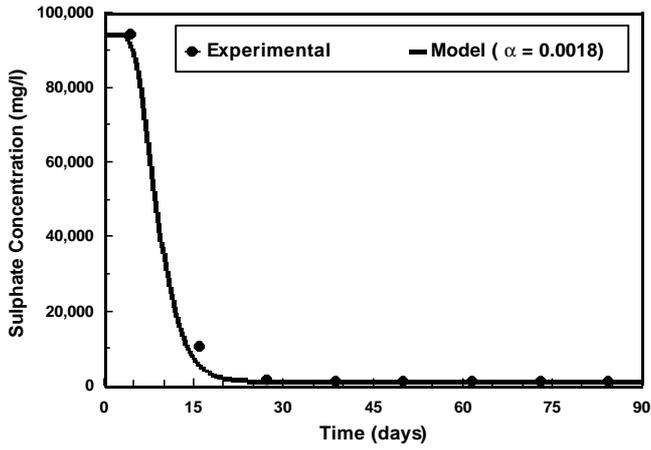
¹ The original value was below the detection limit (<0.1%), hence a minimum value of 0.13% was assumed to avoid a negative soluble mass in the computations.

Table 3. Residual leachate concentrations (90 days)

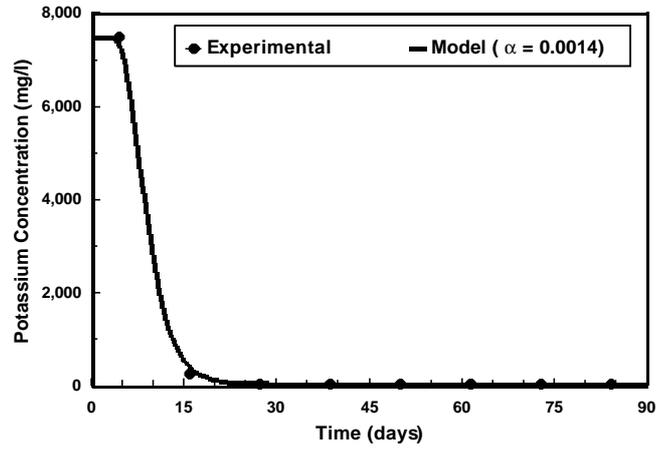
Species	Residual concentrations (mg/L)			
	HPA		HAPS	
	model	experiment	model	experiment
SO_4	1,100	1,034	650	645
Cl	<1	<1	<1	<1
Na	330	358	13.8	160
K	44	40	17	31

6.0 CONCLUDING REMARKS

The theoretical model developed appears to capture reasonably well the major mechanisms of leaching of coal ash which exist in saturated or near-saturated conditions. It appears that the leaching under these conditions are dominated by initial wash-off and advective flow. While this form of model represents the field condition in ash ponds, other factors such as lateral flows, ash burial process, densification of ash due to overburden stresses and perhaps, the subsequent reductions in permeability should still be considered. In addition, the modelling of field conditions such as aged ash deposits in dry land would require the consideration of unsaturated flow and non-regular infiltration. Hence, the model will need to be extended to cover unsaturated flow in order to apply for these situations.

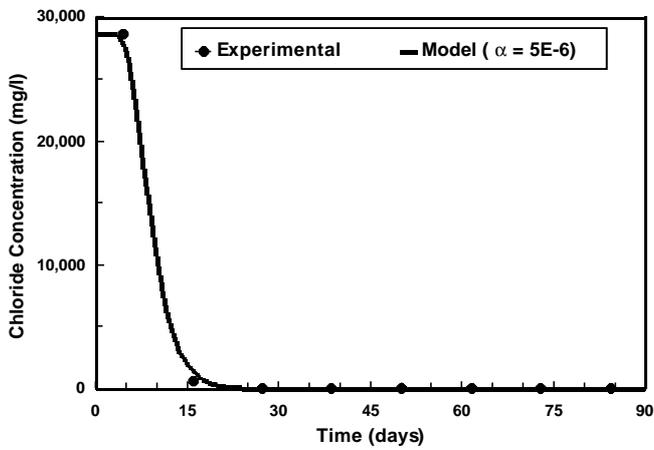


(a) Leaching of SO₄

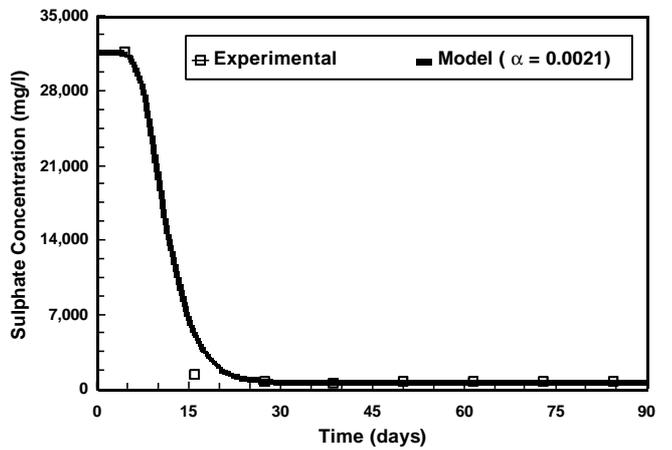


(d) Leaching of K

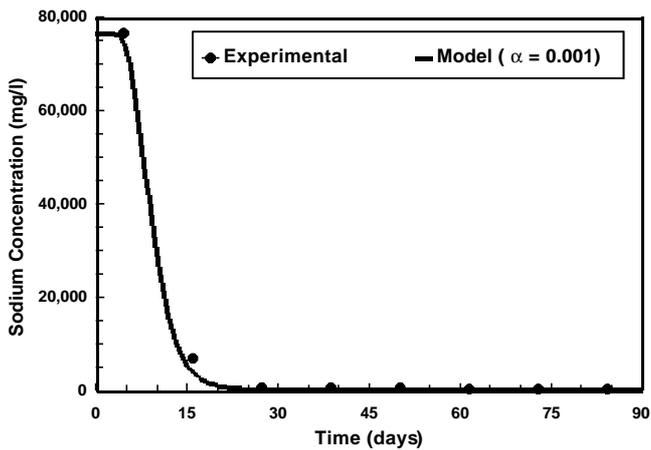
Figure 1. Comparison of experimental and model results of Hazelwood Precipitator ash.



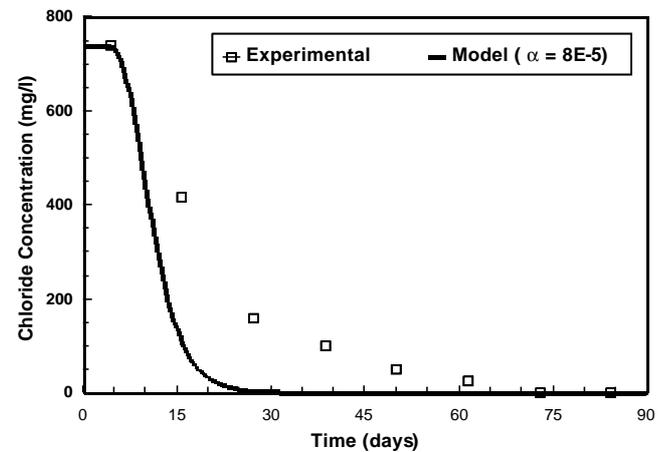
(b) Leaching of Cl



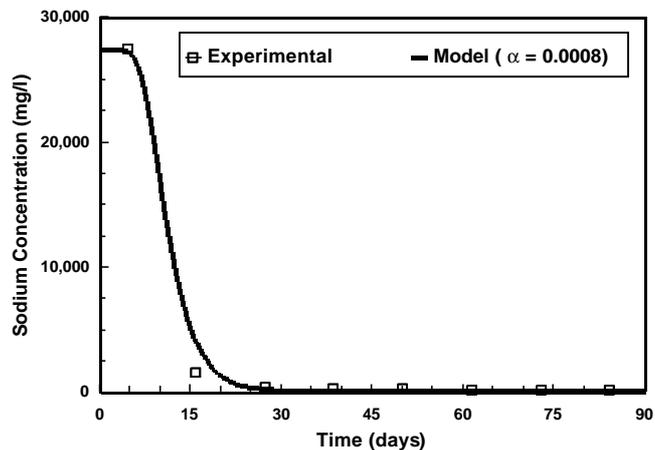
(a) Leaching of SO₄



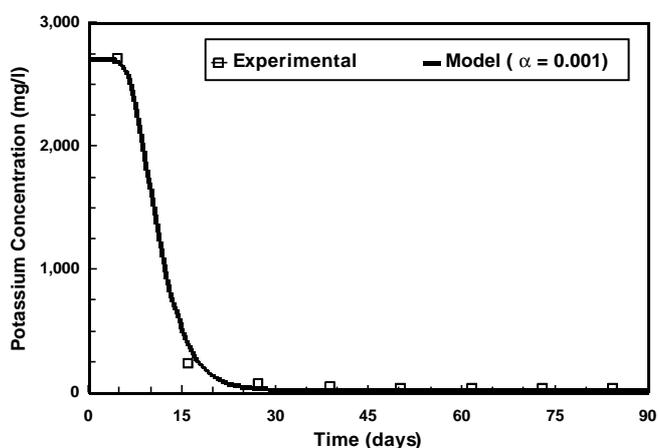
(c) Leaching of Na



(b) Leaching of Cl



(c) Leaching of Na



(d) Leaching of K

Figure 2. Comparison of experimental and model results of Hazelwood pond sediment.

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