Modelling and assessment of the long-term leachate generation potential in deposits of ferro-chromiun slags

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Synopsis

The environmental impact of solid waste materials is closely linked to their potential to produce a hazardous leachate once deposited in a landfill. This potential is conventionally assessed with simple laboratory batch leach tests, which find more and more frequent application also in the minerals and metals industry. Such tests are intended to help distinguish between high and low risk wastes, but are completely unsuitable to allow quantitative prediction or modelling of the long-term leachate generation potential.

In the present approach the leachate generation process is perceived as a combination of bulk convective transport, stagnant zone and inner particle diffusion, as well as reaction kinetic effects. Model equations are formulated accordingly. A modelling framework, WASTESIM, has been developed at UCT, which allows flexible combination of the model components and simulation of leach scenarios. Quantitative model parameters are obtained from a systematic laboratory study on the waste material in question. The combined assessment and modelling approach is demonstrated with a study on Cr(VI) leaching from a ferro-chromium slag material. Although not straightforward, the approach is particularly useful in determining long-term liabilities in the context of waste disposal sites with considerably more reliability than has previously been possible.

Keywords: waste deposits, waste leaching, heap leaching, environmental, risk assessment, Cr(VI), ferro-chromium, slag.

Introduction

The environmental impact of landfill deposits is closely associated with the potential of the stored waste material to generate a hazardous leachate. While the problem has long been recognised in the context of municipal waste disposal and the associated co-disposal of certain industrial wastes, environmental concerns regarding wastes originating from mining and metallurgical operations have been voiced only in more recent times[1,2].

The emergence of a hazardous leachate in ground or surface waters in the vicinity of a waste deposit is usually delayed over many years due to the slow progression of leachate generation and migration in the deposit and the surrounding soil. Consequently there is considerable reluctance by environmental authorities to issue closure certificates to the operators of those disposal sites for which the long-term environmental stability cannot be assured[3].

The environmental hazard potential of a particular waste material is commonly assessed with simple laboratory leach tests, such as the Toxicity Characteristic Leaching Procedure (TCLP), devised by the US Environmental Protection Agency (US EPA)[4]. Based on the outcome of such tests the waste is classified in terms of its hazardousness and must be disposed of correspondingly. In South Africa guidelines for the classification and disposal of hazardous wastes are detailed in the Minimum Requirements document by the Department of Water Affairs and Forestry (DWAF)[5].

Waste assessment tests, which have by now found widespread application in the minerals industry, are, however, limited to broad waste classification, often in terms of a 'worst case' scenario[6]. As such they are only useful in assessing the short to medium term environmental risk of a particular waste material, but they are far too simplistic to allow meaningful prediction of the long-term leachate generation behaviour[7]. To be able to make such predictions, an in-depth understanding of the underlying processes is required. These are discussed in this paper and a modelling framework is formulated on the basis of this understanding. Combined with suitably designed laboratory test procedures this provides a powerful tool for the prediction of leachate generation in waste deposits typical of the mining and metallurgical industry. The application of this approach is demonstrated on studies involving a ferro-chromium slag material.

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The leachate generation process

At its simplest the process of leachate generation can be described as dissolution of soluble substances contained in the solid waste material into rain or process water percolating through the deposit (Figure 1). High concentrations of leached contaminants would emerge at the base of the deposit almost instantaneously and gradually decrease over time as the deposit is leached out.

In practice this description is overly simplistic and the process is likely to be complicated by a number of factors. These relate to aspects of

- ➤ Bulk transport of the aqueous phase through the deposit
- ➤ Diffusion effects of dissolved species in a porous matrix and
- ➤ Chemical reaction mechanisms.

Bulk transport

Bulk transport of an aqueous phase through a porous matrix is unlikely to proceed in strictly one-dimensional direction. In a packed bed of particles a random lateral distribution of flow can be expected with preferential flow paths, areas of trickling flow and completely stagnant zones (Figure 2). Saturation of pore spaces also influences bulk transport significantly. Fully saturated flow conditions exist in groundwater flow, but not in surface landfill deposits, where often only a small portion of the pore space is filled with the aqueous phase, with the remainder containing air. Furthermore, the irregularity of rainfall results in highly variable bulk flow rates, and the degree of saturation of the pore spaces is subject to seasonal drying and wetting, particularly in zones near the external surfaces of the deposit.

Diffusion effects

Chemical species dissolved in the bulk aqueous phase are transported not only by overall movement of the bulk fluid, but also by molecular diffusion within the aqueous phase. Usually this effect is ignored since convective movement of fluid is orders of magnitude faster than diffusion through the fluid. However, in waste deposit, where the bulk fluid moves slowly and intermittently, diffusion effects can be the predominant mode of transport.

More significant, however, is diffusion through stagnant zones and through micro-pores within particles. Stagnant zones exist where fluid is trapped in dead-end pores and in regions of inhomogeneously packed material, which are removed from preferential flow paths. Species that dissolve at the solid liquid interface within a stagnant zone migrate to the bulk fluid exclusively by diffusion. Even if bulk movement is rapid, this stagnant pore diffusion can considerably retard the release of contaminant from a deposit.

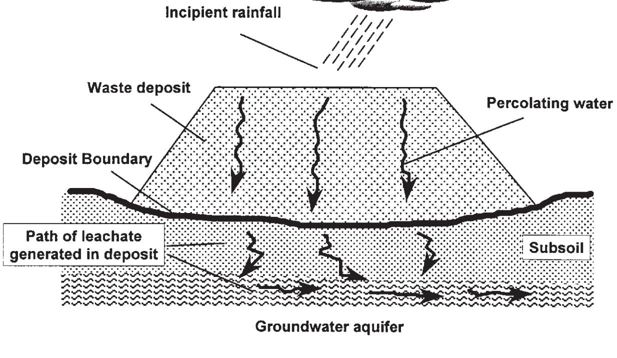

Figure 1—Conceptual leach process

Similar diffusion effects also govern transport through the micro-porous structure of the particles of which the bed is composed. These commonly exhibit a network of micro-pores defined by the mineralogical nature of the solid material (Figure 3). Transportation through these pores is limited to molecular diffusion, but this can result in soluble species engrained within the solid to migrate gradually to the surface and from there into the surrounding fluid. Hence, diffusion controlled leaching from large particles can significantly retard the emergence of hazardous species in the leachate from a deposit.

Chemical reaction

The release of chemical species from the solids into the passing aqueous phase can rarely be described as instantaneous and complete dissolution. The solubility of solid compounds is governed by thermodynamic equilibrium, and the rate at which this equilibrium is achieved is in many cases retarded by kinetic constraints or even inhibited. The

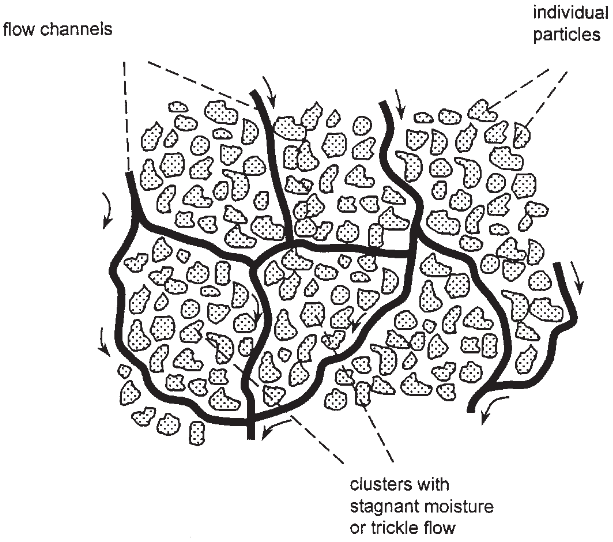

Figure 2—Distribution of flow in a packed bed

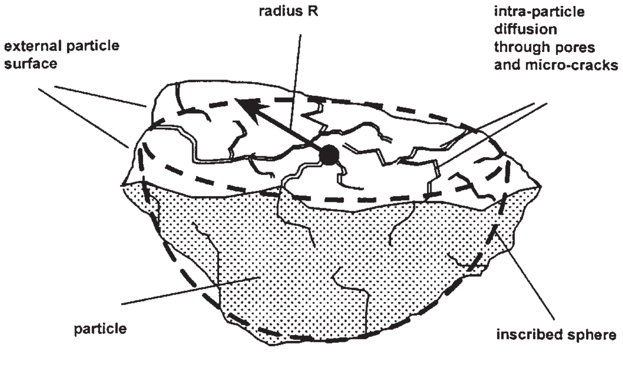

Figure 3—Cross-section through a porous mineral particle

net rate of removal of a chemical species from the solid matrix is a combination of the dissolution kinetics and the rate at which the equilibrium is shifted through removal of dissolved species by transport effects.

Although the aqueous dissolution of solid compounds is probably the most significant release mechanism in waste leaching, other mechanisms are also common, such as desorption of adsorbed species, chemical reaction (oxidation, acid attack) and complexation. Furthermore, removal mechanisms also need to be considered, such as adsorption of dissolved species and precipitation. All of these mechanisms are governed by equilibrium thermodynamics and many constrained by kinetic effects.

A modelling framework

It is easy to recognize from the above description that the process of leachate generation is composed of a number of sub-processes, each of which can be described by a suitable mathematical model. The modelling approach described here has been adopted from a heap leach model formulated by Dixon[8,9], recognizing that the leachate generation process in waste deposit is similar to phenomena encountered in heap leaching.

One-dimensional bulk transport of a dissolved chemical species i can be described as follows

$$-v_s \frac{\partial c_{b,i}}{\partial z} + D_h \frac{\partial^2 c_{b,i}}{\partial z^2} + Q_{C,i} = \varepsilon_b \frac{\partial c_{b,i}}{\partial t} \qquad [1]$$

where $c_{b,i}$ is the dissolved concentration of i in the bulk fluid, v_s the superficial (or Darcy) velocity of the fluid, D_h the hydraulic dispersivity and ε_b the bed liquid volume fraction. $Q_{c,i}$ denotes a source term.

Diffusion transport through spherical, porous particles can be described by

$$D_{e,i}\left[\frac{\partial^2 c_{p,i}}{\partial r^2} + \frac{2}{r}\frac{\partial c_{p,i}}{\partial r}\right] + \varepsilon_p \sum_j R_i^j = \varepsilon_p \frac{\partial c_{p,i}}{\partial t} \qquad [2]$$

where $c_{p,i}$ denotes the dissolved concentration of i in the pore fluid, $D_{e,i}$ is the effective pore diffusivity, ε_p the particle porosity. R_i^j is the rate of production of species i due to reaction j.

Release from the solid phase of the dissolution, $S \rightarrow A + B$, could be described by the following first order kinetic model:

$$R_A^{kin} = R_B^{kin} = -\frac{dc_S}{dt} = kc_S \qquad [3]$$

where c_s denotes the solid concentration of the dissolving solid species S, and k is a first order kinetic constant.

These three models describing individual processes (bulk transport, diffusion through porous particles and reaction) can be linked together through the reactive terms: The rate of dissolution of i described in Equation [3] can link directly into transport Equation [2] and the rate of diffusion from particle pores into the bulk fluid can be linked into Equation [1] via the following expression:

$$Q_{c,i} = -\sum_n \frac{3(1-\varepsilon_h)w^{(n)}}{R^{(n)}} D_{e,i}\left(\frac{\partial c_{p,i}}{\partial r}\right)_{r=R^{(n)}} \qquad [4]$$

where (n) is a counter over all particle size classes of radius $R^{(n)}$ and mass fraction $w^{(n)}$. The gradient term represent the pore concentration gradient at the particle surface.

The present scenario precludes analytical solution of the underlying differential equations and numerical solution using a computer is necessary. For this the waste deposit is divided into disks nodes as indicated in Figure 4. Within each disk there is a population of particles of given size. These are subdivided into shell nodes, as indicated. For each node the current concentrations of the dissolved species i are computed. The various model equations are represented in suitable numerical solution algorithms (Lagrangian approach to Equation [1]; Crank-Nicholson methods for Equation [2], Runge-Kutta methods for the reaction equations, etc.).

The overall solution algorithm steps in discrete time increments. For each step new concentrations are computed for all inner particle nodes via the reaction model [3]. Diffusion transport is then modelled for each particle size class on each disk level, employing the particle transport model [2]. For each disk, then, the bulk concentration is calculated by accounting for the contributions from the particle population using the pore-bulk diffusion Equation [4]. Finally bulk transport through the deposit is modelled using Equation [1], before the process is repeated in the next time-step. Concentrations computed in the bottom-most disk correspond to those of the leachate at that point in time.

When combining the model equations into a computer algorithm a certain degree of flexibility—in terms of which model equations are available and in which way they are combined—should be allowed for. This enables the modelling of a large number of different waste leach scenarios with the same software and also some flexibility in the way any particular scenario is modelled, depending on the availability of data. For example, it is easy to replace the kinetic dissolution model [3] with one that describes an adsorption isotherm, or one that describes kinetic reaction with another dissolved species, or even a combination of various simultaneous reaction mechanisms. Likewise the particle diffusion model [2] can be omitted (if particles are too small to warrant its use) and the reaction models directly linked with the bulk nodes, or the bulk transport Equation [1] can be modified to take account of more complex flow phenomena.

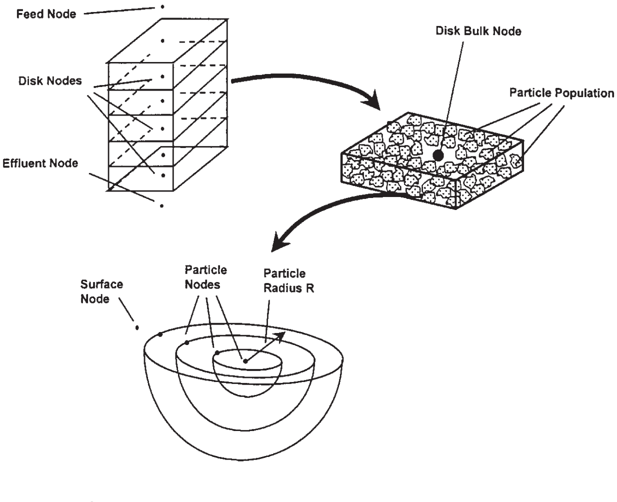

Figure 4—Subdivision of waste heap and individual particles

A prototype of such a flexible algorithm, or modelling framework, has been realized at UCT with the WASTESIM code[10]. WASTESIM (originally programmed in Turbo Pascal® as a DOS executable program) maintains the model equations describing bulk transport, pore diffusion and reaction mechanisms as independent modules or sub-routines in a code library. An overall modelling algorithm for any particular simulation scenario is then assembled from these modules by user selection on an interactive screen. All necessary input parameters, such as deposit dimensions, mineral composition, particles size distribution, porosities, reaction matrix and rate constants etc., are also entered. WASTESIM then drives the simulation through systematic calls to the various sub-routines and generates curves of leachate concentration versus time for selected components. The parameters and results of any particular run are saved in data files and can be recalled from within WASTESIM to allow comparisons between different model selections or sensitivity studies on selected input parameters.

Laboratory assessment

In order to obtain input parameters for any modelling scenario, laboratory leach tests for the quantitative assessment of the leaching and reaction behaviour of the stored waste material remain a necessity. With the help of the modelling framework it is possible to achieve scaling of such laboratory data to full scale and long-term waste leach scenarios. However, meaningful scale-up can only be achieved if the laboratory data has been obtained in a chemical environment which is comparable to that likely to exist in the waste deposit, and if the overall release of any particular species is discerned in terms of the underlying reaction phenomena and their kinetics.

In this sense, once off, short-term leach tests involving relatively aggressive lixiviants, such as are commonly applied in waste characterization tests[11], have little value for predicting the time dependent leachate generation behaviour of a waste material. Therefore, a more systematic approach for the assessment of the leachate generation behaviour is needed.

A comprehensive integrated assessment and modelling approach is illustrated in Figure 5. A good indication of the prevailing physico-chemical conditions in a deposit scenario (in terms of pH, permeability, predominant species, etc.) can be achieved in a laboratory scale, short-term column study on a relatively small sample of material. These indicators are used to design appropriate bench-scale batch leach tests (particularly in terms of leach pH and lixiviant aggressiveness). Further tests, involving variable solid-to-liquid ratios, adsorption studies, studies at elevated temperatures, variable test duration, etc. may be devised as necessary. Careful interpretation of the measured leach data is required at all times, in order to ensure all phenomena are clearly identified and quantified.

In this way, judicious bench scale leach testing will result in a quantified set of reaction mechanisms taking place at the particle level. These are used to compile a model of the leachate generation process in WASTESIM, together with other parameters, such as particle size distribution, density, porosity, etc. obtained from other analyses. As a first test of the model the leach curves obtained from the initial column study are simulated and compared to the experimental data. If good agreement is achieved, the model can now be applied to simulate a full-scale scenario with some confidence, simply by changing the parameters describing bed dimensions and flow rates. If discrepancies are observed, more test work or a re-evaluation of the model equations may be required.

Application of the approach

The methodology proposed above was put to the test with a low-carbon ferro-chromium slag (LCS) material. 500 kg of material were sampled run of production at a smelter in the Mpumalanga Province. A preliminary water leach test would suggest that only Na, K and Ca leach to any significant extent (Table I) and the material can be classified as relatively low risk environmentally. However, most of the Cr leached in the preliminary experiment was found to be the toxic Cr(VI) and some concerns regarding the behaviour of this species remained.

Material characterization

The slag material was in the form of blue-grey, highly porous granules, with an average particle size around 2 mm. The particle size distribution is given in Table II. The larger particles were nearly spherical, hollow globules that crushed easily between the fingers. Smaller particles were mostly

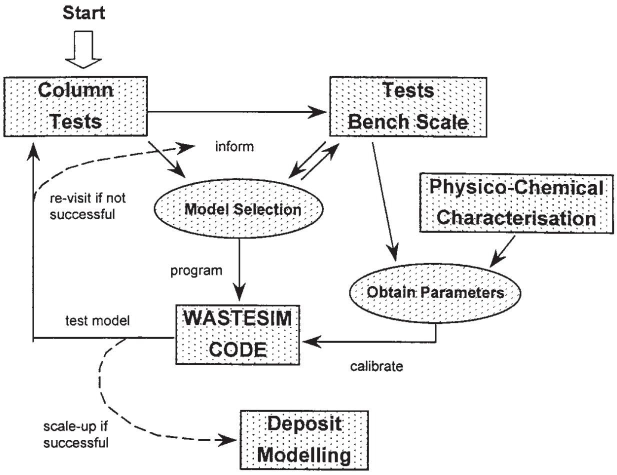

Figure 5—The integrated waste assessment and modelling approach

Table I

Results from preliminary 1:10 water wash on LCS

Element	mg/L	mg/g dust
Na	13.61	0.2722
K	6.64	0.1328
Ca	23.68	0.4736
Mg	0.95	0.019
Cr_{tot}	0.32	0.0064
Cr (VI)	0.31	0.0062
Fe	0.04	0.0008
pH	11.35	

Table II

Particle size distribution of LCS

Sieve size [mm]	% retained
min	1.67
212	1.13
300	2.19
425	0.89
500	9.08
850	5.83
1000	13.75
1400	10.85
2000	41.76
4000	8.21
5600	4.65
9500	0.0

identified as debris of crushed larger particles. The material contained a high degree of moisture (19.7% by mass), resulting from a quenching process to which the hot slag was subjected when poured. The true density was 2900 kg/m^3, porosity was assessed as 50% on average.

Elementary analysis of the slag is given in Table III, established by sodium peroxide fusion digest. Assuming all metals are present as their common oxides, about 15% of the slag mass is unaccounted for. This is assumed to be made up of alumina-silicates, which were not analysed for, but are common components in this type of material[12].

Column experiments

The LCS material was first subjected to a column experiment. The column consisted of a glass tube, 225 mm in diameter, into which the material was filled onto a base support consisting of layers of glass marbles, glass beads, and a sheet of glass fibre for solids retention (Figure 6). The bed height was 50 cm. Lixiviant (an artificial acid rain mixture, well-aerated distilled water acidified with a 6:4 mixture of sulphuric to nitric acid to pH 4) was sprinkled evenly over the top of the bed at a daily flow rate of around 200 ml. The leachate was collected in a beaker placed at the base of the column. The beaker was exchanged daily in order to monitor the flow rate. The collected leachate was analysed from time to time. Evaporative loss of fluid was around 20% of the daily feed. It was observed that the uppermost 10 cm of the bed was somewhat drier than the rest, indicating that it is here where most evaporation occured.

The concentration-time profiles for Cr are given in Figures 7 and those for Na and K in Figure 8. The leachate pH was 10.0, gradually increasing to around 11.2 over the 50-day experimental period. Cr in the leachate was analysed for both Cr(VI) using a spectrophotometric method and total Cr using atomic absorption. In excess of 95% of all Cr measured was Cr(VI), as the yellow colour of the leachate would indicate. The concentration profile for Cr shows the presence of around 10 mg/L as soon as there is leachate emerging at the bottom of the column. Concentrations increase further to a maximum after 18 days (14 mg/l), after which they decline gradually. The leach curves of the alkalis Na and K show a somewhat different behaviour. In both peak concentrations are reached within the first 5 days after breakthrough, after which they decline to within 10% of the peak value after 30 days.

Table III

Elementary analysis of LCS

Element	mass %
Fe	0.17
Cr	1.89
Mn	0.07
Ni	0.04
Mo	<0.01
Ca	47.38
Mg	9.61
K	0.080
Zn	<0.01
Pb	<0.01
Ti	0.400
Cu	<0.01
Sn	<0.01
V	<0.01
Ag	0.0005
Cd	<0.0001
Hg	n/a

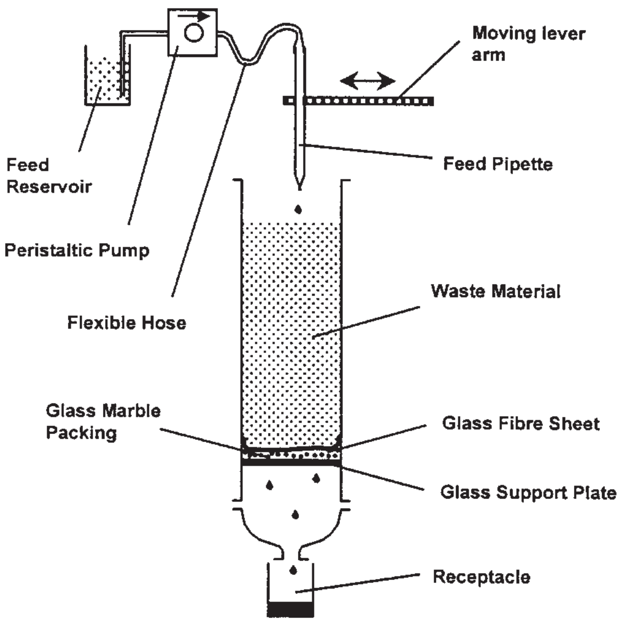

Figure 6— Schematic of slag leach column

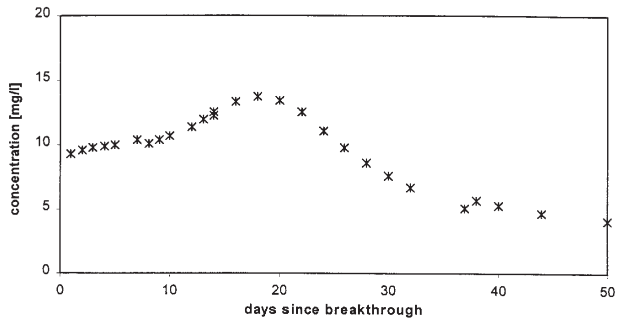

Figure 7—Cr leach profile from column experiment

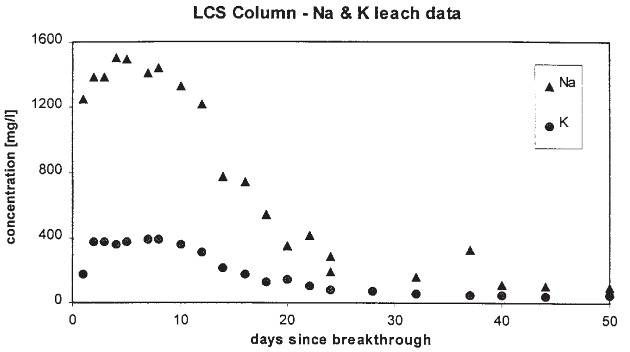

Figure 8—Na and K leach profiles from column experiment

After 50 days of the regular column experiment a tracer study using Li was conducted. Approximately 830 mg/l Li^+ (as Li_2SO_4) was added to the feed solution and supplied for 36 days, before the solution was switched back to the acid rain mixture used before. The appearance of Li in the leachate was closely monitored. Li concentrations versus time in the leachate are shown in Figure 9. Only 82% of the Li supplied were recovered within 21 weeks of starting the Li supply. It was observed in a preliminary experiment that Li does not adsorb to or react with the LCS material to any significant extent. The long tail end in the tracer response curve is typical of flow through granular bed in which there exist large stagnant zones, i.e. liquid trapped in dead-end pores and crevices which is not moving with the bulk flow[13]. Analysis of the tracer study with the WASTESIM code is discussed further below.

Batch leach tests

In parallel to the column test, the LCS material was subjected to a number of bench-scale leach experiments. In most experiments 90 g of material (dry basis) were mixed with 1.8 *l* solution (i.e. at a solid to liquid (S:L) ratio of 1:20) in a 2l glass bottle rotated top over bottom at 30 rpm for 24 hours. Solution composition, leach times as well as S:L ratios were varied in some of the experiments. Small samples (5–10 ml) were taken at regular intervals, filtered and analysed for the components of interest.

The standard TCLP fluid (0.1 M acetic acid), distilled water and 0.1 M NaOH (mild caustic) were used as lixiviants in 24-hour tests. The results of the TCLP tests are plotted in Figures 10a (Na and K) and 10b (total Cr and Cr(VI)); similarly for distilled water in Figures 11a and 11b and for mild caustic in Figures 12a and 12b (K only, since Na is in excess through NaOH lixiviant). The final leachate pH were 5.6 in the TCLP test, 11.3 in the water test and 12.8 in the mild caustic test.

Comparing the results for the species considered here, it is immediately clear that the TCLP returns the highest

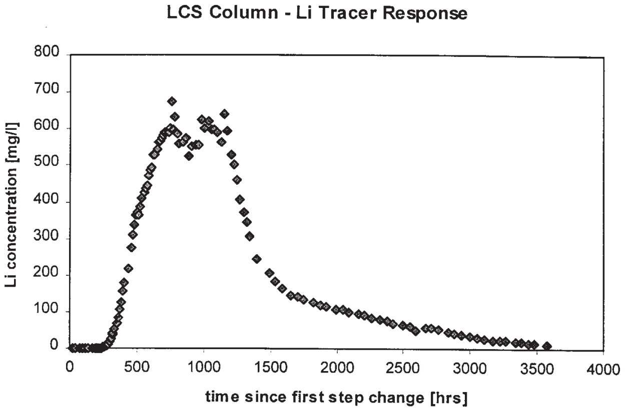

Figure 9—Li tracer concentrations in leach profile of column experiment

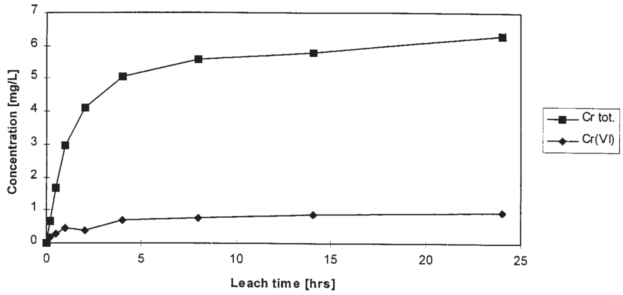

Figure 10a—TCLP leach curves for Cr and Cr(VI)

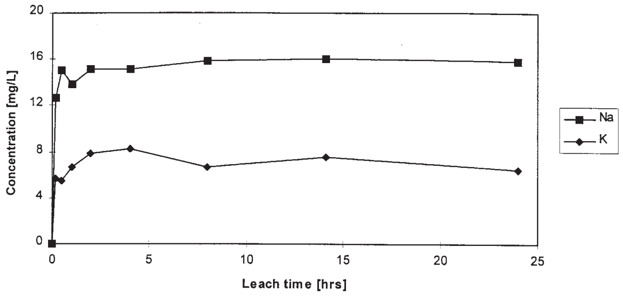

Figure 10b— TCLP leach curves for Na and K

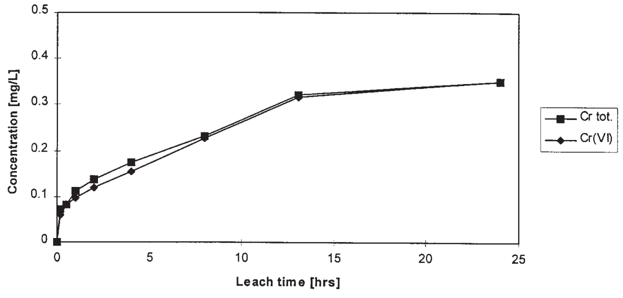

Figure 11a—Water leach curves for Cr and Cr(VI)

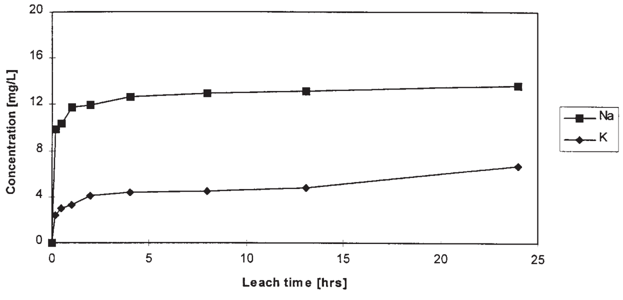

Figure 11b— Water leach curves for Na and K

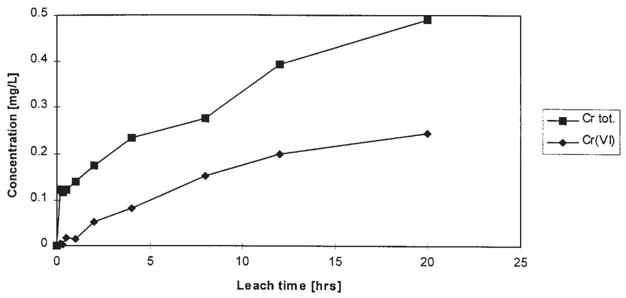

Figure 12a—0.1 M caustic leach curves for Cr and Cr(VI)

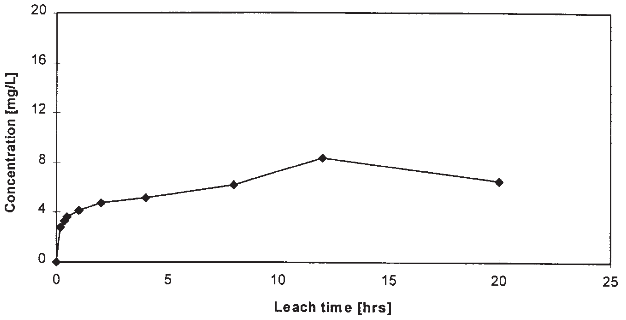

Figure 12b—0.1 M caustic leach curve for K

leachate concentrations, which would support its choice as a worst case indicator, whereas the final leachate pH of the water wash is closest to that observed in the column experiment. While the leaching of Cr(VI), Na and K decreases with increasing leachate pH, total Cr appears to go through a minimum. This is explained by the amphoteric behaviour of Cr(III), which is soluble at both low and high pH, but nearly insoluble at pH 6 to 11. In all runs the leach curves of Na and K rise rapidly (within the first 2 hours) before they settle at a final concentration towards the end of the 24-hour leach period. For Cr the same trend is observed only in the TCLP experiment, whereas both total Cr and Cr(VI) concentrations appear to still be rising at the end of the water leach experiment, indicating the reaction had not gone to completion within 24 hours. A 7-day leach in distilled water at 1:10 S:L was conducted to study the effect over a longer time-span. The result, shown in Figure 13, indicates that the release of Cr(VI) is indeed kinetically controlled.

Furthermore, the adsorption behaviour of Cr(VI) onto the LCS material was investigated. For this a number of 24-hour leach runs were conducted at 1:20 S:L in distilled water to which various quantities of Cr(VI) had been added. The results are given in Table IV. It is assumed that no Cr(VI) was initially adsorbed onto the material. The amount of Cr(VI) released by leaching (0.6 mg/l) is indicated by the first experiment in pure distilled water. This was assumed to be the same in all experiments. The amount of adsorbed Cr(VI) was calculated from the difference between the concentrations measured after 24 hours and what was added at the beginning, plus the 0.6 mg/l leached. Adsorbed concentration has been plotted versus final solution concentration in Figure 14. The data points clearly indicate an adsorption isotherm of the Langmuir or Freundlich types. Both models correlate well for solution concentrations up to 20 mg/l, which is well within range of the concentrations observed in the column leach experiment.

Model compilation

The experimental evidence obtained from the column and batch leach experiments has been carefully evaluated in order to suggest a scheme of reactions taking place at the solid-liquid interface and transport phenomena within the particle bed. A model to simulate the column experiment was then compiled in WASTESIM on the basis of this evaluation[14].

The release of K and Na were taken to be controlled by more or less instantaneous dissolution of salts, which is to some extent controlled by pH. As the final leach pH in the

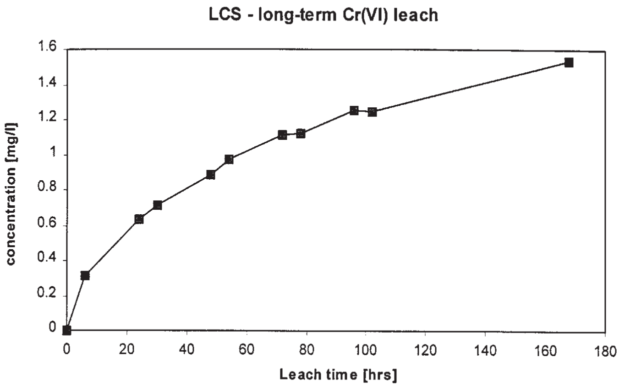

Figure 13—Batch leach profile for Cr(VI)

Table IV

Results from Cr(VI) adsorption experiments

Initial Cr(VI) mg/g	Final Cr(VI) mg/g	Expected mg/g	Cr(VI) adsorbed mg/g
0.0	0.6	0.6	0.0000
2.0	2.4	2.6	0.0044
5.0	5.3	5.6	0.0058
10.6	10.7	11.2	0.0093
18.8	18.7	19.4	0.0130
40.7	40.6	41.3	0.0130
81.0	80.9	81.6	0.0152

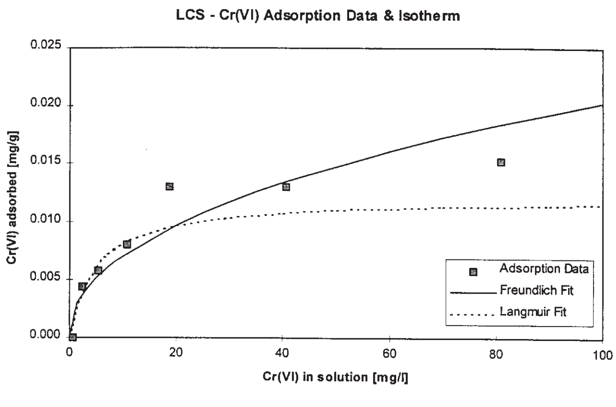

Figure 14—Cr(VI) adsorption curves

distilled water experiment is closest to that observed in the column leachate, the soluble concentration of Na was evaluated as 300 mg/kg LCS and that of K as 100 mg/kg LCS.

The release of Cr(VI), on the other hand, is seen to be controlled by three simultaneous mechanisms: Marginal instantaneous dissolution, adsorption that can be described by a Langmuir type isotherm, and first order kinetic dissolution. All reaction parameters were obtained from the available experimental data and are given in Table V.

In terms of transport effects, particle level diffusion as described in Equation [2] is not rate controlling as the LCS particles were too small and too porous. This was supported by a sensitivity study with WASTESIM in which first order Cr(VI) leaching was simulated for particles of different sizes and porosities[10]. Only for particles larger than 10 mm and porosities lower than 5% did diffusion kinetic begin to dominate over the kinetics of the reaction. For the present study, therefore, the various reactions models (as implicit in Equation [3]) were directly coupled to the bulk model.

The bulk transport model was chosen from evidence of the Li tracer study. This had indicated that simple linear plug flow (as implied in Equation [1]) cannot be assumed in the present case, but that there is a distribution of flow velocities and/or a significant presence of stagnant zones. Multiple flow velocities can be approached by modelling the bed to consist of a number of parallel columns through which the fluid travels in plug flow fashion, but at different velocities. The overall leachate concentrations are then calculated by conceptually mixing the parallel streams back into one. In the present study only two parallel streams were considered.

Stagnant zones can be approached by considering the bed to consist of clusters of particles with stagnant fluid in the interstitial spaces (see Figure 2) and the bulk fluid flowing along preferential paths between these. The clusters are modelled as 'pseudo-particles' and transport through the interstitial spaces as diffusion through their 'pores'. Both approaches were used to model the tracer data and subsequently the column experiment.

Other relevant model parameters are listed in Table VI. The fractional saturation of the interstitial pore space was estimated from the liquid hold-up in the column. This was established from the mass of liquid fed to the bed before the first drop of leachate was recorded and an estimate of the losses to evaporation. It was assumed that the liquid was evenly distributed throughout the bed.

Column simulations

The tracer experiment was simulated employing the WASTESIM code with three different bulk transport models. The simulated curves and experimental data are given in Figure 15. Clearly the uniform flow model (plug flow with dispersion) does not fit the experimental data well. The split flow model (two parallel plug flow columns at different flow rates) much better captures the crest of the peak and part of the extended tail end. The stagnant zone model (using large pseudo particles) emulates only a narrow peak, but captures the extended tail best. The true flow profile is therefore likely to involve both multiple flow velocities, stagnant zones and, in all likelihood, zones of different moisture content. No model is as yet available to account for all these effects simultaneously.

Given the best-fit parameters for the three different bulk transport models, the actual column leach experiment was simulated. The simulated curves for Cr and Na are shown, together with the experimental data in Figures 16 and 17. The curves modelled for K are very similar in trends as those for Na and therefore not discussed here. All leachate concentrations are slightly over-predicted by some 10%, but all simulated curves capture the experimental data well in trends.

Similar to the tracer study the uniform flow model does not appreciate tail-end effects. These are better captured with the split flow and stagnant zone models. Regarding the Na leach curve, only the stagnant zone model is able to emulate the initial rise in concentration observed over the first 10 days.

Regarding Cr, for which a more complex reaction scheme was identified, all models capture the 'hump' in the leach

Table V

Parameters describing Cr(VI) reaction scheme for LCS

Reaction 1: Instant Cr(VI) dissolution	
Reaction Constant	$c_{cr(VI)}{}^0 = 0.002$ mg/g
Reaction 2: Kinetic Cr(VI) dissolution	
Reaction Model: Reaction Constants:	first order in solid Cr(VI) concentration $k = 3.2 \bullet 10^{-6}\ s^{-1}$ $c_{cr(VI)}{}^0 = 0.02$ mg/g
Reaction 3: Cr(VI) Langmuir adsorption	
Reaction Constants:	$K_{ads} = 0.201$ l/mg $c_{max} = 0.012$ mg/g $c_{ads}{}^0 = 0.0$mg/g

Table VI

Other simulation parameters

Total bed height	0.5 m
Bed porosity	0.70
Fractional pore saturation	0.35
Daily flow rate	175 ml/d
True solid density	2900 kg/m^3

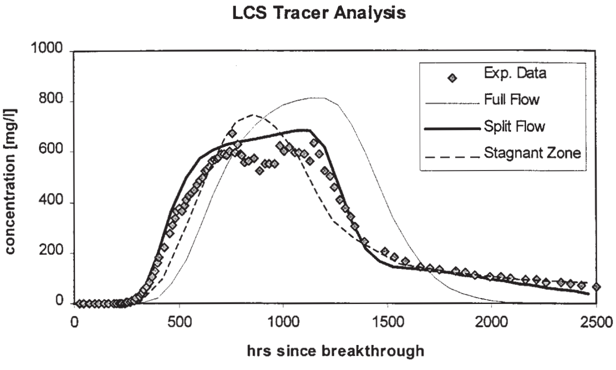

Figure 15—Modelling of the Li tracer experiment with various bulk flow models

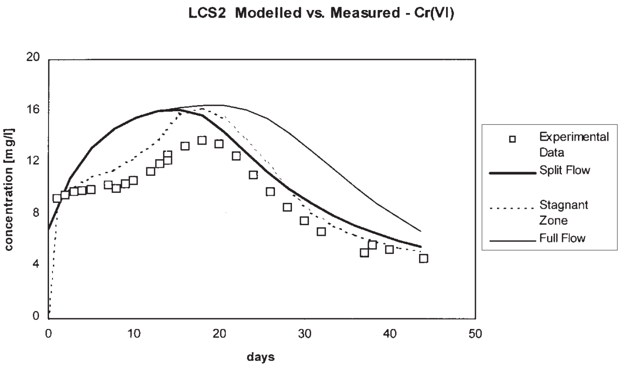

Figure 16—Modelling the Cr(VI) leach profile for the column experiment using various flow models

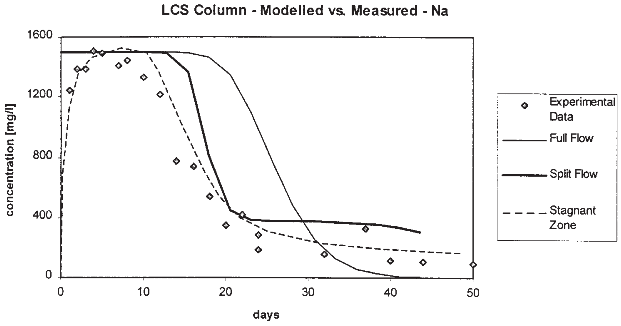

Figure 17—Modelling the Na leach profile for the column experiment using various flow models

curve, which is associated with the kinetically slow release and a more gradual decline in concentration (as compared to the Na curve) due to the presence of an adsorption/desorption buffer. However, only the stagnant zone model captures the distinct initial step in the leach curve.

Thus, overall, the stagnant zone model appears to emulate the real bulk transport effects most appropriately, but too little experimental evidence was gathered to confirm that the stagnant zone concept is indeed correct. The model compiled for the LCS material has not as yet been tested against a full-scale disposal scenario.

In evaluating the quality of the model predictions it should be stressed that all the simulated curves were generated on the basis of independent data, i.e. at no stage of the laboratory assessment approach were the data of the original column leach experiment itself used to calibrate the model. It would be tempting to manipulate certain model parameters, such as initial concentrations, flow rates, particle sizes, etc. to obtain a better fit to the experimental data, but this defeats the objective of the overall approach. The fact that relatively good model fits were achieved without such manipulations only supports the claim that the complex leachate generation process can indeed be assessed through the combination of a suitably designed experimental study with a carefully compiled model. The WASTESIM modelling framework is an excellent tool for this integrated approach.

Conclusions

Short-term laboratory leach tests are insufficient to describe quantitatively the long-term leachate generation behaviour of waste materials. Such a description is, however, necessary to allow a meaningful assessment of the liabilities associated with a particular waste disposal practice and in obtaining a reasonable degree of certainty with regard to future environmental risk when issuing closure certificates to such operations.

The modelling framework developed at UCT, which was introduced here, is a versatile and powerful tool for long-term predictions on the basis of a rigorous understanding of the processes underlying waste leaching. However, it can only be applied in combination with a systematic laboratory study to provide the required model parameters. This approach has been demonstrated successfully in a study on Cr(VI) leaching from a ferro-chromium slag material.

It is recognized that the proposed methodology is not straightforward and may require considerable experimental effort and expert evaluation of the resulting data. In this sense it is not intended to supersede conventional waste assessment methods, but may be used as an additional resource if the long-term stability of a disposal operation is questioned. Large-scale disposal sites containing waste materials, whose leachate generation potential may be borderline between hazardous and non-hazardous, such as the ferro-chromium slag investigated here, are not uncommon in the metallurgical industry. Evaluation of such scenarios in terms of the proposed methodology may help clarify the long-term liabilities of the operators.

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AMIRA rides research wave into South Africa*

A track record of successful minerals research projects conducted by the University of Queensland's Julius Kruttschnitt Mineral Research Centre in South Africa is helping other Australian-based R & D providers access projects for the Republic's base metals market - particularly in platinum group metals.

According to AMIRA International's South African Research Coordinator Professor Peter Gaylard, the JKMRC/AMIRA P9 project is a proven catalyst sparking a wave of interest in AMIRA's suite of mineral processing, pyrometallurgy and mining projects.

"The JKMRC's name is highly respected in South Africa, and having their name attached to P9 made a huge impact with many of the South African sponsors who joined the project in the past few years,' Professor Gaylard said.

With the rapid growth of the P9 project in South Africa, AMIRA realized they needed someone on the ground in SA, preferably from the mineral processing field where the major market for R & D has developed.

Coming from industry with a minerals processing, pyrometallurgy and hydrometallurgy background, Peter Gaylard started AMIRA International's South African office in March last year after secondment to the University of Cape Town from his former position as consulting metallurgist at Billiton.

'We now see the need for a second person, preferably in mining, as we begin to expand the office to capture some of the other opportunities that are arising,' Professor Gaylard said.

The office is located in Cape Town to draw on UCT's Mineral Processing Research Unit infrastructure through which a large slice of AMIRA's SA research is conducted, particularly in P9.

'AMIRA has been active in the Republic for quite a few years, but essentially on the exploration side through links between South African companies and their Australian subsidiaries,' Professor Gaylard said.

Research activity in mineral processing rose sharply in 1996 at the start of the P9L project, with South Africa's largest platinum producers - Amplats, Implats, Lonmin, and Northam - joining the project as major sponsors.

By the end of 1998 there were 17 SA companies sponsoring P9L, including a number of equipment and chemical suppliers.

'The fact that most of these companies have rejoined the P9M project in 2000 indicates they receive good value,' Professor Gaylard said.

SA's three largest platinum producers have extended their involvement in AMIRA's research program, recently signing on for the P479 project on slags and refractories in smelting, with research being conducted by the GK Williams Cooperative Research Centre in Melbourne.

'The project has been modified to suit SA platinum producers' concerns over the effect of chromium in their smelting operations,' Professor Gaylard said.

AMIRA International has delved further into pyrometallurgy, with plans to bring GK Williams and South African researchers Mintek together for a project on the deportment of minor elements in base metal smelting.

Other AMIRA projects attracting attention in South Africa include P260C on surface chemistry aspects in flotation, and P523 on interfacial chemistry and water minimization in tailings management, both undertaken by the Ian Wark Research Institute at the University of South Australia.

'Although Amplats is the sole SA platinum sponsor of P260C at present, interest in the project has been expressed by other producers,' Professor Gaylard said.

But it's not all mineral processing and pyrometallurgy that has attracted South African interest in AMIRA.

The South African Government's 'Deep Mine' initiative has given researchers an opportunity to provide the required know-how to go ever deeper.

'The big challenge is to go down to 'ultra' deep levels below 4000 metres,' Professor Gaylard said.

'There is more gold in the gold fields of the former Transvaal than has yet been extracted.

'It's just that it is very deep and applied research is required to find ways to extract it economically, which in itself presents major challenges for researchers.'

Other AMIRA projects finding significant South African support include cyanide remediation in the gold industry, dewatering and thickening of tailings, and a Cape Technikon -CSIRO joint initiative on pumping of high density slurries. ◆

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