CHAPTER VI

TRANSPORT OF HEAVY METALS OF KHAM BON LANDFILL LEACHATE IN SOIL

6.1 Column Experiments

Column leaching experiments provide information about heavy metal release and transport in soil. KBS-2 (sand) and KBS-3 (silty loam sand) as the representative of soil in the landfill area were used to study heavy metals transported through soil. Plexiglas column (5 x 10 cm) was uniformly packed with soil following its bulk density. Columns were slowly saturated with deionized water with the aid of a peristaltic pump in up flow mode to prevent preferential flow. The cell was then leached with a continuously supplies heavy metals solution, actual leachate and synthetic leachate system, in 10 mgL^{-1} of monometal or mixed metals. The effluent leachate from the column was then collected at frequent intervals. After the effluent concentration (C) divided by influent concentration (Co) is approximately to 1, the feed solution was switched to be deionized water which assume as natural leaching in the field. The breakthrough curve (BTC) are represented by a normalized concentration (effluent concentration (C) divided by the influent constant concentration (Co)) as a function of pore volume. Bromide was used as a tracer to determine dispersion coefficient of soil samples. Twenty four transport experiments were carried out as listed in Table 6.1 (Appendix B).

6.1.1 Bromide Tracer Breakthrough Curves

Figure 6.1 shows the bromide breakthrough curve. The tracer breakthrough curve was nearly symmetrical. From the above bromide breakthrough curve data, the dispersion coefficient value is 0.98 cm^2/hr. This value was used for modeling the transport of metal through soil column.

6.1.2 Monometal Transport Modeling

The breakthrough curves for monometal studies of heavy metals (Cd, Cr, Cu, Cd, and Zn) through soil column treated with actual leachate and synthetic leachate.

Table 6.1 Experimental conditions for column studies.

Soil Type	Type of solution	Column No	Heavy metal	Co (initial)	pH	Soil(g)	Bulk density (g m^{-3})	Porosity (n)	Flow rate (ml min^{-1})
KBS-2	Actual leachate	1	Cd	9.340	8.16	261.8659	1.58	0.40	17.74
		2	Cr	10.300	8.16	261.8659	1.58	0.40	19.43
		3	Pb	10.000	8.16	261.8659	1.58	0.40	17.08
		4	Cu	11.720	8.16	261.8659	1.58	0.40	16.25
		5	Zn	9.575	8.16	261.8659	1.58	0.40	20.86
KBS-3	Actual leachate	6	Cd	9.340	8.16	268.4953	1.62	0.39	18.89
		7	Cr	10.300	8.16	268.4953	1.62	0.39	18.00
		8	Pb	10.000	8.16	268.4953	1.62	0.39	18.00
		9	Cu	11.720	8.16	268.4953	1.62	0.39	17.25
		10	Zn	9.575	8.16	268.4953	1.62	0.39	20.86
KBS-2	Synthetic leachate	11	Cd	10.225	8.16	261.8659	1.58	0.40	20.48
		12	Cr	11.840	8.16	261.8659	1.58	0.40	20.50
		13	Pb	10.540	8.16	261.8659	1.58	0.40	19.00
		14	Cu	9.700	8.16	261.8659	1.58	0.40	17.00
		15	Zn	9.123	8.16	261.8659	1.58	0.40	23.50
KBS-3	Synthetic leachate	16	Cd	10.225	8.16	268.4953	1.62	0.39	20.00
		17	Cr	11.840	8.16	268.4953	1.62	0.39	19.50
		18	Pb	10.540	8.16	268.4953	1.62	0.39	22.10
		19	Cu	9.700	8.16	268.4953	1.62	0.39	22.30
		20	Zn	9.123	8.16	268.4953	1.62	0.39	19.00
KBS-2	Competitive Actual leachate	21	Mixed	10.000	8.16	261.8659	1.58	0.40	18.00
KBS-3	Competitive Actual leachate	22	Mixed	10.000	8.16	268.4953	1.62	0.39	17.40
KBS-2	Competitive Synthetic leachate	23	Mixed	10.000	8.16	261.8659	1.58	0.40	22.80
KBS-3	Competitive Synthetic leachate	24	Mixed	10.000	8.16	268.4953	1.62	0.39	19.23

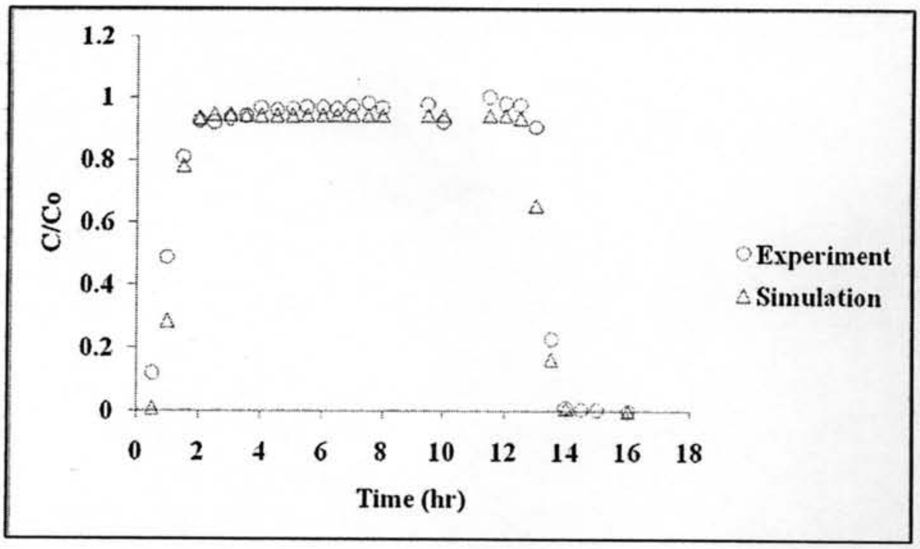

Figure 6.1 Breakthrough of Bromide tracer transport though soil column

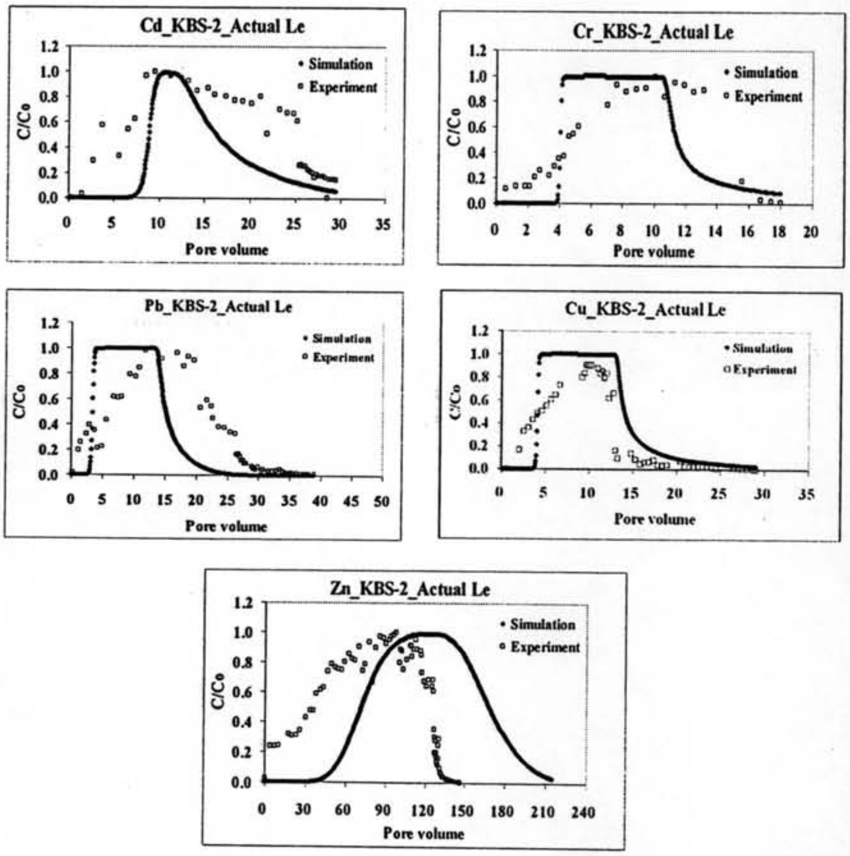

Figure 6.2 Breakthrough curves of Cd, Cr, Pb, Cu, and Zn of KBS-2 soil treated with actual leachate

are illustrated in Figures 6.2 through 6.5, respectively. The breakthrough curves of competitive metals combined with actual leachate and synthetic leachate are given in Figures 6.6 through 6.9.

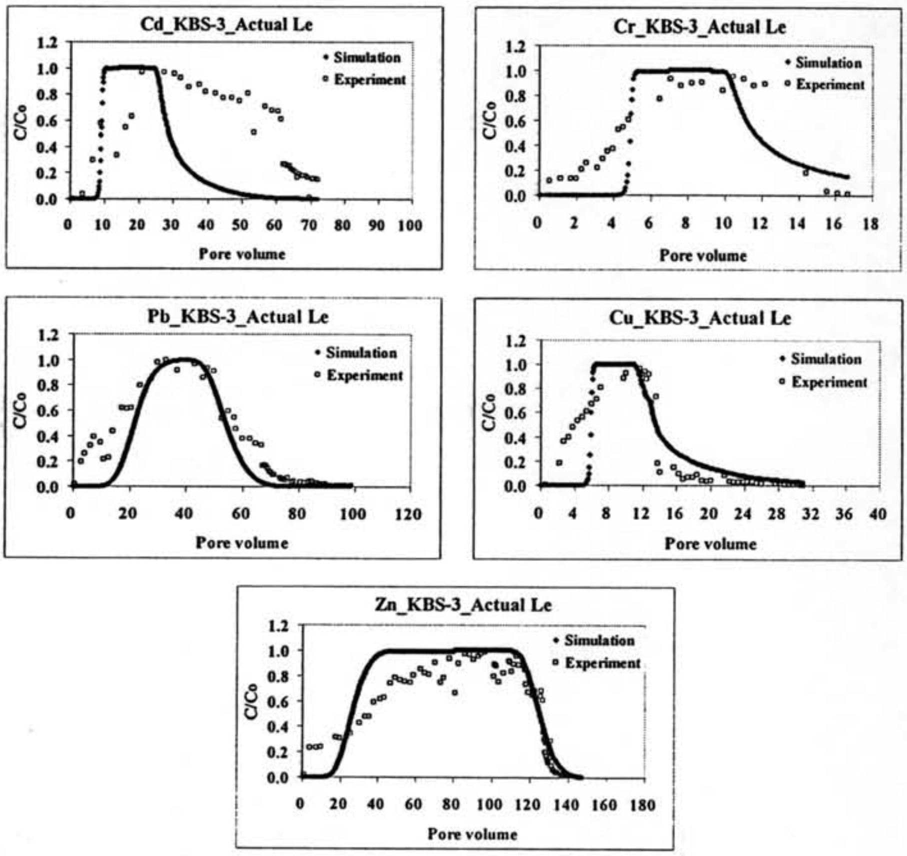

Figure 6.3 Breakthrough curves of Cd, Cr, Pb, Cu, and Zn of KBS-3 soil treated with actual leachate

Considering breakthrough curves of soil treated with actual leachate, KBS-2 soil, Cd started breakthrough curves at pore volume 10 while breakthrough curves of Cr, Cu, and Pb were observed at pore volume 10, 9.7, and 12.9, respectively. Breakthrough curve of Zn exhibited at pore volume 98.1. These shape of breakthrough presented long-tailed desorption process. The heavy metals adsorption increased in the following order Zn > Pb > Cd > Cr > Cu. The breakthrough curves of Cd, Cr, Cu, Pb, and Zn in KBS-3 soil were recorded at pore volume 23, 9.3, 10.3, 32.7, and 98.3, respectively. The high affinity sequence of heavy metals in KBS-3 soil treated with actual leachate is in the order of Pb > Zn > Cd > Cu > Cr. Column experiment in soil treated with synthetic leachate revealed that Cd, Cr, Cu, and Zn started breaking through at pore volume 111, 11.5, 11.4, and 167, respectively in KBS-2 while breakthrough curve of Pb was not reached the unity of one. Breakthrough curves of heavy metals in KBS-3 soil were presented at pore volume 196.6, 9.3, 6.7, and 157.9 for Cd, Cu, Cr, and Zn, respectively.

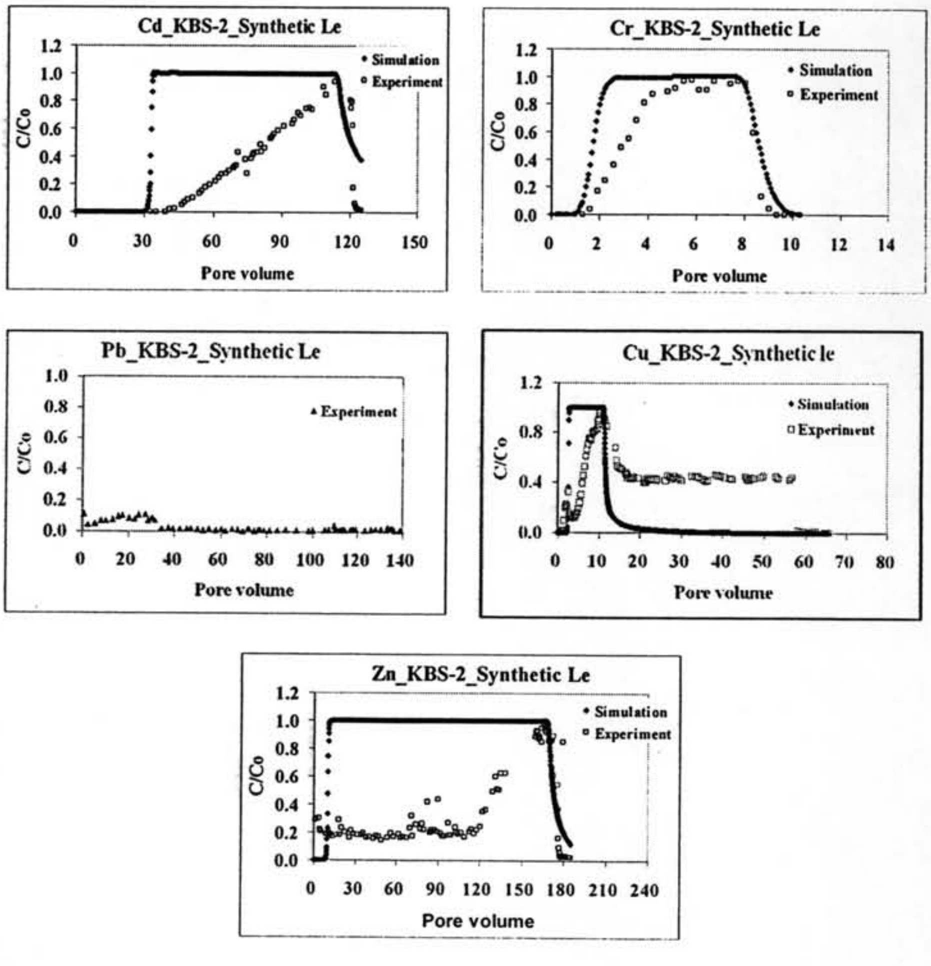

Figure 6.4 Breakthrough curves of Cd, Cr, Pb, Cu, and Zn of KBS-2 soil treated with synthetic leachate

Again, breakthrough curve of Pb was not reached at the unity of one. This is because Pb is strongly adsorbed and the long time required to conduct the experiment would result in varying input concentrations due to precipitation reactions (Pang et al., 2002). The selectivity sequence of sorption capacity in the order of Pb > Cd > Zn > Cu > Cr.

Results of study depicted that the high retention heavy metals was observed in soil treated with synthetic leachate. It can imply that the organic and inorganic substance containing in actual leachate play important role in promoting the mobility of heavy metals in Kham Bon landfill soil. Moreover, these affinity sequences of retention of heavy metal in column breakthrough curve confirmed the batch sorption study. Moreover, it can be observed that after flushing with deionized water as natural leaching the very steep slope of the desorption front of heavy metal indicated the small amount of heavy metal was left in the column as can be seen from Cr and Zn behavior. These may indicate outer-sphere complex interaction.

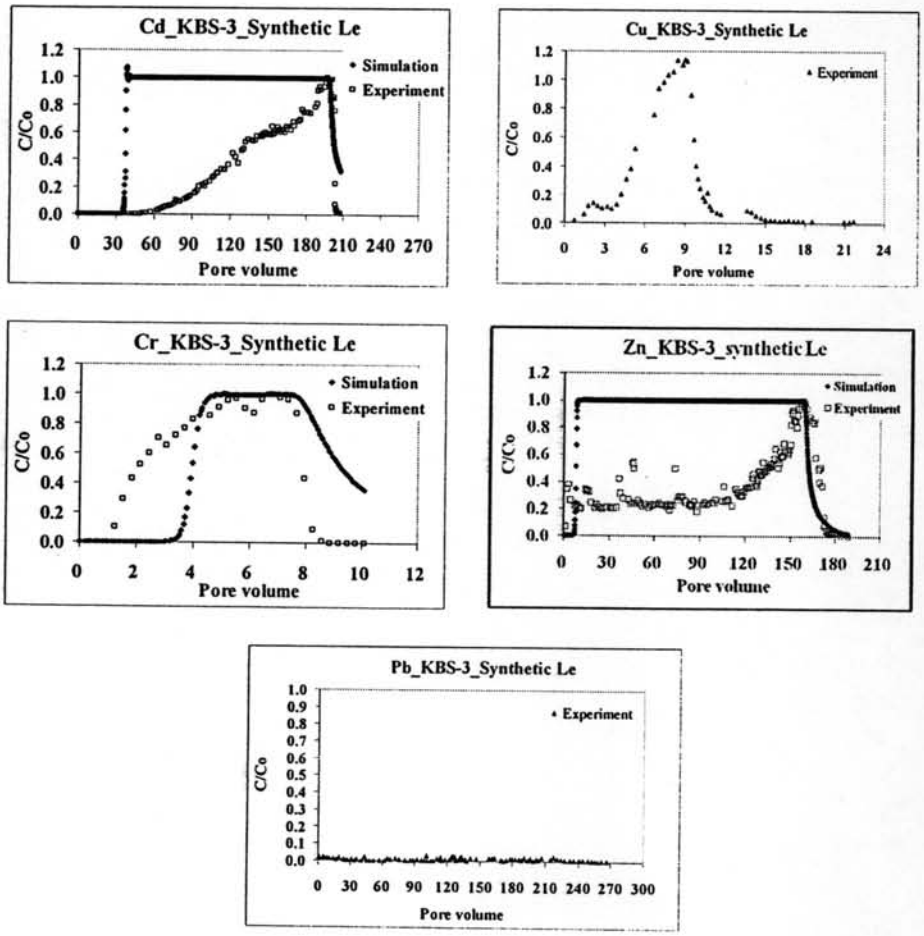

Figure 6.5 Breakthrough curves of Cd, Cr, Pb, Cu, and Zn of KBS-3 soil treated with synthetic leachate

The breakthrough curves are simulated using HYDRUS 2D Model. Langmuir type parameters obtained from batch experiment were performed to this simulation. Result showed that parameters from batch test failed significantly to describe the experimental breakthrough curve of Cd, Pb, and Zn. The unsuccessful results for local equilibrium assumption model were reported (Osathaphan, 2001)

The early slope of the breakthrough curve of these at the adsorption front was steep and followed by a slower increase toward the C/Co reached the unity one. The shape of all breakthrough curves showed non-ideal behavior with asymmetrical shape and long-tailing. Asymmetrical Breakthrough curves with long tailing behavior were observed in all soil which is indicative of both nonlinear and rate-limit adsorption. (Pang et al., 2002). Moreover, the selectivity sequence of these soils displayed in the same pattern but different in amount of sorbed metals. There are other factors that affected to the discrepancy of breakthrough curve: the pore velocity and retardation factor (Pang et al., 1999; Simpson et al., 2004; Pang et al., 2005). At the low flow, the metals have a longer retention times in soil columns allowing more complete sorption. And, retardation value increased significantly when the flow is dropped from the intermediate flow to the low flow. Cadmium, copper and zinc in all soil and all treatment were interfered by retardation mechanism

6.1.3 Competitive Metals Transport Modeling

Breakthrough curves of competitive metals in soil with treated actual leachate are shown in Figures 6.6 to 6.7. The breakthrough curve of cadmium showed a dip from C/Co = 1 to C/Co = 0.8 after the competitive ions were introduced in the column experiment. This depicted the enhancement an effect of other metals in the system. Breakthrough curves of KBS-2 soil treated with actual leachate begun at pore volume 10.8, 3, 87, and 102 for Cr, Cu, Cd, Zn, respectively and pore volume yielding breakthrough curve for KBS-3 soil was observed at 12, 8.7, 96, and 99 for Cr, Cu, Cd, and Zn, respectively. It can be seen that breakthrough curve of Pb increased slowly to reach the unity one. The sequence of retention of heavy metals in decreasing order is Pb > Zn > Cd > Cr > Cu; Pb > Zn > Cd > Cr > Cu for KBS-2 and KBS-3 soil respectively. Figures 6.8 to 6.9 showed transport of competitive ions in soil treated with synthetic leachate. Concerning with KBS-2 soil, Cr started breaking through curve at pore volume 32 while Cu showed lowest metal retention at pore volume 7.15 whereas breakthrough curve of Cd and Zn were revealed at pore volume 136 and 167, respectively. The affinity sequence of heavy metals interacted with KBS-2 soil in decreasing order of Pb > Zn > Cd > Cr > Cu.

Maximum adsorption capacity and binding energy constants obtained from the Langmuir isotherm was performed for breakthrough curve fitting using the HYDRUS 2D model. Figures 6.6 to 6.9 also show the prediction of model transport in all soil. The model prediction revealed that the breakthrough curve is unfit because the portion C/Co not reached to one; the fluctuation of breakthrough curves themselves; the desorption front, and this breakthrough did not fit with Langmuir isotherm.

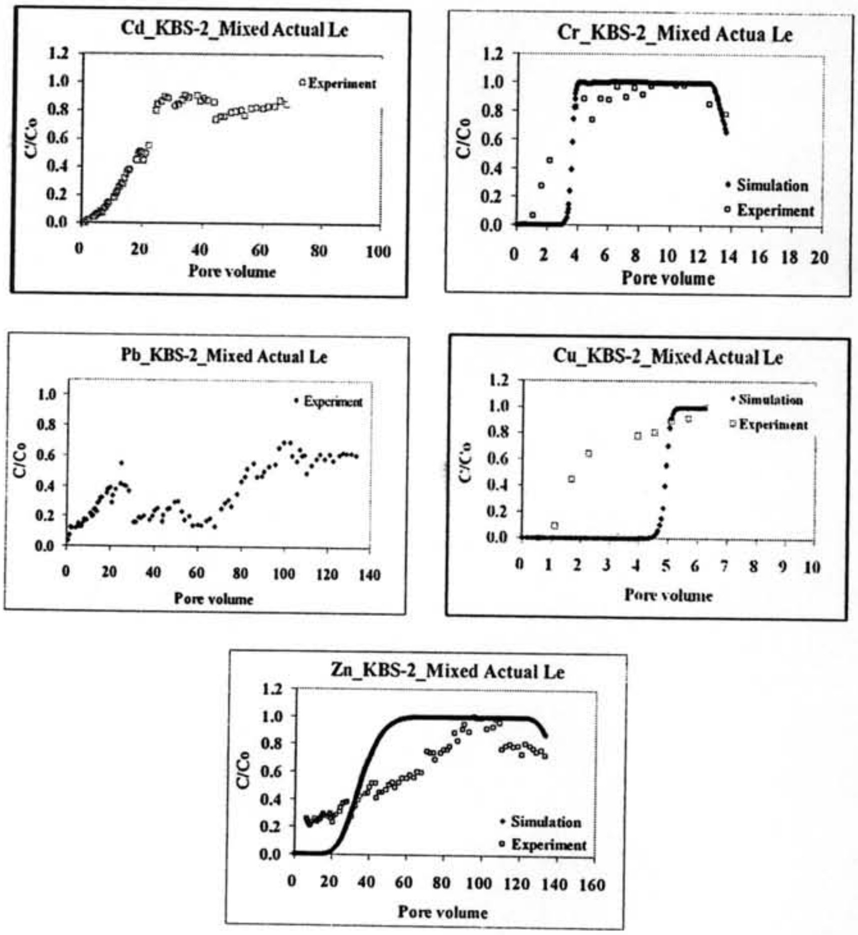

Figure 6.6 Breakthrough curves of competitive metals of KBS-2 soil treated with actual leachate

Due to the failure to fit of breakthrough regarding retardation in soil column, R_{area} method is an alternative to calculate the retardation of heavy metals in each soil (Maraqa, 2001). In the area method, the retardation coefficient (R_{area}) was calculated as :

$$R_{area}=PV_1-\sum_{i=0}^{PV1}(C/C_o)\Delta PV \tag{6.1}$$

where C is the effluent concentration, Co is the influent concentration, and PV_1 is the number of pore volumes at which the relative concentration is 1.

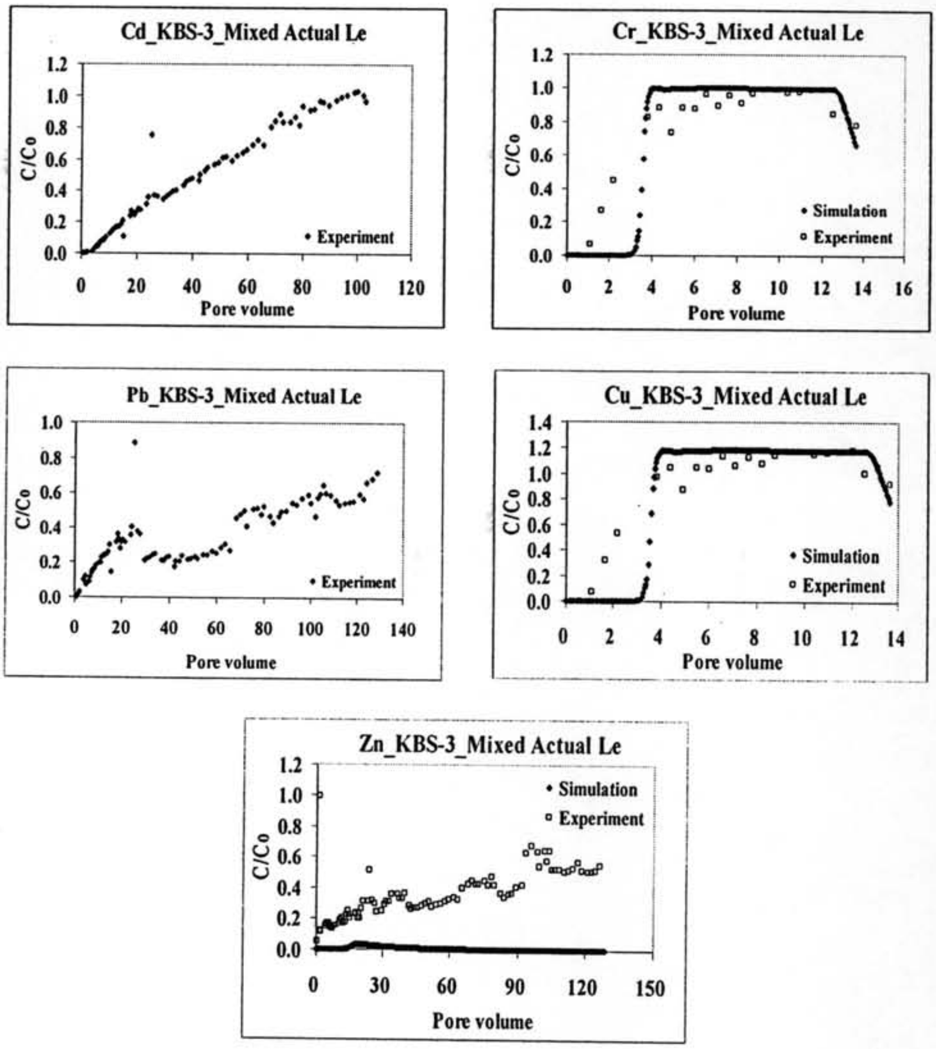

Figure 6.7 Breakthrough curves of competitive metals of KBS-3 soil treated with actual leachate

Apart from retardation factor, dispersion coefficient of each soil can be calculated from column test. Dispersion coefficient can be calculated from longitudinal dispersivity (0.2934 cm) which obtained from tracer analysis multiply by pore water velocity (cm sec^{-1}). Parameters calculations are given in Table 6.2.

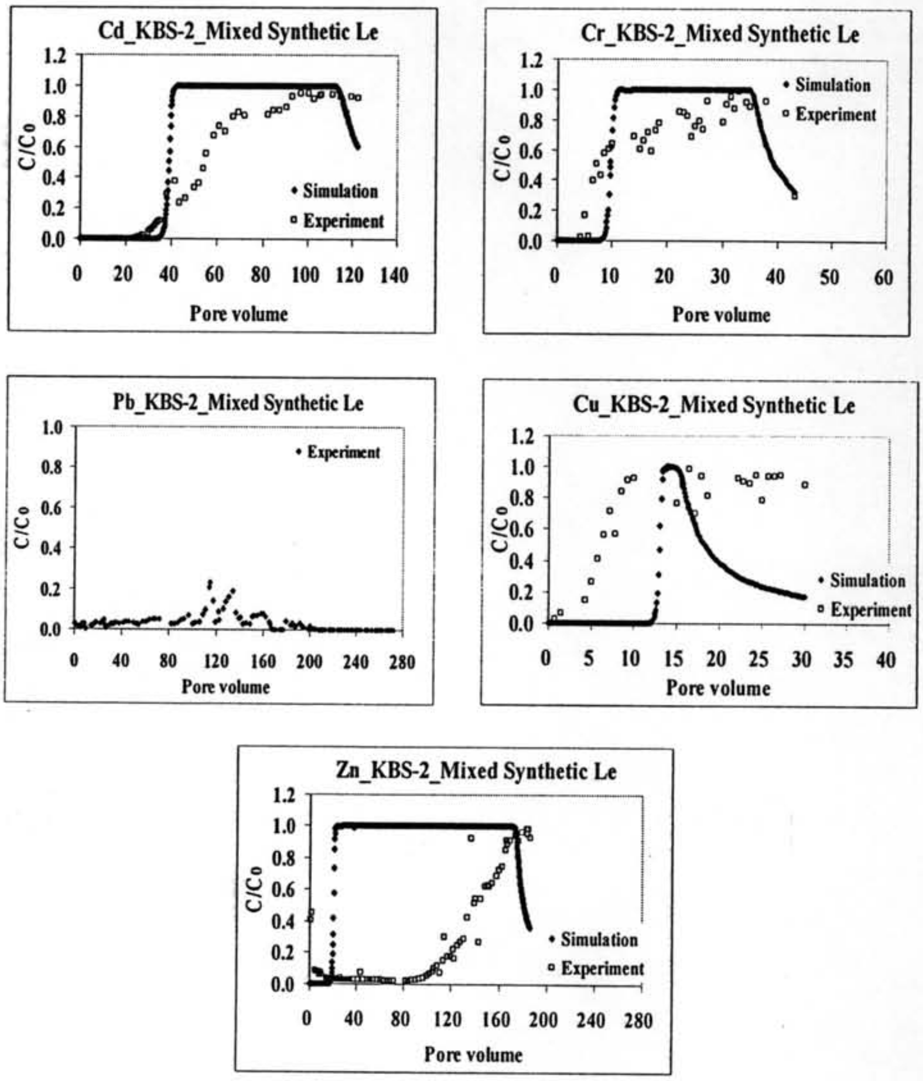

Figure 6.8 Breakthrough curves of competitive metals of KBS-2 soil treated with synthetic leachate

As can be seen in Table 6.1, the highest retardation of Zn except Pb was observed in the experiment while the lowest retardation was Cu. The retardation value of Zn and Cd was in agreement with Pang et al., (2005). It should be noted here that the retardation factors estimated in this study is applicable only to the specific conditions of this study.

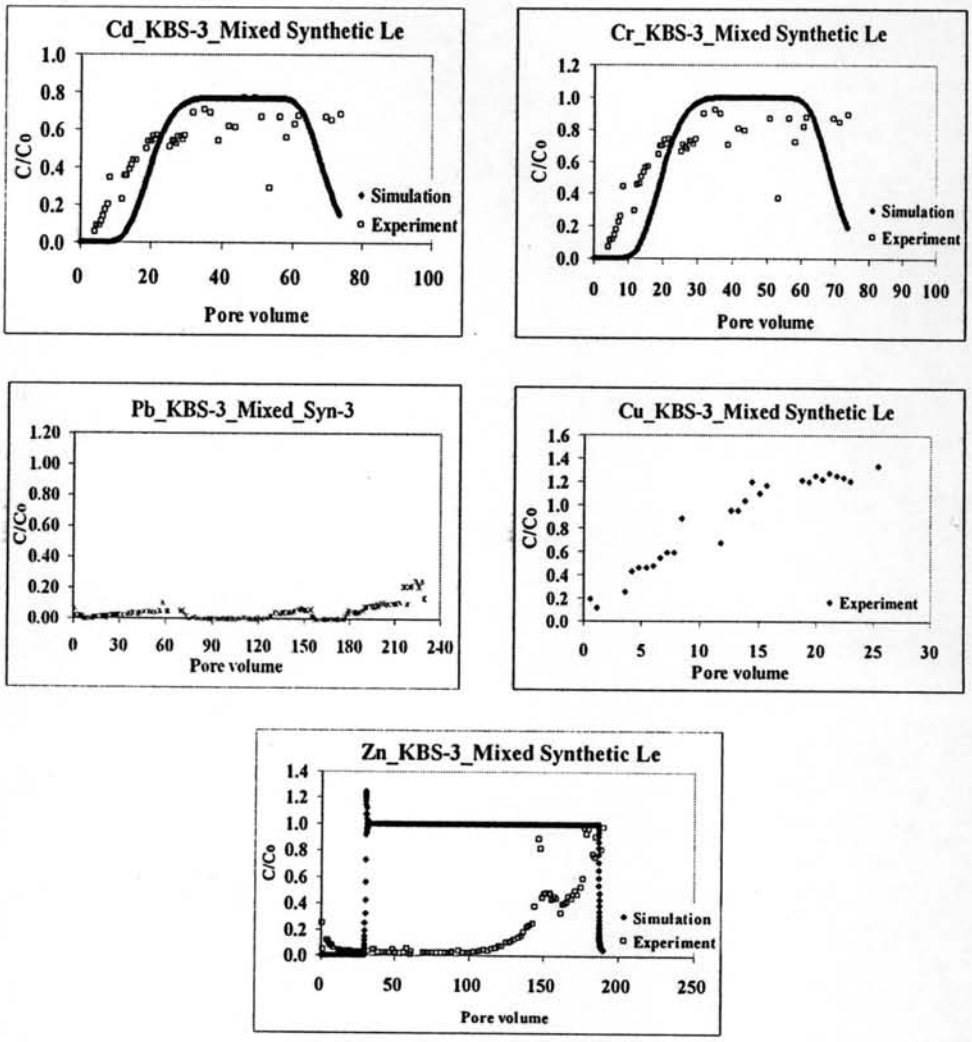

Figure 6.9 Breakthrough curves of competitive metals of KBS-3 soil treated with actual leachate

Table 6.2 Parameters calculation from column test

Soil type	Solution condition	Column No	Heavy metal	R_{area}	D (cm^2/sec)
KBS-2	Actual	1	Cd	5.16	2.40x10^{-2}
		2	Cr	4.81	6.01x10^{-2}
		3	Pb	5.96	2.19x10^{-2}
		4	Cu	4.03	5.03x10^{-2}
		5	Zn	36.57	6.46x10^{-2}
KBS-3	Actual	6	Cd	12.60	5.70x10^{-2}
		7	Cr	4.46	5.43x10^{-2}
		8	Pb	15.15	5.43x10^{-2}
		9	Cu	4.72	5.21 x10^{-2}
		10	Zn	27.13	6.30 x10^{-2}
KBS-2	Synthetic	11	Cd	81.32	6.34 x10^{-2}
		12	Cr	3.18	6.34 x10^{-2}
		13	Pb	-	5.88 x10^{-2}
		14	Cu	4.84	5.26 x10^{-2}
		15	Zn	-	7.27 x10^{-2}
KBS-3	Synthetic	16	Cd	135.73	6.04 x10^{-2}
		17	Cr	4.60	5.89 x10^{-2}
		18	Pb	-	6.67 x10^{-2}
		19	Cu	6.12	6.73 x10^{-2}
		20	Zn	8.77	5.74 x10^{-2}
KBS-2	Competitive Actual leachate	21	Cd	1.22	5.57 x10^{-2}
			Cr	-	
			Pb	-	
			Cu	4.62	
			Zn	48.39	
KBS-3	Competitive Actual leachate	22	Pb	-	5.25 x10^{-2}
			Cd	44.78	
			Cr	3.07	
			Cu	2.42	
			Zn	1.33	
KBS-2	Competitive Synthetic leachate	23	Cd	48.72	7.05 x10^{-2}
			Cr	13.09	
			Pb	-	
			Cu	6.37	
			Zn	123.27	
KBS-3	Competitive Synthetic leachate	24	Cd	12.01	5.80 x10^{-2}
			Cr	-	
			Pb	-	
			Cu	-	
			Zn	157.32	

6.2 Environmental Implication

The retardation factor obtained from batch experiment using equation 5.1 is shown in Table 6.3 and the retardation factor estimated from transport model is presented in Table 6.4. Result from Table 6.3 reveal that the higher retardation factor of soil treated with actual and synthetic leachates was observed in monometal than competitive metals. When comparing the retardation factor of soil treated with actual leachate to soil treated with synthetic leachate, it was seen that the retardation factor of soil treated with synthetic was higher than that of soil treated with actual by a factor of 1 to 9.

Table 6.3 Retardation factor calculated from sorption experiment

Properties		Retardation Factor			
		Soil treated with actual leachate		Soil treated with synthetic leachate	
Sample No.	Metals	Monometal	Competitive metals	Monometal	Competitive metals
KBS-1	Cd	193	154	208	192
	Cr	110	47	317	15
	Pb	376	3939	2834	4453
	Cu	89	67	171	137
	Zn	462	2433	895	95
KBS-2	Cd	40	43	65	37
	Cr	44	18	250	12
	Pb	135	36	171	3344
	Cu	14	17	19	29
	Zn	47	136	42	319
KBS-3	Cd	51	72	104	78
	Cr	43	70	271	10
	Pb	130	129	1123	547
	Cu	21	2616	19	21
	Zn	58	169	72	191

The compared values of R_f were determined from the batch experiment to the values of R_f estimated from transport model (Table 6.4), it is indicated that the retardation factor calculated from the batch experiment was observed higher than the retardation factor obtained from transport model. These may be resulting from (i) high solution-to-soil ratio in batch studies, and (ii) shaking and centrifuging samples in batch studies. These conditions would lead into higher adsorption capacities for the batch conditions. However, the retardation factor obtained from both experiment were expressed the affinity sequence in the same order of Pb > Zn > Cr > Cd > Cu.

Table 6.4 Retardation factor calculated from transport model

Properties		Retardation Factor			
		Soil treated with actual leachate		Soil treated with synthetic leachate	
Sample No	Metals	Monometal	Competitive metals	Monometal	Competitive metals
KBS-2	Cd	5.16	1.22	81.32	48.72
	Cr	4.81	a	3.18	13.09
	Pb	5.96	a	a	a
	Cu	4.03	4.62	4.84	6.37
	Zn	36.57	48.39	a	123.27
KBS-3	Cd	12.6	a	135.73	12.01
	Cr	4.46	44.78	4.6	a
	Pb	15.15	3.07	a	a
	Cu	4.72	2.42	6.12	a
	Zn	27.13	1.33	8.77	157.32

a : breakthrough was insufficient to estimate sorption parameters

The retardation factors from both experiments in each soil and each treatment can be explained by considering that the KBS-1 soil posses a considerable capacity to attenuate the key inorganic contaminant in landfill leachate. The silty clay loam (KBS-1) may significantly retard the transport of these heavy metals. In contrast to the KBS-2 and KBS-3, they illustrated the lower ability to retard heavy metals into themselves. That means the Kham Bon landfill and it vicinity has a chance to contact with landfill leachate. This reason can be described by considering that (i) physical and chemical properties of the KBS-2 and KBS-3 soils display the lower of: clay content; cation exchange capacity; organic matter and Fe-Mn oxide content. These properties play important role in retarding heavy metals in soil, (ii) these soil are deposited in the direction of discharging of landfill leachate. Therefore, location of KBS-2 and KBS-3 soils should be considered as mitigation plan in protecting heavy metals before discharging into environmental receptors.