2001 International Ash Utilization Symposium, Center for Applied Energy Research, University of Kentucky, Paper #86.

http://www.flyash.info

Combined Statistical Model for the Leaching of Heavy Metals from Fly Ash Solidified/Stabilized Wastes

Lucy Mar Camacho[1], Stuart Munson McGee[2]

[1]Universidad Autónoma de Ciudad Juárez, Engineering and Technology Institute, Ave. del Charro 610, Ciudad Juárez, Chih., México; [2]New Mexico State University, Chemical Engineering Department, Box 30001/Dept. 3805/ Las Cruces, New Mexico 88003

KEYWORDS: Cadmium, chromium, aluminum, 2^{6-3} factorial, simplex-centroid, leaching, process parameters, composition variables

ABSTRACT

An adequate method for the disposal of hazardous wastes without causing pollution of groundwater is the solidification/stabilization process. This method consists of combining fly ash material with waste to obtain a solidified form. The United States Environmental Protection Agency (EPA) has developed the toxicity characteristic leaching procedure (TCLP) to establish the environmental acceptability of the solidified/stabilized waste for land disposal. In this test, the waste is contacted with an acidic media under non-equilibrium conditions. The concentration of material leached from the waste after 18 hours of continuous agitation is measured.

The purpose of this article is to present the results obtained from the application of a combined statistical model developed to quantify the amount of heavy metals released from the solidified/stabilized waste to the leaching solution. The TCLP test is run in a semi-batch mode during 100 hours to simulate real environmental conditions. Three metals of relevant importance in the environmental pollution are analyzed namely, chromium, cadmium and aluminum. The model would allow selecting the most appropriate process conditions in the formation of the solidified waste and to minimize the release of the metals. The model is based on a simplex-centroid and a 2^{6-3} fractional factorial experimental design. Fitted equations representing the maximum and final metal release to the leaching solutions are developed. A linear polynomial equation was found to quantify the amount of chromium and cadmium release, while a third degree polynomial was required for the same purpose for aluminum.

INTRODUCTION

In an experimental design, when interest lies in investigating the interactions between mixture variables and process variables as well as in the effect that these interactions might have in the implementation of a process, a combined experimental design can be selected (Cornell and Gorman, 1984; Duineveld et al., 1993; Wieling, et al., 1993; Clayton, et al., 1997). However, since a combined experimental design may become large, fractionation of the design may be necessary. In the case where six process variables at two levels and three mixture components are considered as affecting variables for a given experiment, then 448 model coefficients, or parameters, plus an error term would have to be estimated (Khuri, 1987). Based on that, 449 experiments would have to be performed in order to represent a mixture design with every combination of process variables of the factorial design and to represent a factorial design with all compositions of the mixture (Khuri, 1987). Performance of this number of experiments would be not only economically unfeasible but also time consuming. Therefore a reduction of the total number of experiments is required.

A combination of a simplex-centroid design and a 2^{6-3} fractional factorial design was used in order to investigate the effect of both the mixture components and the process variables on the leaching of heavy metals from fly ash solidified/stabilized waste when subjected to the toxicity characteristic leaching procedure test. The fly ash solidified/stabilized waste in the present study was made by mixing fly ash with a modified evaporator bottoms. In the simplex-centroid mixture design, leaching of heavy metals from the solidified/stabilized waste is analyzed only as a function of the proportions of the components present in the waste. The response is not affected by the amount of the mixture. In the factorial design, leaching is studied only as a function of the combination of the process variables that are present in the solidification/stabilization process. By combining these two models, the effect of both process combinations and mixture components can be statistically analyzed.

Based on previous studies on the effect of process variables in the leaching of heavy metals from fly ash solidified/stabilized wastes (Parsa, 1994), six process variables were selected for the formation of the combined model, namely, acid strength, acid/waste ratio, pH of the slurry, slurry/ash ratio, pressure, and aging of the solidified/stabilized material. Based on solubility-pH diagrams for heavy metals present in an original evaporator bottoms formulation, three metals were also included in the combined model, namely, chromium (III), cadmium (II), and aluminum (III).

In the present paper, the results of the development of a combined statistical model are presented. The model is used to quantify the amount of heavy metals released from the fly ash solidified/stabilized waste to the leaching solution. The Toxicity Characteristic Leaching Procedure (TCLP test) modified to a semi-batch mode and extended to 100 hours is used to simulate the leaching of the metals under real environmental conditions. Induction atomic spectroscopy is used to quantify the amount of metals released during the application of the test. Statistical analysis of the data is made using the software SAS-PROC GLM.

EXPERIMENTAL PROCEDURE

Materials

Leaching samples from solidified/stabilized wastes subjected to the TCLP test were prepared based on the combined statistical experimental design described above. The solidified/stabilized wastes were prepared by mixing grade C fly ash with a simplified hazardous waste formulation. The fly ash was obtained from the Plain Scalante Generation Station in New Mexico. Composition of the fly ash is presented in Table 1 as obtained from the inductively coupled argon plasma spectroscopic analysis conducted by the SWAT laboratory at the New Mexico State University. The simplified formulation was based on an original formulation provided by Los Alamos National Laboratory, and consisted on a simulated evaporator bottoms waste produced during their plutonium purification process. Specifications for the waste are presented in Table 2 as given by Los Alamos National Laboratory (Parsa et al., 1994).

Table 1 Inductively coupled plasma atomic spectroscopic analysis of selected Plain Scalante fly ash.

Test Parameter	Content (mg/kg)	Detection Limit (mg/kg)
Aluminum in digest of solids	93700	10
Arsenic in digest of solids	3.8	0.3
Barium in digest of solids	4644	1
Cadmium in digest of solids	2	1
Calcium in digest of solids	138400	200
Chromium in digest of solids	26	1
Iron in total digest of solids	25400	20
Lead in digest of solids	40	5
Magnesium in digest of solids	18300	10
Mercury in digest of solids	35	20
Total P in solids	3720	1
Selenium in digest of solids	1	1
Silver in digest of solids	less than	1
Sodium in digest of solids	7480	10
Titanium in digest of solids	1250	5

Table 2 Original hazardous evaporator bottoms formulation (Parsa et al., 1994).

Chemical	Formula	Mass (grams)	Concentration (ppm)
Ferric (III) nitrate nonahydrate	$Fe(NO_3)_3.9H_2O$	168.75	112,231
Aluminum nitrate nonahydrate	$Al(NO_3)_3.9H_2O$	53.41	35,521
Calcium nitrate tetrahydrate	$Ca(NO_3)_2.4H_2O$	52.84	35,142
Magnesium nitrate hexahydrate	$Mg(NO_3)_2.6H_2O$	44.88	29,848
Potassium nitrate	KNO_3	56.82	37,789
Ammonium nitrate	NH_4NO_3	50.56	33,626
Sodium nitrate	$NaNO_3$	98.30	65,376
3.5 M nitric acid	HNO_3	411.66	273,783
Cadmium nitrate tetrahydrate	$Cd(NO_3)_2.4H_2O$	1.25	831
Chromium (III) nitrate nonahydrate	$Cr(NO_3)_3.9H_2O$	89.40	59,457
Lead (II) nitrate	$Pb(NO_3)_2$	0.73	486
Water (deionized)	H_20	475.0	316,000

The composition of the simplified formulation varied according to the parameter specifications presented in the combined experimental model. The selection of the three metals included in the formulation was based on the pH at which their minimum solubility occurred (Figure 1). Table 3 gives the composition and parameter ranges of the simplified formulation. The main components of the waste were hydrated metal nitrates, nitric acid and deionized water. Fisher certified standard chemicals, analytical reagent grade, were used to prepare the mixture. Deionized water was obtained via MilliQ® system.

A hydraulic compaction press was required to apply pressure to the fly ash-waste mixture in order to obtain the solidified samples. The hydraulic compaction press consists of a compaction chamber, a hydraulic cylinder with a piston, a pump with 1.5 HP motor, a hydraulic control valve, and a pressure gauge.

Table 3 Simplified Hazardous Evaporator Bottoms Formulation.

Chemical	Formula	Concentration variations
Chromium (III) nitrate nonahydrate	$Cr(NO_3)_3.9H_2O$	500-50,000 ppm
Cadmium nitrate tetrahydrate	$Cd(NO_3)_2.4H_2O$	500-50,000 ppm
Aluminum nitrate nonahydrate	$Al(NO_3)_3.9H_2O$	500-50,000 ppm
Nitric acid	HNO_3	1M-4M
Water (deionized)	H_20	Constant
Sodium hydroxide	NaOH	As required to meet pH of 5-10

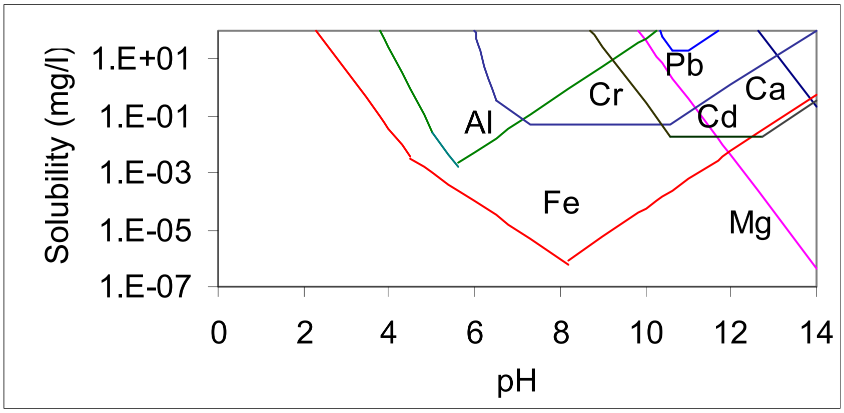

Figure 1 Solubility-pH diagram for the heavy metal in the original simulated hazardous evaporator bottoms formulation (Snoeyink and Jenkins, 1980; Lindsay, 1979; Baes and Mesmer, 1977).

Two TCLP-test agitation apparati, each of them supporting six, 2-liter polyethylene extraction vessels were used to run the TCLP-test in order to cause the leaching of wastes from the solidified samples. Both agitation apparati were capable of rotating the extraction vessels in an end-over-end fashion at 30 rpm as specified by the TCLP test. Concentration of metals leached from the toxicity characteristic leaching procedure was made using an inductively coupled-plasma emission spectrometer model ICP JY38S (Jovin Yvon Emission Instruments).

Procedure

A total of 80 different samples were prepared in such a way that for each of the eight experimental points in the 2^{6-3} fractional factorial design (designated number one through eight), 10 different mixture compositions (designated from letter “a” through “j”) were made. The eight experimental points corresponded to the eight different combinations of the six process variables in the solidification/stabilization process. The ten mixture experiments corresponded to the seven points of the simplex-centroid design plus the three augmented points. Each of the 80 samples was prepared completely independent and in a random order to avoid inaccuracies in the study. In doing this, 100 grams of 1 M or 4 M nitric acid was mixed with the metal nitrates in a ratio of 19:1 or 1996:1, which corresponded to a waste concentration of 50,000 or 500 ppm respectively. After that, sodium hydroxide was added to reach the desired pH of 5 or 10. The slurry was then mixed with fly ash in a ratio of 1:7 or 1:8 and subject to 600 or 3000 psi in the compaction press for approximately 5 seconds. The compacted samples were placed in a plastic bag and aged at room temperature for a period of 24 hours or 28 days. The obtained solidified/stabilized samples weighed 300 grams and had dimensions of 2.5”x5”X0.5”. Table 4 presents the six process variables and the three mixture components in the combined model.

For the application of the TCLP test, 94 grams of the solidified/stabilized sample were pulverized and mixed with 1,880 grams of an acetic acid solution of pH 2.88 ± 0.10. The suspension was then tumbled for 100 hours in the TCLP apparatus. Samples of 4 ml were collected, filtered in 0.6 to 0.8 μm TCLP filters and stored at 4^0C for subsequent metals analysis. Leachate pH was also recorded every hour in the beginning and

Table 4 Combined experimental design for six process variables and three mixture components.

Sample (non-randomized)	Process Variable					
	A	B	C	D	E	F
	(psi)		(days)	(M)		
1a –1j	600	1:7	1	4	10	1991:1
2a –2j	3000	1:7	1	1	5	1991:1
3a – 3j	600	1:8	1	1	10	19:1
4a – 4j	3000	1:8	1	4	5	19:1
5a –5j	600	1:7	28	4	5	19:1
6a – 6j	3000	1:7	28	1	10	19:1
7a – 7j	600	1:8	28	1	5	1991:1
8a – 8j	3000	1:8	28	4	10	1991:1

then with decreasing frequency until the TCLP test finished.

COMBINED STATISTICAL MODEL

For the development of the combined statistical model, a simplex-centroid design and a 2^{6-3} fractional factorial design were selected. The simplex-centroid design was selected in order to study the leaching behavior of the three metals as a function of their respective concentration in the simplified formulation of the solidified/stabilized waste. These metals were chromium, cadmium, and aluminum and were represented as x_1, x_2, and x_3 respectively. The design consisted of 10 experimental points: 3 points for the pure components (for example 1,0,0), 3 points for the binary mixtures (for example1/2,1/2,0), an overall centroid point (1/3,1/3,1/3) and three additional points located at the interior of the experimental space (Table 5).

Table 5 Location of points in the simplex-centroid mixture design.

Location	No.	x_1	x_2	x_3
Vertices	a	1	0	0
	b	0	1	0
	c	0	0	1
Edges	d	½	½	0
	e	½	0	1/2
	f	0	½	1/2
Centroid	g	1/3	1/3	1/3
Additional	h	2/3	1/6	1/6
	i	1/6	2/3	1/6
	j	1/6	1/6	2/3

These three additional points were included to check the fit of the model inside the experimental space. The experimental region was represented on a tri-linear coordinate system as shown in Figure 2.

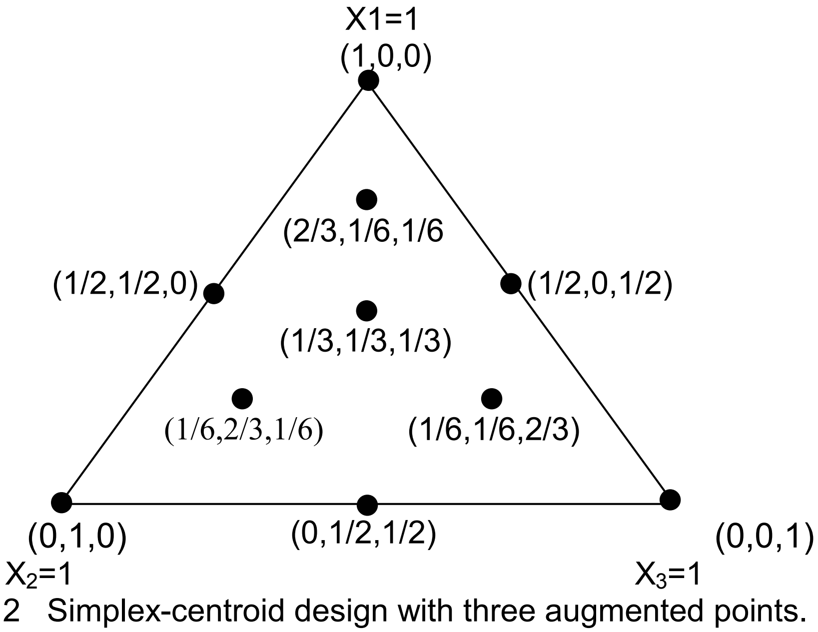

Figure 2 Simplex-centroid design with three augmented points.

The 2^{6-3} fractional factorial design was selected in order to study the leaching of the three metals as a function of the process variables that may affect the solidification/stabilization process. These variables were pressure, slurry/ash ratio, aging, acid strength, pH of the slurry, and waste/acid ratio and were represented by the capital letters A through F respectively (Table 6). The assignment of letters to the factors was made randomly to avoid sources of errors (Mason et al., 1989). The lower and upper levels to which each factor was constrained were coded with -1 and +1, respectively (Table 7).

By running the 2^{6-3} fractional factorial design, that is, an 8th fraction of a full 2^6 factorial design, the number of experiments required to study the effect of the six process variables was reduced from 64 to 8. This reduction was possible by selecting a resolution III design which assumes first, that high order interactions are negligible, second, that main effects are not confounded with main effects, and third, that main effects are confounded with two-factor and higher-order interactions. With this model, it was possible to obtain economically accurate information on the effect of the six process variables.

Prior to the statistical analysis, standardization of the process variables was required in order to control their relative effects on the response. Standardization of the mixture component variables x1, x2 and x3, representing chromium, cadmium and aluminum concentrations, respectively,

Table 6 Range of analysis for process factor variables.

Factor	Coded Identification	Levels
Acid strength	D	1M - 4M
Acid:waste	F	19:1- 1991:1
pH of slurry	E	5 - 10
Ash:slurry	B	1:7 - 1:8
Pressure	A	600 psi - 3000 psi
Aging	C	1 day - 28 days

Table 7 2^{6-3} Fractional factorial design (coded).

Run	Constant	Factor Combination						Factor Interaction		
	I	A	B	C	D = AB	E =AC	F =BC	ABD	ACE	BCF
1	+	-	-	-	+	+	+	+	+	+
2	+	+	-	-	-	-	+	+	+	+
3	+	-	+	-	-	+	-	+	+	+
4	+	+	+	-	+	-	-	+	+	+
5	+	-	-	+	+	-	-	+	+	+
6	+	+	-	+	-	+	-	+	+	+
7	+	-	+	+	-	-	+	+	+	+
8	+	+	+	+	+	+	+	+	+	+

was not required since simplex-centroid designs are specified in terms of coded components values that are suitably standardized (mason et al., 1989).

RESULTS AND DISCUSSION

The complete results from the 80 experimental samples were reported by Camacho (2000). For the statistical analysis only maximum and final concentrations obtained after 100 hours of leaching were considered. The maximum concentrations represented the maximum amount of metal released from the solidified/stabilized waste to the leaching solution. A graphical representation of the combined model used to analyze the concentration data for the 80 samples is presented in Figure 3.

In general, two different behaviors for the metals studied were observed during the application of the TCLP test. Some of the samples subjected to 24 hours of solidification showed a maximum chromium concentration during the first hours of the leaching process. After certain time the concentration decreased slowly and reached a final concentration of about 0.5 ppm, which is the final concentration for most of the samples. On the other hand, the chromium concentration for the majority of the samples subjected to 28 days of stabilization showed an asymptotic increase and reached equilibrium after approximately 25 hours of leaching. For the case of cadmium, a peak was also observed in all the samples subjected to 28 days of stabilization, while the asymptotic increase until the concentration reached equilibrium was observed in the majority of the samples subjected to 24 hours of stabilization. An aluminum peak was also observed in all samples subjected either to 24 hours or 28 days of stabilization but the first (24 hours) required more time to equilibrate. Figures 4, 5 and 6 respectively, present representative samples of the observed chromium, cadmium and aluminum concentration behavior. The application of the combined statistical model helped in determining the process and mixture conditions that contributed to the observed metals behavior. The results are presented as follows.

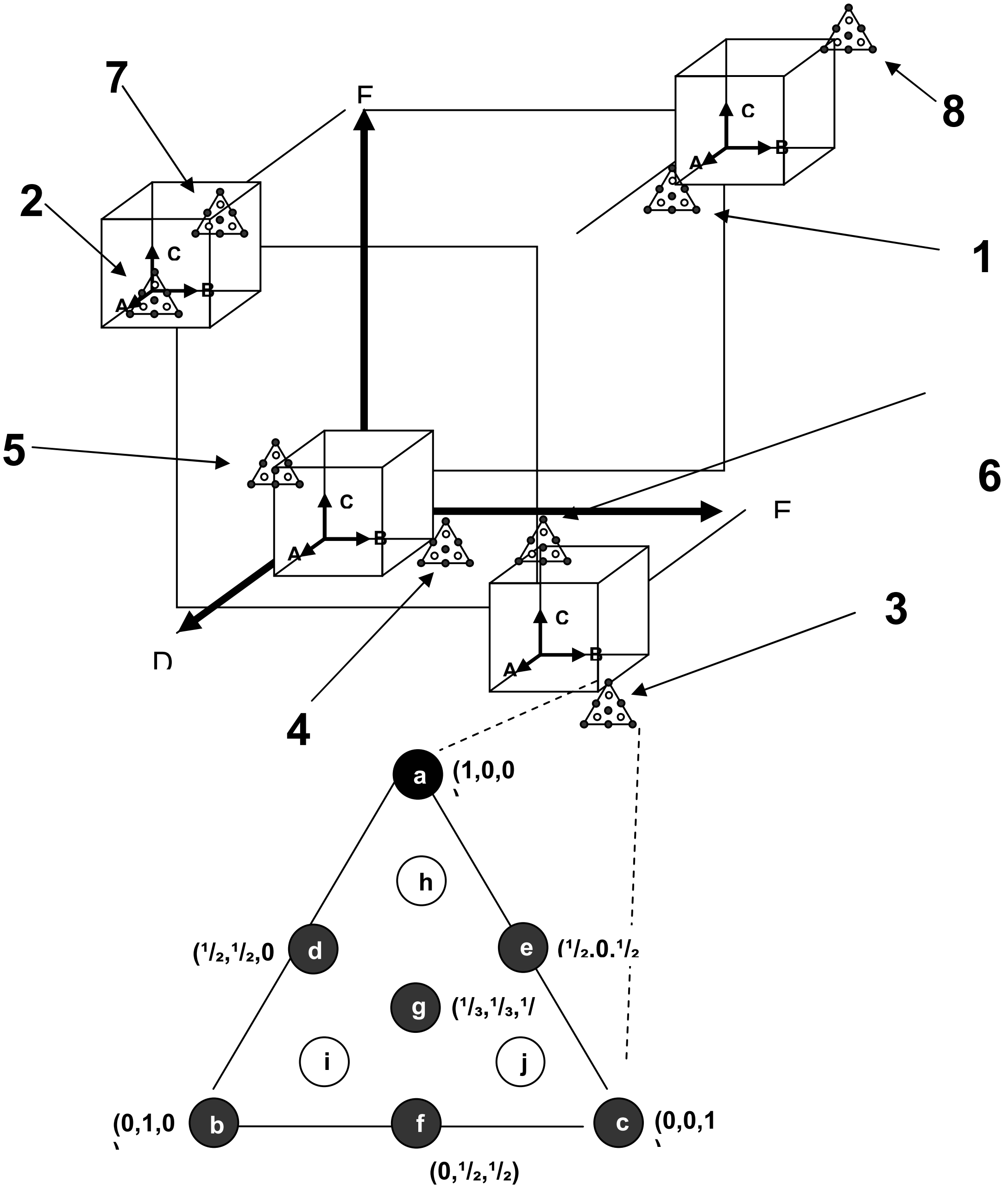

Figure 3 Graphical representation of the experimental space.

The process factor combinations are represented by the cubic spaces while the composition factor space is represented by the triangular spaces. Within the composition space, the solid circles represent points used to determine the coefficients of the statistical model while the open circles represent points used to determine the model's lack-of-fit. The numbers beside each triangle are the coding used to identify the various process factor combinations in the dissertation and the letters inside the points in the composition space are the coding used to identify the mixture combinations in the dissertation.

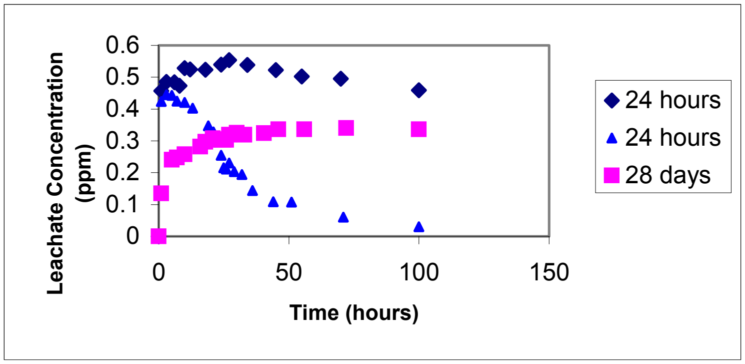

Figure 4 Leaching behavior of chromium for selected samples after 24 hours or 28 days of stabilization.

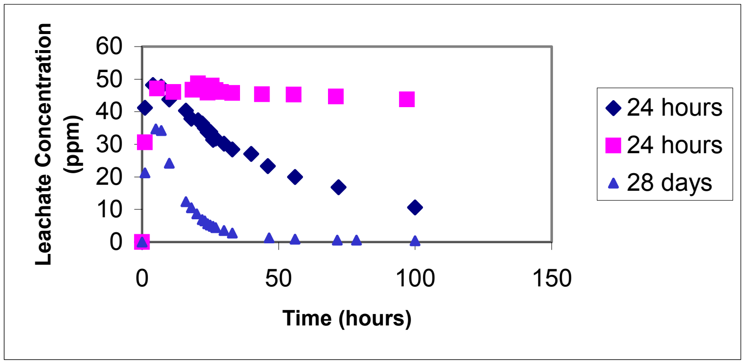

Figure 5 Leaching behavior of cadmium for selected samples after 24 hours or 28 days of stabilization.

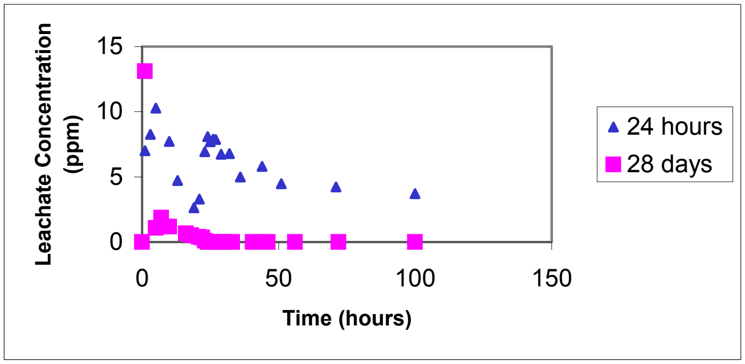

Figure 6 Leaching behavior of aluminum for selected samples after 24 hours or 28 days of stabilization.

Statistical Model Approach

Equation 1was used to represent the simplex-centroid design and is a special cubic polynomial (Khuri and Cornell, 1987):

$$y(x) = \beta_1 x_1 + \beta_2 x_2 + \beta_3 x_3 + \beta_{12} x_1 x_2 + \beta_{13} x_1 x_3 + \beta_{23} x_2 x_3 + \beta_{123} x_1 x_2 x_3 + \varepsilon \qquad (1)$$

Considering the assumption of linearity in the factor effects when applying a two-level factorial design (Montgomery, 1997), a linear regression equation (Equation2) was considered appropriate to represent the main effect of the six process parameters in the 2^{6-3} fractional:

$$y(z) = \alpha_0 + \alpha_a z_a + \alpha_b z_b + \alpha_c z_c + \alpha_d z_d + \alpha_e z_e + \alpha_f z_f + \varepsilon \qquad (2)$$

The model equation was developed by taking the coefficients of the cubic polynomial as the response variables for the process-factor, fractional factorial experiment. In this way, a single polynomial expression was obtained to describe both the effects of composition and processing on the predicted metals concentration. The equation was given as follows Equation3:

$$
\begin{aligned}
Y(x,z) = {} & (\alpha_0 + \alpha_a z_{ai} + \alpha_b z_{bi} + \alpha_c z_{ci} + \alpha_d z_{di} + \alpha_e z_{ei} + \alpha_f z_{fi})\beta_1 x_1 + \\
& (\alpha_0 + \alpha_a z_{ai} + \alpha_b z_{bi} + \alpha_c z_{ci} + \alpha_d z_{di} + \alpha_e z_{ei} + \alpha_f z_{fi})\beta_2 x_2 + \\
& (\alpha_0 + \alpha_a z_{ai} + \alpha_b z_{bi} + \alpha_c z_{ci} + \alpha_d z_{di} + \alpha_e z_{ei} + \alpha_f z_{fi})\beta_3 x_3 + \\
& (\alpha_0 + \alpha_a z_{ai} + \alpha_b z_{bi} + \alpha_c z_{ci} + \alpha_d z_{di} + \alpha_e z_{ei} + \alpha_f z_{fi})\beta_{12} x_1 x_2 + \\
& (\alpha_0 + \alpha_a z_{ai} + \alpha_b z_{bi} + \alpha_c z_{ci} + \alpha_d z_{di} + \alpha_e z_{ei} + \alpha_f z_{fi})\beta_{13} x_1 x_3 + \\
& (\alpha_0 + \alpha_a z_{ai} + \alpha_b z_{bi} + \alpha_c z_{ci} + \alpha_d z_{di} + \alpha_e z_{ei} + \alpha_f z_{fi})\beta_{23} x_2 x_3 + \\
& (\alpha_0 + \alpha_a z_{ai} + \alpha_b z_{bi} + \alpha_c z_{ci} + \alpha_d z_{di} + \alpha_e z_{ei} + \alpha_f z_{fi})\beta_{123} x_1 x_2 x_3
\end{aligned}
\qquad (3)
$$

In Equation, x_1, x_2 and x_3 represent the concentration of chromium, cadmium and aluminum in the solidified waste respectively. The β coefficients represent the linear and non-linear effects of the mixture components on the mixture design, the z's are coded variables ($-1 \leq z_i \leq +1$) of the six process variables A, B, C, D, E and F present in the factorial design, namely pressure, ash/slurry ratio, aging, acid strength, pH of slurry and acid/waste ratio respectively and the α's are regression coefficients representing the linear effect of the process variables on the factorial design.

Equation 3 was simplified with Equation 4:

$$Y = b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3 \qquad (4)$$

where the b coefficients are functions of the process variables as given by Equations 5-11:

$$b_1 = \gamma_{10} + \sum_{i=a}^{f} \gamma_{1i} z_i \tag{5}$$

$$b_2 = \gamma_{20} + \sum_{i=a}^{f} \gamma_{2i} z_i \tag{6}$$

$$b_3 = \gamma_{30} + \sum_{i=a}^{f} \gamma_{3i} z_i \tag{7}$$

$$b_{12} = \gamma_{120} + \sum_{i=a}^{f} \gamma_{12i} z_i \tag{8}$$

$$b_{13} = \gamma_{130} + \sum_{i=a}^{f} \gamma_{13i} z_i \tag{9}$$

$$b_{23} = \gamma_{230} + \sum_{i=a}^{f} \gamma_{23i} z_i \tag{10}$$

$$b_{123} = \gamma_{1230} + \sum_{i=a}^{f} \gamma_{123i} z_i \tag{11}$$

The γ coefficients are obtained from Equations 12-17:

$$\gamma_{io} = \beta_i \alpha_0 \tag{12}$$

$$\gamma_{ijo} = \beta_{ij} \alpha_0 \tag{13}$$

$$\gamma_{ijko} = \beta_{ijk} \alpha_0 \tag{14}$$

$$\gamma_{ii} = \beta_i \alpha_i \tag{15 }$$

$$\gamma_{iji} = \beta_{ij} \alpha_i \tag{16}$$

$$\gamma_{ijki} = \beta_{ijk} \alpha_i \tag{17}$$

The subscript i on the process variable z represents the lower, -1, or the higher level, +1. With help of the statistical software SAS-PROC GLM (General Linear Model Procedure) (SAS Institute Inc, 1990a) the least square technique was applied to estimate the regression coefficients of the model. Camacho (2000) presented the details on the technique.

In order to obtain a constant variance in the results when running the SAS program, a Poisson transformation, which is a modification of the square root transformation $Y_i^* = \sqrt{(1+Y_i)}$, was applied. Figure 7 shows the experimental data versus the predicted data using the Poisson transformation for maximum and final metals concentration.

Statistical Analysis

Initially a test of significance about the form of the model (Equation 4) was performed in order to determine if the special cubic polynomial Equation 1that represented the effect of the mixture concentrations was required to explain the metals leaching, or if a lower degree polynomial was sufficient to meet same purpose. This was done by fitting the combined model with help of the ANOVA table of the SAS-GLM program. The details about the test are given by Camacho (2000). Results from the test are presented in Tables 8 and 9.

It was found that second and higher order terms are insignificant for the models that represented the maximum and final chromium and cadmium concentrations. That is, $\gamma_{ijk} = \gamma_{ij} = 0$ since their calculated F-values do not exceed the theoretical $F_{\alpha, r, n-p-1}$ value at the α=0.05 level of significance. Second and higher order terms were also found

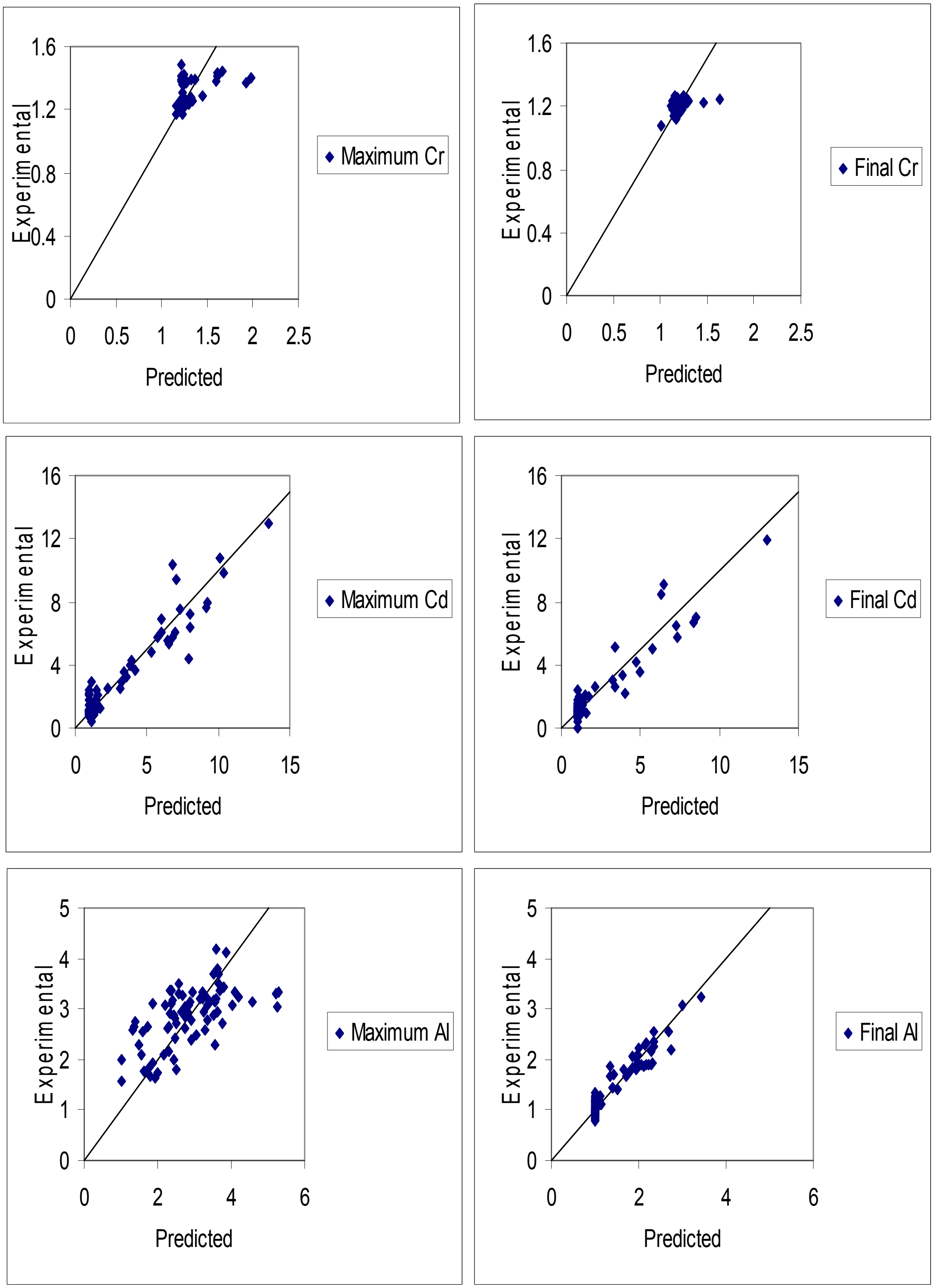

Figure 7 Experimental versus predicted data using Poison transformation for maximum and final metals concentration.

Table 8 Test of significance about the polynomial form of the transformed maximum metal concentration models.

Model	n	P	r	SSE	F_{cal}	$F_{005,7,30}$
Chromium						
Combined with special cubic R^2 = 0.9953 ESD=0.1410	80	49	7	0.616	0.33	3.38
Combined with quadratic R^2 = 0.9950 ESD= 0.1321	80	42	21	0.663	1.44	1.97
Combined with linear R^2 = 0.9910 ESD= 0.1429	80	21		1.205		
Cadmium						
Combined with special cubic R^2 = 0.9763 ESD= 1.029	80	49	7	32.800	0.22	3.38
Combined with quadratic R^2 = 0.9751 ESD= 0.9526	80	42	21	34.480	1.18	1.97
Combined with linear R^2 = 0.9584 ESD=0.9769	80	21		57.637		
Aluminum						
Combined with special cubic R^2 = 0.9910 ESD= 0.7179	80	49	7	15.976	3.09	3.38
Combined with quadratic R^2 = 0.9619 ESD=0.8506	80	42	21	27.491	0.958	1.97
Combined with linear R^2 = 0.9412 ESD= 0.8482	80	21		42.440		

Table 9 Test of significance about the polynomial form of the transformed final concentration models.

Model	n	p	r	SSE	F_{cal}	$F_{005,7,30}$
Chromium						
Combined with special cubic $R^2 = 0.9981$ ESD = 0.085	80	49	7	0.223	1.883	3.38
Combined with quadratic $R^2 = 0.9980$ ESD = 0.078	80	42	21	0.231	0.740	1.97
Combined with lineal $R^2 = 0.9972$ ESD = 0.075	80	21		0.328		
Cadmium						
Combined with special cubic $R^2 = 0.9668$ ESD= 0.883	80	49	7	24.175	0.168	3.38
Combined with quadratic $R^2 = 0.9655$ ESD = 0.813	80	42	21	25.125	1.147	1.97
Combined with lineal $R^2 = 0.9430$ ESD = 0.838	80	21		41.481		
Aluminum						
Combined with special cubic $R^2 = 0.9877$ ESD = 0.282	80	49	7	2.465	4.837	3.38
Combined with quadratic $R^2 = 0.9738$ ESD = 0.372	80	42	21	5.247	0.808	1.97
Combined with lineal $R^2 = 0.9621$ ESD = 0.359	80	21		7.591		

insignificant for the model that represented the maximum aluminum concentration. However, higher order terms were found significant for the model that represented the final aluminum concentration. For this metal the null hypothesis of $\gamma_{ijk} = 0$ was rejected against the alternative hypothesis of $\gamma_{ijk} \neq 0$. Therefore, a linear polynomial equation for the mixture components combined with the linear polynomial equation for the process variables was considered sufficient to explain the observed maximum chromium, cadmium and aluminum concentrations as well as the observed final chromium and cadmium concentrations. A third degree polynomial for the mixture components in combination with a linear polynomial equation for the process variables was required to explain the observed final aluminum concentration.

Based on the R^2 values, approximately 99%, 95% and 94% of the variability in the maximum chromium, cadmium, and aluminum concentrations, and 100%, 94%, and 99% of the variability in the final chromium, cadmium, and aluminum final concentrations respectively, was explained with the selected models. The estimated error standard deviations (ESD) were relative small and were considered appropriate for the models.

To validate the adequacy of the selected models, a lack-of-fit test was required. In doing this, the three augmented points of the simplex centroid design (h, i and j) for each of the eight process parameter combinations (1 through 8) were taken as nearest neighbors (Mason et al., 1989). To test the lack-of-fit, a level of significance of 0.05 (α=0.05) was selected. A more in depth analysis is presented in Camacho (2000). Since the calculated F-values were smaller than the theoretical $F_{\alpha,fLOF, fP}$ values, the null hypothesis of adequacy of the models was accepted versus the alternative hypothesis of lack-of-fit. This implied that the terms in the selected models were adequate to capture all of the assignable causes of variation in the response variables. The model for the maximum aluminum concentration showed a similar value for both, calculated and theoretical F-values. This implied that the selected models were just enough to represent its behavior. Results of the test are shown in Tables 10 and 11.

Table 10 Test of lack-of-fit of the fitted linear combined models for maximum metal concentrations.

METAL	SOURCE	D.F.	SS	MS	F_{CALC}	$F_{0.05,42,16}$
Chromium	Model	21	131.17	6.246		
	Error	58	1.205			
	Pure error	16	0.340	0.021		
	Lack-of-fit	42	0.865	0.021	0.97	1.89
Cadmium	Model	21	1326.92	63.187		
	Error	58	57.637			
	Pure error	16	55.128	3.446		
	Lack-of-fit	42	2.509	0.060	0.017	1.89
Aluminum	Model	21	678.98	32.333		
	Error	58	42.444			
	Pure error	16	7.105	0.444		
	Lack-of-fit	42	35.339	0.841	1.895	1.89

Since it was also important to determine if all the individual parameters in the models were statistically significant, a test of hypothesis concerning the individual parameters was also performed. The test consisted on comparing the absolute value of the calculated t-value for each parameter with the two tailed critical t-value at the level of significance α=0.05 and at the degree of freedom associated with the estimate, s^2 = MSE. For the case of the final aluminum concentrations, the null hypothesis H_o: $\gamma_{io} = \gamma_{ijo} = \gamma_{ijko} = \gamma_{il} = \gamma_{ijl} = \gamma_{ijkl} = 0$ was rejected in favor of the hypothesis H_a: $\gamma_{io} \neq 0$, $\gamma_{ijo} \neq 0$, $\gamma_{ijko} \neq$

Table 11 Test of lack-of-fit of the fitted combined models for final metal concentrations.

Metal	Source	d.f.	SS	MS	F_{calc}	$F_{\alpha,fLOF,fP}$
Chromium	Model	21	117.29	5.585		
	Error	58	0.328			
	Pure error	16	0.161	0.010		
	Lack-of-fit	42	0.167	0.004	0.40	1.89
Cadmium	Model	21	687.22	32.725		
	Error	58	41.481			
	Pure error	16	20.45	1.278		
	Lack-of-fit	42	21.031	0.501	0.39	1.89
Aluminum	Model	21	192.925	9.187		
	Error	58	7.591			
	Pure error	16	1.941	0.121		
	Lack-of-fit	42	0.524	0.012	0.309	2.44

0, $\gamma_{il} \neq 0$, $\gamma_{ijl} \neq 0$, $\gamma_{ijkl} \neq 0$. For the other cases, the null hypothesis Ho: $\gamma_{io} = \gamma_{il} = 0$ was rejected in favor of the hypothesis Ha: $\gamma_{io} \neq 0$, $\gamma_{il} \neq 0$. Tables 12 and 13 include those significant coefficient estimates whose absolute t-value exceeded the corresponding critical t-value.

Table 12 Significant estimates for maximum metal concentration.

Parameter	Chromium		Cadmium		Aluminum	
	t-value	p-value	t-value	p-value	t-value	p-value
X_1	34.42	0.0001	4.22	0.0001	12.72	0.0001
$F*x_1$	-	-	-	-	2.55	0.0135
X_2	34.64	0.0001	24.12	0.0001	14.42	0.0001
$F*x_2$			18.43	0.0001	-	-
X_3	33.82	0.0001	5.91	0.0001	11.63	0.0001
$F*x_3$	-	-	-	-	2.15	0.0001

Table 13 Significant estimates for final metal concentrations.

Parameter	Chromium		Cadmium		Aluminum	
	t-value	p-value	t-value	p-value	t-value	p-value
X_1	62.65	0.0001	4.33	0.0001	14.22	0.0001
$C{*}x_1$	-	-	-	-	4.01	0.0004
X_2	61.51	0.0001	17.43	0.0001	16.69	0.0001
$A{*}x_2$	-	-	2.77	0.0075	-	-
$B{*}x_2$	-	-	8.71	0.0001	-	-
$C{*}x_2$	-	-	9.90	0.0001	6.50	0.0001
$F{*}x_2$	-	-	11.92	0.0001	-	-
X_3	62.55	0.0001	5.98	0.0001	14.64	0.0001
$C{*}x_3$	-	-	-	-	4.30	0.0002
$A{*}x_1{*}x_2$	-	-	-	-	3.35	0.0021
$E{*}x_1{*}x_2$	-	-	-	-	3.40	0.0019
$X_1{*}x_2{*}x_3$	-	-	-	-	2.12	0.0425
$A{*}x_1{*}x_2{*}x_3$	-	-	-	-	3.50	0.0014
$C{*}x_1{*}x_2{*}x_3$	-	-	-	-	2.26	0.0310
$E{*}x_1{*}x_2{*}x_3$	-	-	-	-	3.45	0.0016

Based on the significant parameters, it was concluded that both the maximum and final chromium release to the leaching solution were only affected by the presence of the single mixture components and not by the different process parameter combinations. This result was in agreement with observations made by Camacho (2000) when plotting the concentration as a function of time and the solubility as a function of pH.

The maximum cadmium release seemed to be affected not only by the presence of the three single components but also by the combination of the process parameter F with the single component cadmium. The process parameter F represented the acid/waste ratio, which ranged between 19:1 and 1991:1. The first level corresponded to an initial concentration of 50,000 ppm of cadmium in the waste, and the second level to an initial concentration of 500 ppm. The final cadmium concentrations were affected by the presence of the single components chromium, cadmium, and aluminum, but also by the interaction of the single component cadmium with the process parameters A, B, C, and F. Here, A represented the applied pressure, B the slurry/ash ratio, C the aging, and F de acid/waste ratio. This combined effect seemed to be responsible for the reduction of cadmium release from the waste to the leaching process. However, due to the resolution III of the model and taking the assumption that there was no interaction effect when linear polynomial models applied, the effect was considered only due to the main factors alone.

The maximum aluminum release was also affected by the F parameter. This effect was observed not only when aluminum was combined with the pure component chromium but also when it was combined with the pure component aluminum. The confounded effect of the process parameter F with the two-factor interactions BC and DE due to the resolution III of the models became negligible by having a first-degree polynomial representing the response of the systems. On the other hand, the final aluminum concentrations seemed to be affected not only by the presence of the single, the binary, and the tertiary mixture components but also by the combinations of these mixture components with all the process parameters except D. Two more coefficients were eliminated from the final aluminum model, namely x1*x2*x3 and C*x1*x2*x3, since they were found insignificant ($p>0.05$) after running the SAS program with only those coefficients that were found significant (Table 13). By looking at the remaining coefficients it could be observed that C was the process parameter that played a more important role for the single components since it had a combined effect together with the pure chromium, cadmium, and aluminum components. In contrast, A and E were the only process parameters that were present in combination with the binary and tertiary mixture components. Here it was not possible to differentiate between main effects and two-factor interaction effects due to the resolution III of the model and due to the third degree polynomial (Equation 1) required in the final aluminum model. Since there was no prior knowledge about the magnitude or importance of these factors effect on aluminum, attention has to be paid on the confounding effects of the process parameters in the final aluminum concentrations.

The fitted equations representing the maximum and final concentrations for the three metals after adjusting the models to the significant parameters are given by Equations 18-23 as:

$$Y_{Cr(max)} = \underset{(0.03)}{1.2849}x_1 + \underset{(0.03)}{1.2933}x_2 + \underset{(0.03)}{1.2596}x_3 \tag{18}$$

$$Y_{Cd(max)} = \underset{(0.25)}{1.0935}x_1 + (\underset{(0.25)}{6.2347} - \underset{(0.25)}{4.9525}f)x_2 + \underset{(0.25)}{1.5060}x_3 \tag{19}$$

$$Y_{Al(max)} = (\underset{(0.22)}{2.8122} - \underset{(0.22)}{0.5349}f)\,x_1 + \underset{(0.22)}{3.1966}x_2 + (\underset{(0.22)}{2.5700} - \underset{(0.22)}{0.4539}f)x_3 \tag{20}$$

$$Y_{Cr(final)} = \underset{(0.02)}{1.2192}x_1 + \underset{(0.02)}{1.1966}x_2 + \underset{(0.02)}{1.2179}x_3 \tag{21}$$

$$Y_{Cd(final)} = \underset{(0.22)}{0.9512}x_1 + (\underset{(0.22)}{3.8126} + \underset{(0.21)}{0.5623}a + \underset{(0.21)}{2.0467}b - \underset{(0.21)}{2.3046}c - \underset{(0.21)}{2.6851}f)x_2 + \underset{(0.22)}{1.3005}x_3 \tag{22}$$

$$Y_{Al(final)} = (\underset{(0.09)}{1.3431} - \underset{(0.09)}{0.3408}c)x_1 + (\underset{(0.09)}{1.6282} - \underset{(0.09)}{0.6460}c)x_2 + (\underset{(0.09)}{1.4214} - \underset{(0.09)}{0.4320}c)x_3$$

$$+ (\underset{(0.48)}{1.2738}a - \underset{(0.48)}{1.2828}e)x_1x_2 - (\underset{(3.11)}{7.0893}a - \underset{(3.11)}{6.4494}e)x_1x_2x_3 \qquad (23)$$

The numbers in parentheses below the parameter estimates represent the estimated standard errors.

From the interpretation of the individual coefficient estimates in the maximum fitted model equations the following conclusions were drawn:

- Since in the maximum chromium model $\gamma_{20} \approx \gamma_{10} \approx \gamma_{30}$, it implies that the three single components increase in about the same magnitude the release of the maximum chromium concentration.

- By having $\gamma_{20} \gg \gamma_{2f} \gg \gamma_{30} \approx \gamma_{10}$ in the maximum cadmium model, it implies that the maximum cadmium concentration release is affected in a lesser form by the presence of single components of aluminum or chromium. It might be that no competing effects are present between those metals and cadmium. The negative sign in the coefficient γ_{2f} implies that the larger ratio (1991:1) results in less release of maximum cadmium concentration than it is with the lower acid/waste ratio (19:1).

- Since $\gamma_{20} > \gamma_{10} \approx \gamma_{30} > \gamma_{1f} \approx \gamma_{3f}$ in the aluminum concentration model, it implies that single component of cadmium controls the release of maximum aluminum concentration. The negative signs in the coefficients γ_{1f} and γ_{3f} implies that the larger ratio (1991:1) results in smaller aluminum or chromium release than with the lower acid/waste ratio.

The following conclusions were drawn from the interpretation of the individual coefficient estimates in the final fitted model equations:

- Since $\gamma_{10} \approx \gamma_{20} \approx \gamma_{30}$ in the final chromium model it implies that the single components of chromium, cadmium, and aluminum contribute in approximately the same way to maintain low final concentrations.

- Since $\gamma_{20} \gg \gamma_{2c} \approx \gamma_{2f} > \gamma_{2b} > \gamma_{30} > \gamma_{2a} \approx \gamma_{10}$ in the final cadmium model, it implies that the final cadmium concentrations are more affected by itself and by its combination with the process parameters C, F, and B than by the presence of single components of chromium or aluminum. The negative sign in the coefficient estimates γ_{2c} and γ_{2f} might imply that high acid/waste ratios (1996:1) and long aging periods (28 days) helped to obtain final lower concentrations. The positive sign in the coefficients γ_{2a} and γ_{2b} might suggest that high pressures (3000 psi) and high slurry:ash ratios (1:8) increase the stability of the system and, therefore, low final concentrations can be obtained.

- By having $\gamma_{123a} > \gamma_{123e} \gg \gamma_{20} \approx \gamma_{30} \approx \gamma_{10} \approx \gamma_{12e} \approx \gamma_{12a} > \gamma_{2c} \approx \gamma_{3c} \approx \gamma_{1c}$ in the final aluminum model, it implies that the final aluminum concentrations are controlled by the combination of the tertiary mixture with process parameter A and E. Factor A represents the pressure applied to obtain a solid form, and E represents the pH of the slurry. The negative sign of the coefficient estimate γ_{123a} might suggest that the lower final concentrations of aluminum are greater at the high pressures (3000 psi) than at lower pressures (600 psi). The positive sign of the coefficient γ_{123e} might mean that the high final aluminum concentrations are significantly greater at the high levels of pH of the slurry (pH=10) than at its lower levels (pH=5).

CONCLUSIONS

A combined statistical model was developed to analyze the leaching of heavy metals from solidified/stabilized wastes. The purpose of the analysis was to determine the most adequate metal composition and the best process parameter conditions in the formation of fly ash solidified/stabilized wastes to minimize the leaching of heavy metals. A linear polynomial for the mixture components was found sufficient to quantify the maximum and final chromium and cadmium release. However, a linear and a third degree polynomial for the mixture components were required to quantify the maximum and final aluminum release, respectively.

The statistical model equations for the maximum and final chromium concentrations release suggested that the chromium behavior during the leaching process is affected to the same extent by the presence of the metal itself and by the addition of cadmium or aluminum to the waste.

The linear polynomial equations fitted to the cadmium statistical model established that there are no competing effects between the pure component cadmium with the other two metals added to the process. However the effect of some process parameters is present in the equations. Large ratios of acid/waste result in less release of maximum metal concentration. Long aging periods helped obtain final lower concentrations. Also, high pressures and high slurry/ash ratios increased the stability of the system and helped obtain low final concentrations.

The minimization of aluminum release from wastes being subjected to long periods of time to the leaching solution is more complex than it is for cadmium and chromium, as established by the third degree polynomial for the final metal concentration in the combined model. The ratio of acid/waste which represented the amount of metal added to the waste was considered an important main factor to affect the release of large amounts of aluminum. The amount of aluminum released at the end of the leaching process is controlled by the combination of the tertiary mixture with the process parameters pressure and the pH of the slurry.

Even though confounded interaction effects with the pressure and the pH of the slurry were not excluded from the analysis due to the inclusion of the third degree polynomial, these two main factors seemed to be the ones that could considerably affect the amount of aluminum released to the leaching solution after long periods of time. High pressures and low pH of the slurry contributed to the minimization of aluminum release.

Attention has to be paid to the effect of the process parameter C which represents the aging of the solidified samples for 24 hours or 28 days. This parameter appeared in the cadmium and aluminum final concentration models and was in agreement with the observed lower release of these two metals from the majority of the samples.

Finally, the combined statistical models outlined in the present study can be used to find the independent variables that minimize the amount of heavy metals leached out of solidified/stabilized wastes. At the same time, the model can be helpful in maximizing the metal content in the waste. However, if the model is used to extrapolate past the range of the parameter levels included in the experiment or if it used to include other metals, then the behavior of the actual system may appear entirely different. Therefore, a generalization of the combined model to other fly ash-waste systems is recommended.

ACKNOWLEDGEMENTS

The authors would like to thank the Waste Management Education and Research Consortium (WERC) and also to the Programa Nacional para la Excelencia Académica (SUPERA), México for the support given to this project. To the Universidad Autónoma de Ciudad Juárez, México, for giving also suport one of the authors. We are grateful for their help.

REFERENCES

Baes, C. F. Jr., and Mesmer, R. E. (1977). *The Hydrolysis of Cations*. John Wiley & Sons, New York.

Camacho, L. M, (2000). “Modeling the Leaching Behavior of Fly Ash Solidified/Stabilized Wastes.” Ph.D. Dissertation, New Mexico State University, Las Cruces, NM.

Clayton, C. A., Goldberg, M. M., and Potter, B. B. (1997). “Design and analysis of an experiment for assessing cyanide in gold mining wastes.” *Chemometrics and Intelligent Laboratory Systems*, 36, 181-193.

Cornell, J. A., and Gorman, J. W. (1984). “Fractional design plans for process variables in mixture experiments.” *Journal of Quality Technology*, 16, 20-38.

Duineveld, C. A., Smilde, A. K., and Doornbos, D. A. (1993). “Designs for mixture and process variables applied in tablet formulations.” *Analytica Chimica Acta*, 277, 455-465.

Khuri, A. I., and Cornell, J. A. (1987). *Response Surfaces*. Marcel Dekker, Inc., New York.

Lindsay, W. L. (1979). *Chemical Equilibria in Soils*. John Wiley & Sons, Inc., New York.

Mason, R. L., Gunst, R. F., and Hess, J. L. (1989). *Statistical Design and Analysis of Experiments.* John Wiley & and Sons, New York. Montgomery, D. C. (1997). *Design and Analysis of Experiments*. Fourth edition, John Wiley & Sons, New York.

Parsa, J., Munson-McGee, S. H., and Steiner, R. (1994). “Stabilization/Solidification of hazardous wastes using fly ash.” *Journal of Environmental Engineering*, 122(10), 935-940.

SAS Institute Inc. (1990a). *SAS Procedure Guide*. Version 6, third edition. SAS Institute Inc., Cary, NC.

Wieling, J., Dijkstra, H., Mensink, C. K., Jonkman, J. H., Coenegracht, P. M., Duineveld, C. A., and Doornbos, D. A. (1993). “A fractionated combined mixture and factorial design for the modeling of the recovery of five tricyclic amines from plasma after liquid-liquid extraction prior to high-performance liquid chromatography.” *Journal of Chromatography*, 629, 181-199.

Snoeyink, V. L., and Jenkins, D. (1980). *Water Chemistry*. John Wiley & Sons, New York.