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AN EXPERIMENTAL DESIGN FOR THE PRELIMINARY STUDY
OF GEOCHEMICAL PROCESSES

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Water and Wastewater Research
Earth Sciences Section
ENVIRONMENTAL AND RADIOLOGICAL SCIENCES

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PACIFIC NORTHWEST LABORATORY

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AN EXPERIMENTAL DESIGN FOR THE PRELIMINARY STUDY OF GEOCHEMICAL PROCESSES

L. L. Ames, Jr. and B. F. Hajek

Introduction

As the geochemist proceeds from a relatively simple study such as element distribution to the study of the natural processes that yielded the element distribution, experimental precision is very likely to decrease. The extent of the decrease in precision is commensurate with the degree to which the independent variables in the experiment can be controlled and their number. Many experimental designs already are available for use in geochemical process investigations. Several of these designs, including the factorial designs, allow measurement of the effects of several different variables and their relationships simultaneously. The two-level factorial design is especially valuable in exploratory work, yielding a maximum of useful information for a given level of experimental effort.

The usual experimental method is to hold all of the independent variables except one at some level, while determining the effect of the one independent variable on the dependent variable under study. Interactions between factors can be missed by examination of only one factor at a time.

It is the purpose of this paper to examine several examples of geochemical investigations using factorial designs and their analyses to give the reader a better notion of the utility and shortcomings of such designs.

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Cation Exchange Reactions

A simple factorial design to study the removal of tracer level cesium-134 and strontium-85 by a local soil is shown in Fig. 1. (In this design, two concentration levels of each of four factors (NaNO_3 , HNO_3 , KNO_3 and $\text{Ca}(\text{NO}_3)_2$) were combined in all possible combinations to give a total of 2^4 or 16 combinations.) Solutions were made up to correspond to the 16 combinations plus cesium-134 or strontium-85 and numbered as per Fig. 1. A local soil was selected and quartered to 16 one-gram samples. The samples were placed in straight sealing tubes with fritted glass discs, and one of the 16 solutions recirculated through the one-gram soil column until equilibrium was attained as indicated by frequent solution sampling and counting. In the case of strontium-85, the amount of activity removed by the soil column was low, so the column itself was counted rather than the solution. In both cases, the volumetric comparison between the original solution counts and final solution or column counts gave a cesium or strontium distribution. The dependent variable (cesium or strontium distribution), and the effects of factor variation on the dependent variable, was sought and analyzed. The Yates method of factorial analysis (1937) was used with the results given in Table 1. The dependent variable in Table I is C/C_0 where C = the cesium-134 counts/nl/min remaining in solution after soil solution equilibrium, and C_0 = the cesium-134 counts/ml/min in the original solution. The cesium C/C_0 values represent an average for four replicates of this design. As the t-test shows, HNO_3 , KNO_3 , $\text{Ca}(\text{NO}_3)_2$ and NaNO_3 are all statistically significant at the 5% level. Three and four-factor interactions were arbitrarily chosen for an estimation of error.

Table I. Analysis of cesium-134 removal data using the Yates data treatment method.

Solution number	Experimental C/C_0	Effect Totals	Identification	Predicted C/C_0
1	0.1195	5.9553	Grand total	0.1217
2	0.2802	1.3063*	A (HNO_3 main effect)	0.2849
3	0.2408	0.8279*	B (KNO_3 main effect)	0.2251
4	0.4123	-0.0215	AB	0.3883
5	0.2085	0.5583*	C ($\text{Ca}(\text{NO}_3)_2$ main effect)	0.1915
6	0.3318	0.0421	AC	0.3547
7	0.2573	-0.1203	BC	0.2949
8	0.4687	0.1975	ABC	0.4581
9	0.2512	1.3171*	D (NaNO_3 main effect)	0.2863
10	0.4613	-0.0275	AD	0.4495
11	0.4217	-0.0503	BD	0.3897
12	0.5115	-0.2193	ABD	0.5529
13	0.3707	0.1313	CD	0.3561
14	0.5404	0.0371	ACD	0.5193
15	0.4548	0.0151	BCD	0.4595
16	0.6245	-0.0429	ABCD	0.6227

$$\sigma^2 = 0.00112 \quad \sigma = \pm 0.0335 \quad \sigma \text{ Effect Totals} = (\sqrt{16}) (\pm 0.0335) = \pm 0.134.$$

t at 5% level with five degrees of freedom = 2.571. An effect total is significant if $> \pm 0.345$.

The three and four factor interactions were chosen for the error estimate. Solution numbers correspond to those shown in Fig. 1. C/C_0 is the fraction of the original cesium-134 count remaining in the equilibrium solution. Capital letters identify the effect totals. An asterisk indicates a significant effect total.

It is perhaps easier to visualize a statistically meaningful effect total if a graphical method of presentation, such as that proposed by Daniel (1959) is used. Here the absolute values for the effect totals are plotted on a half-normal scale with the result shown in Fig. 2. Note that the statistically significant values fall off of the line representing the null or no-effect case.

Still further use may be made of the effect totals given in Table I. An equation to describe the response of the dependent variable (C/C_0) is

$$C/C_0 = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_4 x_4 \quad (1)$$

where b_0 through b_4 are regression coefficients and x_1 through x_4 are HNO_3 , KNO_3 , $\text{Ca}(\text{NO}_3)_2$ and NaNO_3 concentrations, respectively, over the ranges studied. Equation (1) is valid only over the concentration ranges of the respective HNO_3 , KNO_3 , $\text{Ca}(\text{NO}_3)_2$ and NaNO_3 used in the experiment. The regression coefficients may be obtained directly from the effect totals by dividing the grand and main effect totals, in this case, by 16. For example, $b_0 = 5.9553/16 = 0.3722$ and $b_1 = 1.3063/16 = 0.0816$. Equation (1) then becomes

$$C/C_0 = 0.3722 + 0.0816(x_1) + 0.0517(x_2) + 0.0349(x_3) + 0.0823(x_4). \quad (2)$$

Experimental and computed C/C_0 values using equation (2) are given in Table I. The agreement between experimental and predicted C/C_0 values is good enough to be useful for predicting other C/C_0 values within the given concentration range of the independent variables, such as a NaNO_3 concentration of 2.6 molar.

The same factorial design also was executed with strontium-85 removal from solution as the dependent variable. The results are shown as a half-normal scale plot in Fig. 3. No statistically significant effect totals were found by analysis, and none are seen to deviate significantly from the null line in Fig. 3.

Much more elaborate experiment designs to study radioisotope removal from soils are possible. A design and analysis by Hawkins and Short (1965) illustrate use of a two-level factorial that would require 2^{11} combinations for total completion.

A Complex Chemical Reaction

A factorial design also was used to study the removal of strontium from solution into an apatite during a chemical reaction between phosphate ion and calcite (Ames, 1959; Ames, 1960). Fifty-gram calcite columns were used with the first liter of effluent solution collected for strontium-85 counting. At least six factors could potentially effect the dependent variable (strontium-85 removal or C/C_0) including the influent solution pH, phosphate ion concentration, system temperature, column flow rate, calcite surface area and strontium concentration. These factors resulted in a design as shown in Fig. 4. Instead of completing all treatment combinations for a total of 2^6 or 64 experiments, a half-replicate was completed with a total of 32 treatment combinations (see Cochran and Cox, 1957, p. 279). The Yates analysis of the strontium removal data is given in Table 2. The solution numbers used in Fig. 4 and Table 2 are identical. Note that even at a t-test level of 1%, calcite surface area, influent solution pH, system temperature-solution pH interaction are statistically significant. A 1% significance level indicates that only one time out of a hundred trials would the experimenter expect the effect total to equal that value. With the exception of calcite surface area, the other statistically significant effect totals at the 1% level are obviously significant to much lower levels than 1%.

The main effect totals from this design also may be used in a regression equation, but the precision is of a lower order than with the cation exchange data due to the use of a single half-replicate in this instance. An extra term could be added to the regression equation to handle the temperature-solution pH interaction.

Table II. Analysis of strontium removal data during a calcite-phosphate reaction from a fractional factorial design.

Solution number	C/C ₀ values	Effect totals	Identification
1	0.7474	9.1467	Grand Total
20	0.1915	1.4565	A (Solution flow rate main effect)
19	0.2232	2.3327*	B (Calcite surface area main effect)
2	0.9516	0.5133	AB
17	0.0799	-0.4265	C (Strontium concentration main effect)
4	0.8164	0.5473	AC
3	0.8760	0.1463	BC
18	0.7223	0.9253	ABC
25	0.0007	-6.8143*	D (Influent solution pH main effect)
12	0.1151	1.0879	AD
11	0.3274	-0.0374	BD
26	0.0616	-0.4333	ABD
9	0.0054	-0.6875	CD
28	0.0006	-0.6649	ACD
27	0.0020	-0.9579	BCD
10	0.1548	-0.6605	ABCD = EF
21	0.0008	-1.4051	E (Total phosphate ion main effect)
8	0.7803	-0.0473	AE
7	0.8474	-0.3911	BE
22	0.1828	0.1703	ABE
5	0.6096	-0.5043	CE
24	0.0033	-0.8721	ACE
23	0.0155	-0.5411	BCE
6	0.9325	4.1987*	ABCE = DF (Temperature-pH interaction)
13	0.0093	1.0671	DE
32	0.0016	0.2299	ADE
31	0.0098	-0.3578	BDE
14	0.3361	0.8001	ABDE = CF
29	0.0146	0.7583	CDE
16	0.0305	-0.4431	ACDE = BF
15	0.0761	0.2191	BCDE = AF
30	0.0206	-6.0851*	ABCDE = F (System temperature main effect)

$$\sigma^2 = 0.01285 \quad \sigma = \pm 0.1135 \quad \sigma \text{ Effect Totals} = (\sqrt{32}) (\pm 0.1135) = \pm 0.642$$

t at 1% level and 10 degrees of freedom = 3.169. An effect total is significant if $> \pm 2.034$.

Solution numbers correspond to those of Fig. 4. The three-factor interactions were used in the estimation of error. An asterisk indicates an effect total significant at the 1% t-test level. The use of a half-replicate leads to several aliases, as noted under identification.

Discussion

Increasingly, geochemists and mineralogists will be studying natural systems and processes with many hard-to-control variables affecting the final results. Examples have been given of factorial experimental designs that enable the investigator to extract a maximum of useful information for his efforts. In the first example, the distribution of cesium-134 and strontium-85 between a soil column and a solution was reported. In the case of cesium-134 removal, all of the independent variables were significant over their respective concentration ranges, while with the removal of strontium-85, none of the independent variables were statistically significant. The lack of significant effects of the independent variables on the dependent variable of strontium-85 removal does not mean that such a statistically significant effect is nonexistent, but only that an independent variable range lying outside of the significant independent variable range was chosen. Later work showed that extending the concentration range of NaNO_3 caused the NaNO_3 main effect total to become statistically significant at the 5% t-test level in its effect on strontium-85 removal. Thus, some thought is required concerning the range of the independent variables before proceeding with the design.

In the soil column work temperature was deleted as an independent variable because nothing but ion exchange reactions were expected as removal processes. However, the addition of temperature as a variable when the reaction type is in doubt is often enlightening because the differences in temperature effects on the dependent variable during chemical, ion exchange and chemisorption removal reactions are usually readily discernible. The main source of error and lack of precision in a cation exchange experiment of this type is the difficulty of obtaining 16 exactly

comparable one-gram soil columns. Several replicates would be necessary, therefore to improve precision and lower the errors involved. Often a single replicate or a fractional replicate will suffice for an exploratory study.

As the reader has probably noticed, the number of experiments required to complete the design rise exponentially with the number of independent variables. The larger the number of independent variables, the more unwieldy and time-consuming the completion of the design becomes. The use of fractional replicates for the larger designs partially solves the problem of large size, but usually at the cost of an increase in the standard deviation of the effect totals. The problem of size, however, is rightly the responsibility of the investigator. The design, two-level factorial or otherwise, should not be criticized for investigator's lack of ability to define his problem.

The second example of a factorial design for the study of strontium removal during a complex chemical reaction illustrates the useful information that can be obtained from a preliminary design of this type. The relatively large effect of temperature and the null effect of strontium concentration on strontium removal strongly suggest that a chemical reaction is involved, assuming that the investigator was uncertain of the reaction type. Calcite surface area and solution pH significance suggest little unless the distribution of the various species in polyprotic H_3PO_4 with pH is known. The interaction of temperature and solution pH could easily have been overlooked if conventional experimental methods had been used in the preliminary investigation.

The two-level factorial design yields no direct indication of the strontium removal mechanism; i.e., there is nothing in the data of Table II which directly

indicates that the strontium is being removed into an apatite, continuously forming by a replacement reaction with calcite and phosphate ion. The data do suggest that a chemical reaction is involved, and therefore give an indication as to the further study required to elucidate the removal mechanism.

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NaNO ₃ Concentration				Ca(NO ₃) ₂ Concentration		KNO ₃ Concentration
1.0M		3.0M				
HNO ₃ Concentration						
0.0M	0.05M	0.0M	0.05M			
7	8	15	16	0.05M	0.001M	0.0M
3	4	11	12	0.0M		
5	6	13	14	0.05M		
1	2	9	10	0.0M		

Fig. 1. Design and solution compositions used in a two-level factorial for the study of the effects of NaNO₃, HNO₃, KNO₃ and Ca(NO₃)₂ on Cesium-134 and Strontium-85 removal from aqueous solutions.

Fig. 2. A plot on a half-normal scale of the absolute factorial effect total values obtained by analysis of the cesium-134 removal data as given in Table I.

Fig. 3. A plot on a half-normal scale of the absolute factorial effect total values obtained by analysis of the strontium-85 removal data from the same design as given in Fig. 1.

Influent Solution pH							
7.3				12.3			
0.01M		0.05M		0.01M		0.05M	
		Temperature, °C					
25	60	25	60	25	60	25	60
1			21		25	13	
	17	5		9			29
	19	7		11			31
3			23		27	15	
	20	8		12			32
4			24		28	16	
2			22		26	14	
	18	6		10			30

300 ml/hr/cm ²		850 ml/hr/cm ²	
Column Flow Rate		Calcitic Surface Area	
0	0.121 m ² /g	0	0.032 m ² /g
0.067	0.121 m ² /g	0.067	0.121 m ² /g
0	0.067	0	0.067
0.067	0.067	0.067	0.067
0	0	0	0
0.067	0.067	0.067	0.067
0	0	0	0
0.067	0.067	0.067	0.067

Fig. 4. A half-replicate, two-level factorial design and solution compositions used to study the effects of influent solution pH, phosphate ion concentration, system temperature, column flow rate, calcite surface area and strontium concentration on the removal of strontium from aqueous solution during a calcite phosphate reaction.