Factorial Experiments in Sequence: the Attainment of Optimum Conditions for a Decontamination Process

M. K. BARNETT, P. M. HAMILTON, and F. C. MEAD, JR.

Mound Laboratory, Monsanto Chemical Company, Miamisburg, Ohio

The advantages of factorial design are first illustrated by a simple experiment devoted to the effect of two *p*H factors and an iron-concentration factor on the efficiency of a decontamination process employing iron sulfide as a scavenging agent. The broadening of the base of an investigation by the expansion of a factorial is illustrated by addition of the sulfide concentration as a factor. Finally the principle of expanded factorials is further utilized in the later phases of the study, in which additional levels are assigned to the *p*H factors in order to arrive at a closer estimate of the optimum conditions for the process.

Factorial experiments, that is, those embracing all possible combinations of the process variables, are peculiarly suited to the prosecution of a systematic approach in laboratory investigations. If such experiments have yet to attain wide usage among chemical workers, one reason must be the excessive advance commitment of time and manpower and resultant loss of flexibility in scientific planning which the execution of an elaborate factorial scheme often requires. This difficulty may be circumvented by employing factorial designs in sequence. Thus initially simple factorial experiments may, as experience accumulates, be successively expanded and perhaps redirected to form more elaborate factorial plans whose relevance to the objectives of the investigation is more assured than if the entire program had been planned in advance.

The utility of such sequential factorials is illustrated by a study devoted to the improvement of a process for removal of radioactivity from liquid wastes. The process employed iron sulfide as a scavenging agent, and the problem was to adjust operating conditions in such a manner that the major portion of the activity became associated with the solid phase. The latter, after separation by settling, could be disposed of by burial.

DESCRIPTION OF WASTE AND PROCESS

To make the results of the study applicable to general laboratory wastes encountered in practice, a complex waste sample was deliberately chosen. Although its exact composition was not established, it was known to contain a wide variety of radioactive species, including both alpha and beta emitters; nonradioactive inorganic salts; and organic material, some of which was visible as suspended matter in the liquid. The initial activity of the waste, measured as alpha plus beta on a 0.5-ml. sample, was 26,453 counts/min. Of this total, 1,850 counts/min. was recorded as alpha only. Also, 17,050 counts/min., or about two thirds of the total, was associated with suspended matter.

The process was studied on a laboratory scale, separation of the solid being effected by filtration. In the first step sulfuric acid was added to 250 ml. of the waste solution until the *p*H attained a previously prescribed value called the *initial* *p*H. Ferrous chloride solution (100 mg. of ferrous iron/ml.) was then added until the iron concentration attained a prescribed value. After addition and solution of a prescribed quantity of finely divided solid sodium sulfide, acid or base was added until the *p*H attained a certain value, called the *final* *p*H. After 30 min., allowed for settling, the solid was filtered off and the filtrate was sampled and mounted in duplicate. Each mount was counted in duplicate for alpha plus beta.

CHOICE OF FACTORS AND LEVELS FOR INITIAL EXPERIMENTS

Although prior knowledge was inadequate for precise prediction, it was freely utilized as a guide in the choice of independent variables, or "factors," and values, or "levels," of these factors for the initial experiment. Previous application (*1*) of the process to a different type of waste had established the initial *p*H, *I*; the iron concentration, *F*; and the final *p*H, *A*, as important factors affecting the extent of decontamination. It was decided to devote the initial work to these factors with two levels to be assigned to each factor. The amount of sulfide reagent was held constant at 0.5 g. The earlier work (*1*) had suggested an iron concentration of 1 mg./ml., an initial *p*H of 1, and a final *p*H of 4 as desirable conditions, and these levels were adopted as one set of factor values for the present study. As the aforementioned level for iron concentration was near the upper economic limit, a lower value, 0.5 mg./ml., was adopted for the second level of this factor. Because of the need for reducing corrosion in the metal equipment in which the large-scale process would be carried out, reduced acidity was desirable. The second levels for the initial *p*H and final *p*H were therefore set at 2 and 6, respectively.

CHOICE OF EXPERIMENTAL DESIGN

There was no reason to suppose that the efficiency of decontamination was a simple additive function of the three factors under study. For example, the effect of changing the iron content on the decontamination might well depend on the levels or values assigned to the other two factors or independent variables included in the study. The complete exploration of the causal relations would require the observation of the effect of each factor under all combinations of values of the others, thus consuming a large number of tests.

The use of the larger number of tests needed for more complete coverage of interrelations among the factors would seem to incur a corresponding reduction in the number of replicate tests, thus decreasing the reliability of the conclusions drawn from the data. This seemed particularly serious in the present case, because previous experience had indicated the presence of considerable uncontrolled variability in the process. The horns of a dilemma thus presented themselves: on the one horn, generality at the expense of precision; on the other, precision at the expense of generality.

A solution of this dilemma was supplied by R. A. Fisher (*2*) some twenty-five years ago when he proposed the factorial design, a plan for simultaneously attaining both maximum reliability and maximum generality, or coverage. This design was adopted for the study of the three factors under consideration. Such a design, by definition, must include all possible combinations of the factors at their different levels, each combination or "treatment" being repeated an equal number of times. In the present case,

---

P. M. Hamilton is at present with Central Research Laboratories, Monsanto Chemical Company, Dayton, Ohio.

because each of the three factors was studied at two levels, there were 2 × 2 × 2 = 8 possible treatments. The treatments were run in triplicate, and the results of the experiment are represented in Table 1.

TABLE 1. RESULTS OF THE 2^3 FACTORIAL EXPERIMENT*

Treatment symbol	F, Iron concentration, mg./ml.	A, Final pH	I, Initial pH	Activity remaining, $\alpha + \beta$ (tens of counts/min./0.5 ml. of filtrate) Block I	Block II	Block III	Average
$F_1A_1I_1$	0.5	4	1	1,065	946	999	1,003
$F_1A_1I_2$			2	689	784	875	783
$F_1A_2I_1$		6	1	244	281	275	267
$F_1A_2I_2$			2	474	387	357	406
$F_2A_1I_1$	1.0	4	1	1,036	1,028	977	1,014
$F_2A_1I_2$			2	869	907	893	889
$F_2A_2I_1$		6	1	167	236	230	211
$F_2A_2I_2$			2	157	165	173	165
Average				587	592	597	592

---

*The eight treatments were carried out in random order in each block.

TABLE 2. MAIN EFFECTS OF THE 2^3 FACTORIAL EXPERIMENT

Conditions	Effect of iron concentration		
$A = A_1, I = I_1$	$F_2A_1I_1-F_1A_1I_1$ =	1,014-1,003 =	11
$A = A_1, I = I_2$	$F_2A_1I_2-F_1A_1I_2$ =	889-782 =	106
$A = A_2, I = I_1$	$F_2A_2I_1-F_1A_2I_1$ =	211-267 =	− 56
$A = A_2, I = I_2$	$F_2A_2I_2-F_1A_2I_2$ =	165-406 =	−241
Average or main effect . . . . =			− 45
	Effect of final pH		
$F = F_1, I = I_1$	$F_1A_2I_1-F_1A_1I_1$ =	267-1,003 =	−736
$F = F_1, I = I_2$	$F_1A_2I_2-F_1A_1I_2$ =	406-783 =	−377
$F = F_2, I = I_1$	$F_2A_2I_1-F_2A_1I_1$ =	211-1,014 =	−803
$F = F_2, I = I_2$	$F_2A_2I_2-F_2A_1I_2$ =	165-889 =	−724
Average or main effect . . . . =			−660
	Effect of initial pH		
$F = F_1, A = A_1$	$F_1A_1I_2-F_1A_1I_1$ =	783-1,003 =	−220
$F = F_1, A = A_2$	$F_1A_2I_2-F_1A_2I_1$ =	406-267 =	139
$F = F_2, A = A_1$	$F_2A_1I_2-F_2A_1I_1$ =	889-1,014 =	−125
$F = F_2, A = A_2$	$F_2A_2I_2-F_2A_2I_1$ =	165-211 =	− 46
Average or main effect . . . . =			− 63

Note: Results in tens of counts per minute per 0.5 ml. of filtrate.

The treatment symbols appearing in the first column of the table utilize the factor symbols with appropriate subscripts. Subscripts 1 and 2 indicate that the lower or higher levels, respectively, of the factors were employed in the treatments. The number representing the activity remaining was computed by averaging the four results obtained from the pair of mounts prepared from each filtrate. The activity is reported as alpha plus beta in tens of counts per minute per 0.5 ml. of filtrate.

PROBLEM OF ERROR CONTROL

To most physical scientists the refinement or stabilization of experimental technique is the most obvious method of error control. A number of unusual refinements were adopted in the present experiment. Thus the pH adjustments and the addition of all reagents were carried out by the same operator throughout the study. Such factors as the rate and manner of addition were thus held as constant as possible. A second operator was responsible for all the filtrations, and a third did all the sampling and mounting. The total time consumed in pH adjustments and addition of reagents was held constant at 7 min., and all solutions were allowed exactly 30 min. for settling. Filtrates were sampled and mounted immediately after filtration, and mounts were counted on the same day that they were prepared.

Error control may also be achieved by suitable arrangement of the experimental tests and conditions in a manner consistent with the over-all experimental design. The present experiment provides an elementary illustration of this type of error control. As indicated in Table 1, the twenty-four tests were segregated into three blocks, each block of eight comprising a complete replication of the factorial experiment. These three blocks were assigned to the 3 days required to complete the experiment. The advantage of this arrangement is that any day-to-day differences in operating conditions will have no influence on the comparisons to be drawn from the experiment. Thus the effect of the iron factor may be formulated by subtracting the average of the four low-iron tests in the first block from the average of the four high-iron tests in the same block. This contrast may also be formulated for each of the other two blocks. The over-all or average iron effect is obtained by pooling the three contrasts from the three blocks, and this pooled contrast, obtained by averaging, is obviously independent of any differences between blocks, i.e., days.

The eight runs within each block were not carried out in the systematic order shown in Table 1 but in random order, a different random order being used for each block. Randomization accomplished two results. First, it greatly reduced the likelihood that bias would be present in comparisons drawn to reveal the effect of a particular factor. If, for instance, some unknown factor increased gradually during each day, the decontamination would be progressively greater or less than it would otherwise have been. If the eight treatments had been carried out in a systematic order, say all the low-iron treatments first followed by the high-iron treatments, then the influence of the accidental factor would be indistinguishable from the effect of the iron factor. The apparent effect of the latter might have been either smaller or larger than its real effect. The second result of randomization is a more valid estimate of the experimental error. This estimate must be based on the observed discrepancies between replicate tests. However, if the same order is used for all three blocks, then replicate tests are likely to be run under more uniform conditions than if different random orders are used. The result will be to make the measured error smaller than the true error present in the experiment. Since the significance of observed effects will be ascertained by comparing them with the measured error, the use of this smaller error would cause experimental effects to appear more significant than they really are.

MAIN EFFECTS OF THE EXPERIMENT

The eight treatment averages shown in the last column of Table 1 provide four unbiased comparisons for the formulation of the effect of each of the three factors. These are shown in Table 2. It is evident that the effect of each of the three factors has been measured under each of the four possible sets of conditions defined by the levels assigned to the other two factors. These four simple effects may be averaged to produce a "main effect" of the factor. The main effect of a given factor, so defined, is obviously equivalent to the excess of the average activity remaining for the four treatments having the higher level of the factor over the average for the four with the lower level of the factor.

The efficiency of the factorial design begins to make itself evident. Not only has each factor been studied under the widest range of conditions, but also, by virtue of the symmetry of the design, all the data have been utilized in formulating the effect of each factor.

It should be noted that a negative effect, if large enough to be significant, indicates that there was less activity remaining at the higher level of the factor and that raising the level was beneficial.

CALCULATION OF INTERACTIONS

The extent to which the effect of a factor depends on the value assigned to a second factor attains simple quantitative formulation in the concept of *interaction*. From Table 2, the average effect of increasing the final *p*H when the iron concentration was at its higher level was $\frac{1}{2}[(-803) + (-724)] = -763$, and the average effect when the iron concentration was at its lower level was $\frac{1}{2}[(-736) + (-377)] = -556$. The influence of raising the iron concentration on the effect of the final *p*H would be given by the difference: $(-763) - (-556) = -207$. Actually, it is preferable to take one half of this difference as the interaction, denoted by FA, as this will identify the interaction with the difference between the average of four treatments and the average of the remaining four and will therefore impart to the interaction the same precision as the main effects. Therefore $FA = -207/2 = -103$.

In a three-factor experiment there are two additional "first-order" interactions. One, denoted by IA, may be formulated as the dependence of the final *p*H effect on the initial *p*H; and the other, denoted by FI, as the dependence of the initial *p*H effect on the iron concentration. This enumeration exhausts the possible first-order interactions, as only one interaction exists between any two factors; thus the effect of the iron concentration on the effect of the final *p*H is identical with the effect of the final *p*H on the effect of the iron concentration.

However, there remains a single "second-order" interaction symbolized by FAI, which represents the dependence of the interaction between any two factors on the level assigned to the third factor. Thus the interaction between the iron concentration factor and the final *p*H factor when the initial *p*H is held at I_2 is, from Table 1, $(-241) + (-106) = -347$, and, when $I = I_1$, is $(-56) + (-11) = -67$. The effect of changing the initial *p*H on the first-order interaction might be taken as $(-347) - (-67) = -280$. Again, to maintain uniformity of precision among the main effects and interactions, the interaction is taken as one fourth of this difference: $FAI = -280/4 = -70$.

The symmetry of the design has permitted utilization of all the data in the formulation of each interaction; and so the four interactions, like the three main effects, have been measured with maximum precision.

EVALUATION OF RESULTS

The seven effects of the experiment are tabulated in the second column of Table 3. Again, because of the symmetry of the experimental structure and the care taken in randomization, a clear-cut straightforward statistical procedure is available for objectively evaluating the results. This procedure, called *analysis of variance*, is discussed in standard texts (*3*). By means of it, the discrepancies among triplicate determinations may be made to furnish certain critical values for judging the significance of an effect. Thus there are but 5 chances in 100 that the experimental error could produce an observed effect as large as 46, and 1 chance in 100 that it could produce one as large as 63.

Examination of Table 3 shows that the outstanding feature of the experiment was the marked beneficial effect of increasing the final *p*H. This effect far exceeded the 1% level of significance. An over-all beneficial effect of increasing the initial *p*H is also present, though the 1% level was not quite achieved. The effect of the iron factor was less pronounced, the main effect falling just short of the 5% significance level. However, the beneficial effect of increasing the iron content makes a firm appearance in the strongly negative FA interaction, indicating that the beneficial effect of increasing the final *p*H was accentuated by operating at the higher iron content. The significantly negative FAI interaction again suggests the beneficial effect of simultaneously raising all three factors to their higher levels. The statistically significant, positive AI interaction presents the only puzzling aspect of the experiment and will be discussed later.

The three block averages, tabulated at the bottom of Table 1, differed but little from one another, and, in fact, a simple extension of the statistical analysis showed that the variation among the three was readily attributable to the same experimental error which operated within the blocks. Thus nothing was gained, so far as the consistency of the seven factorial effects was concerned, by carrying out the experiment in three randomized blocks instead of a single completely randomized block of twenty-four tests. However, the auxiliary information that laboratory technique and operating conditions had been sufficiently uniform to eliminate day-to-day variability was extremely useful and, in fact, was immediately utilized in laying out the succeeding experiment.

TABLE 3. COMPARISON OF THE RESULTS OF THE ORIGINAL 2^3 FACTORIAL WITH THOSE OF THE EXPANDED 2^4 FACTORIAL

Effect	2^3 Factorial	2^4 Factorial
F	− 45	− 17
A	−660†	−677†
I	− 62*	− 56*
FA	−103†	− 77†
FI	− 22	− 11
AI	110†	40
FAI	− 70†	− 24
S		17
FS		− 28
AS		17
IS		− 7
FAS		− 26
FIS		− 12
AIS		+ 70†
$FAIS$		− 46*

*Attains 5% significance level, 46.
†Attains 1% significance level, 63.
Note: Results in tens of counts per minute per 0.5 ml. of filtrate.

TABLE 4. EXPANSION OF 2^3 FACTORIAL INTO A 2^4 FACTORIAL BY INCLUSION OF THE SULFIDE FACTOR (S_1 = 0.25 g., S_2 = 0.50 g.)

Treatment	Count	Treatment	Count
$F_1A_1I_1S_1$	891	$F_1A_1I_1S_2$	1,003
$F_1A_1I_2S_1$	892	$F_1A_1I_2S_2$	783
$F_1A_2I_1S_1$	298	$F_1A_2I_1S_2$	267
$F_1A_2I_2S_1$	197	$F_1A_2I_2S_2$	406
$F_2A_1I_1S_1$	973	$F_2A_1I_1S_2$	1,014
$F_2A_1I_2S_1$	933	$F_2A_1I_2S_2$	889
$F_2A_2I_1S_1$	236	$F_2A_2I_1S_2$	211
$F_2A_2I_2S_1$	180	$F_2A_2I_2S_2$	165

Note: Activity remaining, $\alpha + \beta$, in tens of counts per minute per 0.5 ml. of filtrate.

EXPANSION OF THE 2^3 FACTORIAL BY ADDITION OF THE SULFIDE FACTOR

The initial 2^3 factorial experiment, just described, pointed rather firmly to the desirability of further increases in both initial and final *p*H, while the iron content is maintained at the higher concentration. Before the investigation was extended in this direction, however, it was deemed desirable to check the influence of variations in the sulfide factor, which had been held constant at 0.5 g. of reagent in the initial experiment. Previous experience with this factor had indicated that quantities of sulfide in excess of 0.5 g. tended to give colloidal solutions which passed through the filter and hence retained considerable activity. In fact, some difficulty was experienced in the 2^3 factorial with colloid formation. Therefore the new level of the sulfide factor was set at a lower value, 0.25 g.

The device adopted for incorporating the sulfide factor into the investigation might be called the principle of *expanded factorials*. If, in adding the new factor, one wishes to reap the full advantages of factorial design, he will need to include in the over-all plan all $2 \times 2 \times 2 \times 2 = 16$ treatments. However, eight of these, for which the sulfide was at its higher level, have already been included in the original factorial. To complete the new 2^4 factorial, it will suffice to carry out eight new treatments. These will be identical with the original eight treatments in respect to combinations of levels for iron concentration, initial pH, and final pH but will utilize 0.25 g. of sulfide in place of 0.5 g.

Although the eight additional treatments were carried out in random order, complete randomization of the sixteen was impossible. However, this does not mean that the comparison between the average of the original eight treatments, all having the higher quantity of sulfide, and the average of the new block of eight, all having the lower quantity of sulfide, is a biased comparison unsuitable for measuring the main effect of the sulfide factor. For, except for amount of sulfide used, the new block of eight treatments was carried out under the same conditions as prevailed during the earlier experiment, and, as significant day-to-day variations were absent from the earlier experiments, they were presumably likewise missing from the later experiments. Therefore, the raising or lowering of the apparent main effect of the sulfide factor by interblock differences is highly unlikely.

The results of the additional eight treatments, along with the average results for the original eight, are listed in systematic order in Table 4. The symbolism has been expanded to take care of the new factor, the symbol S denoting the sulfide factor, and S_1 and S_2 its lower and higher levels, respectively.

The widened base of the 2^4 factorial affords answers to a greater variety of questions than was provided by the original experiment. These new effects are the main effect of the sulfide factor; the interactions of this factor with each of the other three, FS, AS, IS; the interactions of the sulfide factor with the others, taken two at a time, FAS, FIS, AIS; and the single third-order interaction, $FAIS$. In addition, the seven effects of the original 2^3 factorial may also be reformulated to provide confirmatory information on their magnitude and significance.

The mechanics of computation is strictly analogous to that used in the 2^3 factorial. Thus, to formulate the main effect of any factor, the average activity remaining for the eight treatments with the low level of the factor is subtracted from the average value for the eight with the high level of the factor. The interactions are likewise formulated in a manner similar to that employed in the simpler case. As was the case in the original factorial, each effect will be based on all the data and will be formed by subtracting from the average of eight of the treatment results the average of the remaining eight. The table of signs (*3*), presented as Table 5, shows how the data must be grouped in order to compute the fifteen different effects.

As previously noted, any over-all difference between the conditions prevailing for the first eight treatments and those for the last eight treatments, though unlikely to exist, would vitiate the evaluation of the main effect of the sulfide factor. However, from Table 5 it is evident that such interblock differences could have no influence on the remaining fourteen effects of the 2^4 factorial. For in each of the fourteen cases the expression for the effect may be written as the sum of two groups of contrasts, one group involving only high-sulfide treatments, the other involving only low-sulfide treatments. In formal language the main effect of the sulfide factor has been "confounded" with blocks, leaving all other effects free from interblock differences.

The fifteen effects of the 2^4 factorial are listed in the last column of Table 3. The values obtained from the expanded experiment are based on twice as many comparisons as was the case with the 2^3 factorial, although this advantage is partly balanced by the circumstance that the eight treatments required for the expansion were not replicated. Since the error prevailing among the last eight treatments was not measured, no rigorous calculation of significance levels for the expanded factorial experiment is possible. As a first approximation, they are assumed to have the same values as in the first experiment.

Consider the question of agreement between the original 2^3 factorial and the expanded 2^4 factorial, as measured by the values obtained for the seven effects not involving the sulfide factor. As far as the first five effects listed in Table 3 are concerned, agreement was good. The effects attaining statistical significance were the same in both experiments, and, furthermore, the level of significance attained was the same. Discrepancies appeared, however, in the AI and FAI interactions. The AI interaction, which was significantly positive in the first experiment, now falls short of significance, and the FAI interaction, though still negative, is no longer large enough to claim reality.

Turning to the main object of the expanded experiment, the evaluation of effects involving the sulfide factor, it appears that neither the main effect of sulfide nor its simple interactions with the other three factors are significant. In the absence of any simple effects

TABLE 5. TABLE OF SIGNS FOR CALCULATION OF EFFECTS OF 2^4 FACTORIAL

	Effect														
Treatment	F	A	I	S	FA	FI	AI	FS	AS	IS	FAI	FAS	FIS	AIS	$FAIS$
$F_1A_1I_1S_1$	−	−	−	−	+	+	+	+	+	+	−	−	−	−	+
$F_2A_1I_1S_1$	+	−	−	−	−	−	+	−	+	+	+	+	+	−	−
$F_1A_2I_1S_1$	−	+	−	−	−	+	−	+	−	+	+	+	−	+	−
$F_2A_2I_1S_1$	+	+	−	−	+	−	−	−	−	+	−	−	+	+	+
$F_1A_1I_2S_1$	−	−	+	−	+	−	−	+	+	−	+	−	+	+	−
$F_2A_1I_2S_1$	+	−	+	−	−	+	−	−	+	−	−	+	−	+	+
$F_1A_2I_2S_1$	−	+	+	−	−	−	+	+	−	−	−	+	+	−	+
$F_2A_2I_2S_1$	+	+	+	−	+	+	+	−	−	−	+	−	−	−	−
$F_1A_1I_1S_2$	−	−	−	+	+	+	+	−	−	−	−	+	+	+	−
$F_2A_1I_1S_2$	+	−	−	+	−	−	+	+	−	−	+	−	−	+	+
$F_1A_2I_1S_2$	−	+	−	+	−	+	−	−	+	−	+	−	+	−	+
$F_2A_2I_1S_2$	+	+	−	+	+	−	−	+	+	−	−	+	−	−	−
$F_1A_1I_2S_2$	−	−	+	+	+	−	−	−	−	+	+	+	−	−	+
$F_2A_2I_1S_2$	+	−	+	+	−	+	−	+	−	+	−	−	+	−	−
$F_1A_2I_2S_2$	−	+	+	+	−	−	+	−	+	+	−	−	−	+	−
$F_2A_2I_2S_2$	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+

TABLE 6. RESULTS OF THE $2 \times 3 \times 3$ FACTORIAL

	$F = F_1$			$F = F_2$		
	$A = A_1$	$A = A_2$	$A = A_3$	$A = A_1$	$A = A_2$	$A = A_3$
$I = I_1$	1,003*	267*	340	1,014*	211*	187
$I = I_2$	783*	406*	557	889*	165*	141
$I = I_3$	499	726	1,115	555	153	113

---

*Taken from the original 2^3 experiment.
Note: Activity remaining in tens of counts per minute per 0.5 ml. of filtrate.
Iron concentration: $F_1 = 0.5$, $F_2 = 1.0$
Final pH: $A_1 = 4$, $A_2 = 6$, $A_3 = 8$
Initial pH: $I_1 = 1$, $I_2 = 2$, $I_3 = 4$

involving this factor, little weight can be assigned to the formally significant *AIS* and *FAIS* interactions.

The failure of the change in sulfide concentration to affect the results constitutes useful information. From the standpoint of economics it means that the quantity of sulfide may be halved without deleterious effect. From the standpoint of operational control, it means that the amount of sulfide might be allowed to vary within wide limits without decreasing the efficiency of the process.

The advantages of exploring the sulfide factor by expansion of the original factorial, rather than by an independent study, are now apparent; first, the sulfide factor, as well as its interactions with the first three factors, has been evaluated with maximum precision; second, the main effects and interactions of the original experiment have been further checked by utilization of the larger number of comparisons afforded by the expanded design.

EXPANSION OF THE 2^3 FACTORIAL BY ADDITION OF NEW LEVELS

Any factorial experiment may be expanded in two ways: by addition of new factors or by increase in the number of levels of the original factors. The first device having been utilized to explore the sulfide factor, the second was adopted to check the influence of further increases in the initial and final *p*H. The new *p*H levels were chosen as $A_3 = 8$ for the final *p*H and $I_3 = 4$ for the initial *p*H. The iron factor was retained at its original levels. The sulfide factor, which had given only negative results, was eliminated by being held constant at the original level of 0.5 g. The expanded factorial was thus a three-factor experiment, with the iron factor at two levels and each *p*H factor at three levels. There were $2 \times 3 \times 3 = 18$ treatment combinations required, of which eight were included in the original 2^3 factorial. The ten additional treatments were carried out in random order.

The outstanding conclusions of the experiment are revealed in a general way in Table 6, in which the results of the eighteen treatment combinations are tabulated in a systematic fashion. The table draws attention to a marked improvement in decontamination attributable to elevating the iron content and also to consistently better results with increasing initial and final *p*H provided the iron is held at the higher level.

The results may be examined more rigorously by computing the effect of each factor for each combination of levels of the remaining two factors. This has been done in Table 7 (*a*), (*b*), and (*c*) for the iron concentration factor, the final *p*H, and the initial *p*H, respectively. As the new treatments were not replicated, no error term is available for rigorous significance tests. However, because of the additional levels included, the consistency of trends is available as a criterion of significance. The maximum efficiency characteristic of the factorial plan again is evident: each of the three tables utilizes all the data. Because of the presence of pronounced interactions and the increasing concentration on specific results as optimum conditions are approached, the main or over-all effects are of only limited interest.

TABLE 7. SIMPLE AND MAIN EFFECTS OF THE 2 × 3 × 3 FACTORIAL EXPERIMENT

(*a*) Effect of Iron Concentration ($F_2 - F_1$)

	$A = A_1$	$A = A_2$	$A = A_3$	Avg.
$I = I_1$	11	− 56	− 153	− 66
$I = I_2$	107	−241	− 417	−184
$I = I_3$	56	−573	−1002	−506
Average	58	−290	− 524	−252

(*b*) Effect of Final *p*H

	$F = F_1$		$F = F_2$		Avg., F_1 and F_2	
	$A_2 - A_1$	$A_3 - A_2$	$A_2 - A_1$	$A_3 - A_2$	$A_2 - A_1$	$A_3 - A_2$
$I = I_1$	−737	73	−803	−24	−770	25
$I = I_2$	−377	151	−725	−24	−551	63
$I = I_3$	228	389	−402	−40	− 87	174
Average	−295	204	−643	−29	−469	87

(*c*) Effect of Initial *p*H

	$F = F_1$		$F = F_2$		Avg., F_1 and F_2	
	$I_2 - I_1$	$I_3 - I_2$	$I_2 - I_1$	$I_3 - I_2$	$I_2 - I_1$	$I_3 - I_2$
$A = A_1$	−220	−284	−124	−335	−172	−309
$A = A_2$	139	320	− 46	− 12	47	154
$A = A_3$	218	558	− 46	− 28	86	265
Average	46	198	− 72	−125	− 13	37

Note: Results in tens of counts per minute per 0.5-ml. of filtrate.

TABLE 8. RESULTS OF THE 4 × 4 FACTORIAL EXPERIMENT

	$A_1 = 4$	$A_2 = 6$	$A_3 = 8$	$A_4 = 10$
$I_1 = 1$	1,014	211	187	163
$I_2 = 2$	889	165	141	114
$I_3 = 4$	555	153	113	62
$I_4 = 6$	567	155	113	44

Note: Activity remaining in tens of counts per minute per 0.5 ml. of filtrate.

The effect of raising the iron concentration is given in Table 7 (*a*) for each of the nine different combinations of initial and final *p*H included in the expanded experiment. The table affords ample evidence of the *FA* interaction: for every *I* value, the iron effect becomes progressively more beneficial with increasing final *p*H. Also an *FI* interaction exists at the two higher levels of final *p*H, the effect of the iron factor becoming more beneficial with increasing initial *p*H.

The effect of a three-level factor requires two comparisons for its expression. Thus the effect of the final *p*H may be expressed as the differences $A_2 - A_1$, and $A_3 - A_2$. In Table 7 (*b*) each of these differences is tabulated for the six iron-concentration–initial-*p*H combinations included in the experiment. The *FA* interaction is again apparent: the beneficial effect of increasing the final *p*H is invariably greater at the higher iron level.

The effect of the initial *p*H, again expressed as two comparisons, is tabulated for each of the six iron-concentration–final-*p*H combinations in Table 7 (*c*). The *FI* interaction is exemplified by the circumstance that increasing the initial *p*H is consistently beneficial only at the higher iron level.

The positive *AI* interaction, suggested by the earlier experiments, is again present. Thus from Table 7 (*b*) the beneficial effect of increasing the final *p*H becomes less pronounced with increasing initial *p*H. Conversely, from Table 7 (*c*), the beneficial effect of increasing the initial *p*H drops off with increasing final *p*H. The positive interaction seems to be associated with the circumstance that with increasing final (initial) *p*H the limiting performance of the process is approached and therefore progressively smaller initial (final) *p*H effects are encountered. It is nonetheless clear from Table 6 that it is desirable to increase both *p*H factors together to attain the best decontamination.

THE 4 × 4 FACTORIAL

The results of the 2 × 3 × 3 experiment indicated that still further increases in nitial and final pH might give greater decontamination. Accordingly, one additional level was assigned to each of the pH factors, namely, $A_4 = 10$ and $I_4 = 6$. The iron concentration factor was eliminated by holding it constant at the higher level.

A factorial experiment, devoted to the two pH factors, each at four levels, required $4 \times 4 = 16$ treatments, seven of which are new. All sixteen results are tabulated in Table 8. The expected improvement, from increasing the final pH to 10, is confirmed for all three initial pH levels. The advantage of increasing the initial pH to 6 is slight and appears only at the highest final pH.

CONCLUSIONS

The decontamination obtained with an initial pH of 6 and a final pH of 10, when an iron concentration of 1 mg./ml. and 0.5 g. of sulfide were used, was the best result observed in the study. Judging from results at the lower pH levels, halving of the amount of sulfide used has no influence on the results. The possibility of further improving the process with still higher values of the pH did not appear attractive because of the smallness of any anticipated effect and the increasing cost entailed by additional chemical treatment.

The value of using a sequence of progressively expanding and contracting factorial designs in a study devoted to the establishment of optimum operating conditions has been clearly demonstrated. Such a procedure generates a series of coherent conclusions characterized by maximum reliability and generality. While the goal of optimum conditions is attained in a highly efficient manner, the functional dependence of the dependent variable on those conditions is thoroughly explored.

ACKNOWLEDGMENT

The services of the following chemists are gratefully acknowledged: T. C. Tesdahl, T. G. Linxweiler, and D. R. Spangler.

Mound Laboratory is operated by Monsanto Chemical Company for the U. S. Atomic Energy Commission under contract AT-33-1-GEN-53.

LITERATURE CITED

1. Lowe, C. S., L. L. Bentz, E. L. Murphy, E. Orban, F. Reichel, C. E. Shoemaker, and T. C. Tesdahl, *MLM*-662 (*Rev.*) (Dec. 28, 1953).
2. Fisher, R. A., "The Design of Experiments," 4 ed., Hafner Publishing Company, New York (1949).
3. Cochran, W. G., and G. Cox, "Experimental Designs," John Wiley and Sons, Inc., New York (1950).

Presented at Nuclear Science and Engineering Congress, Cleveland.

A System for Counting Variables in Separation Processes

MOOSON KWAUK

Hydrocarbon Research, Inc., New York, New York

In the proposed system for counting variables in separation processes the processes are resolved into their simpler component classes, e.g., theoretical plates, heat exchangers, reboilers, distillation columns, etc., and a distinction is made between those variables which are inherent in the systems and those which may be specified for design. Results are presented for the most commonly occurring component classes, and all possible process relations existing among these classes are expressed by a set of generalized equations [(16) to (19)]. The procedure of counting variables is therefore reduced to composition from variables for the component classes by use of the generalized equations.

In the design of processes for physical separation of components by mechanisms involving mass and heat transfer, the first step usually consists of specification of process conditions or independent variables. When the sufficient and necessary independent variables are fixed, the system is determined and other variables may be found by design computations. Normally the variables of a system are interrelated in such a way that only a few of them could be expressed as explicit functions of the others; the remaining ones have to be determined by lengthy calculations.

An example is the design of a distillation column separating a binary mixture of benzene and toluene. The column is to be designed to have one intermediate feed, a partial reboiler with a liquid-bottoms-product stream, and a total condenser with a liquid-distillate-product stream, and it will operate at atmospheric pressure. It is possible to specify for this column the concentration of either benzene or toluene in either the distillate or the bottoms stream, the recovery of either component in either stream, and the reflux ratio, viz., three independent variables. Then the number of theoretical plates both above and below the feed could be found by the familiar McCabe-Thiele diagram, thus determining two implicit dependent variables. A formal analysis shows, however, that for the column there exist four independent variables that could be specified. The fourth variable, not stated above, is implicit in the McCabe-Thiele method, that is, optimum location of the feed plate; the stepwise procedure is to be transferred from one operating line to the other in the vicinity of the intersection of the lines in order to secure a minimum total number of plates.

Another example is a so-called "double-distillation column" separating the ternary mixture, air—N_2, A, and O_2—with vapor air feed to the high-pressure column and a nitrogen-rich vapor distillate stream and an oxygen-rich vapor bottoms stream from the low-pressure column. In this case the number of independent variables that could be specified is not at all apparent. However, without a knowledge of the exact number of independent variables it is difficult, if not impossible, to proceed with a design problem in a systematic way. Often experience helps in setting trial values of certain variables very close to the correct answer, without the need of actually differentiating the implicit from the independent variables. With recent increase in use of electronic computers for design studies, however, it is desirable to know at the outset of a problem the correct number of independent variables as process conditions and to feed into the machine neither more nor less than those variables that can be specified, thus letting the machine perform the trial-and-error loops in finding the correct values of the dependent variables. In such a situation experience could hardly substitute for correct logic.

PRINCIPLES OF THE METHOD OF ANALYSIS

The difficulty of finding the correct number of independent variables was recognized by Gilliland and Reed (*2*), who proposed a method of attack by use of the phase rule and the first law of thermodynamics. Other discussions on the subject can be found in the literature

---

Tabular material has been deposited as document 4807 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for \$5.00 for photoprints or \$2.25 for 35-mm. microfilm.