Considering the XRD traces of the 5, 14 and 27.5% $HCℓO_4$ leached alloy (Figure 5.5 a-c) it can be seen that higher concentrations of acid result in more extensive leaching. Most noticeable are decreases in the $Cu(Zn)Aℓ_2$ phase, together with intergranular Aℓ and Zn. Aluminium leached more extensively than zinc, and in 27.5% perchloric acid no solid Aℓ was present after one hour of reaction. This trend is consistent with the AA data presented in Table 5.6. The CuAℓ phase remained impervious to perchloric acid attack, even at acid concentrations of 14 and 27.5%. The CuAℓ phase was also resistant to caustic leaching (see Chapter 4, Figure 4.7). Elemental copper was observed to be the primary product of leaching in the 27.5% $HCℓO_4$ solution, whilst no Cu(I) or Cu(II) was apparent after 1 hour extraction in perchloric and nitric acid at all concentrations (Figure 5.5).

Leaching Alloy B in 5, 14 and 27.5% $HNO_3$ (Figure 5.7 d-f) did not change the XRD pattern significantly. As the acid concentration was increased, so the *relative* intensity of the $Cu(Zn)Aℓ_2$ phase decreased by less than was observed for leaching in $HCℓO_4$.

Also, the amount of intergranular Aℓ and Zn decreased, with traces of only Aℓ seen after one hour of leaching in 27.5% $HNO_3$. Once again, the CuAℓ phase appeared to be resistant to leaching in all concentrations of nitric acid. Elemental copper was identified in the XRD pattern obtained for Alloy B extracted in 27.5% $HNO_3$, but as expected, was more predominant in the pattern of the 27.5% $HCℓO_4$ leached alloy (Figure 5.5). The XRD traces show that the relative intensities (and hence content) of the 5 and 14% perchloric and nitric acid leached (Figure 5.5 a,d and b,e respectively) alloys are similar. The AA analysis of the catalysts (Table 5.6) is consistent with this trend. Extraction of Alloy B in all concentrations of both acids for 19.5 hours shows that after <u>long</u> reaction times, Aℓ and Zn are depleted to residual levels, whilst the bulk copper content does not exceed a maximum of 76.4wt% (Table 5.6).

## 5.3.4. Statistical optimisation of catalyst preparation variables

Alloy B was selected for the statistical evaluation of three important preparation variables (see Chapter 6). In this case, a $2^3$ factorial design was chosen for investigating the effect of the variable particle size range, acid strength and acid/metal ratio on total catalyst surface area. Catalysts were prepared by leaching Alloy B in nitric and perchloric acids for 1.0 hour according to the design matrix presented in Table 5.7. The leach reaction procedure and conditions were similar to those reported in Chapter 2, Section 2.1.1.

**Table 5.7** **The $2^3$ factorial design matrix for determining the effects of particle size, acid strength and acid/metal ratio at two levels using 8 experiments**

| Standard/ run number | Particle size (μm) | Acid Strength (%) | Acid/Metal ratio |
|---|---|---|---|
| 1 | 300 - 500 (-)[a] | 5.0 (-) | 1:1 (-) |
| 2 | 1180 - 1400 (+) | 5.0 (-) | 1:1 (-) |
| 3 | 300 - 500 (-) | 27.5 (+) | 1:1 (-) |
| 4 | 1180 - 1400 (+) | 27.5 (+) | 1:1 (-) |
| 5 | 300 - 500 (-) | 5.0 (-) | 3:1 (+) |
| 6 | 1180 - 1400 (+) | 5.0 (-) | 3:1 (+) |
| 7 | 300 - 500 (-) | 27.5 (+) | 3:1 (+) |
| 8 | 1180 - 1400 (+) | 27.5 (+) | 3:1 (+) |

[a] Positive and negative signs indicate the high and low levels selected for each of the variables (see Chapter 6.).

The BET surface area responses, together with the bulk catalyst compositions (determined by AA) for the nitric and perchloric acid leached alloys are shown in Tables 5.8 and 5.9 respectively.

Table 5.8 **BET surface area responses and corresponding bulk compositions of the Raney copper catalysts leached in nitric acid**

| Standard/ run number | $S_{BET}$ (response) ($m^2.g^{-1}$) | Bulk Composition (wt%) | | |
|---|---|---|---|---|
| | | Cu | Zn | Aℓ |
| 1 | 2.5 | 64.0 | 10.2 | 25.8 |
| 2 | 1.5 | 57.5 | 14.0 | 28.5 |
| 3 | 1.0 | 67.6 | 9.5 | 22.9 |
| 4 | 1.3 | 56.0 | 14.4 | 29.6 |
| 5 | 0.9 | 63.4 | 12.5 | 24.1 |
| 6 | 0.6 | 62.4 | 17.9 | 19.6 |
| 7 | 0.9 | 68.9 | 6.4 | 24.7 |
| 8 | 1.4 | 58.9 | 14.1 | 27.0 |

Table 5.9 **BET surface area responses and corresponding bulk compositions of the Raney copper catalysts leached in perchloric acid**

| Standard/ run number | $S_{BET}$ (response) ($m^2.g^{-1}$) | Bulk Composition (wt%) | | |
|---|---|---|---|---|
| | | Cu | Zn | Aℓ |
| 1 | 5.1 | 80.7 | 11.0 | 8.3 |
| 2 | 6.5 | 65.5 | 10.5 | 24.0 |
| 3 | 5.0 | 69.8 | 7.6 | 22.6 |
| 4 | 4.3 | 67.9 | 12.6 | 19.5 |
| 5 | 5.8 | 64.9 | 9.9 | 25.2 |
| 6 | 7.7 | 69.6 | 10.6 | 19.8 |
| 7 | 8.8 | 83.5 | 3.6 | 12.9 |
| 8 | 7.0 | 80.9 | 5.3 | 13.8 |

No significant main effects or two factor interactions were observed for either the nitric or perchloric acid statistical experiments, and as a result, three catalysts were randomly chosen from each design on the basis of "high" BET surface area and/or high Zn content for reactor testing. Based on this criteria, Catalysts 1, 4 and 8 were chosen from the nitric acid design, whilst Catalysts 6, 7 and 8 were chosen from the perchloric acid design. Immediately evident from Tables 5.8 and 5.9 are the

extremely low BET surface areas of all 16 Raney copper catalysts relative to those of the caustic extracted samples. The BET and copper surface areas, together with the copper dispersion of the selected catalysts are presented in Table 5.10.

Table 5.10 **Surface area and copper dispersion of selected Raney copper catalysts leached in nitric and perchloric acid**

| Acid Catalyst number | $S_{BET}$ ($m^2.g^{-1}$) | $S_{Cu}$ ($m^2.g^{-1}$) | Copper Dispersion (%) x $10^{-1}$ |
|---|---|---|---|
| N (1)[a] | 2.5 | 0.49 | 2.2 |
| N (4) | 1.3 | 0.05 | 0.3 |
| N (8) | 1.4 | 0.27 | 1.4 |
| P (6)[b] | 7.7 | 0.31 | 1.3 |
| P (7) | 8.8 | 0.46 | 0.2 |
| P (8) | 7.0 | 0.19 | 0.1 |

[a] N = nitric acid leached catalyst, number ... (see Table 5.8)
[b] P = perchloric acid leached catalyst, number ... (see Table 5.9)

From Table 5.10 it can be seen that leaching in both nitric and perchloric acids under the stated conditions resulted in Raney catalysts with negligible copper surface areas and dispersions. Interestingly, the BET surface areas of the perchloric acid leached alloys are at least twice the area observed for the nitric acid extracted samples. XRD analysis (Figure 5.5) showed that more extensive extraction took place during perchloric acid extraction, especially in concentrated solutions. This observation may explain the higher surface areas.

## 5.3.5 Activity and stability of acid leached Alloy B catalysts

### (a) Initial activity

The initial WGS activities of the selected nitric and perchloric extracted alloys are presented in Table 5.11. Specific activities are expressed as the rate (per hour) of moles of carbon monoxide converted as a function of : volume of catalyst particles (Rate a), composite (total) mass of catalyst particles (Rate b), specific copper surface area (Rate c) and BET surface area (Rate d).

**Table 5.11** **Specific activities of Raney copper catalysts leached in nitric and perchloric acid[a]**

| Acid/ Catalyst number | Extraction time (h) | Rate (a) ($mol_{CO}/ml/h$) x $10^{-3}$ | Rate (b) ($mol_{CO}/g_{comp}/h$) x $10^{-3}$ | Rate (c) ($mol_{CO}/m^2_{Cu}/h$) x $10^{-3}$ | Rate (d) ($mol_{CO}/m^2/h$) x $10^{-4}$ |
|---|---|---|---|---|---|
| N (1) | 1.0 | 2.37 | 1.38 | 2.82 | 5.54 |
| N (4) | 1.0 | 0.16 | 0.09 | 1.84 | 0.71 |
| N (8) | 1.0 | 0.85 | 0.49 | 1.78 | 3.48 |
| P (6) | 1.0 | 0.7 | 0.50 | 1.62 | 0.65 |
| P (7) | 1.0 | 0.64 | 0.53 | 1.16 | 0.61 |
| P (8) | 1.0 | 1.10 | 1.09 | 5.67 | 1.56 |

[a] Temperature = 200°C; Total GHSV = $1000\,h^{-1}$; Dry gas composition = 10% CO/90% $N_2$; $CO:H_2O$ = 1:22.5; Catalyst Volume = 2 ± 0.1 ml

From Table 5.11 it can be seen that the copper and total surface area turnover efficiencies (Rates c and d respectively) are significantly higher than the equivalent rates observed for caustic leached Raney copper catalysts, as well as the industrial and co-precipitated alternatives (see Chapter 4, Table 4.9). Rates c and d for the acid leached catalysts are greater than expected because of the high CO conversions observed for low copper surface areas at a GHSV of $1000\,h^{-1}$.

Activities based on catalyst volume and composite mass (Rates a and b respectively) clearly demonstrate that the low surface areas render acid leached Raney copper catalysts inappropriate for commercial operation.

(b) Stability

Long term life-time microreactor runs were conducted on catalysts N(1) and P(8) with EDAX determined zinc contents of 3.2% and 2.0%. The results are shown in Figures 5.6 and 5.7 respectively. In each case, stability was evaluated at temperatures of 200, 250 and 300°C, using the procedure and conditions described in Chapter 2, Section 2.2. Activities were expressed in terms of mass of catalyst copper content.

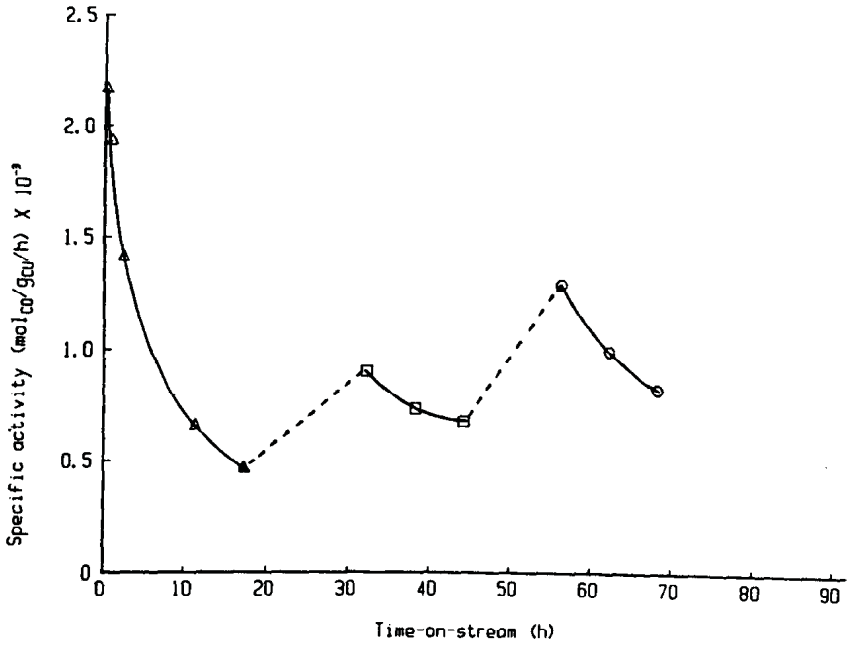


**Figure 5.6** **Stability of a nitric acid leached Raney copper catalyst [N(1)] at various temperatures[a]**

△ = 200°C; ⊡ = 250°C; ⊙ = 300°C

[a] Total GHSV = 1000 $h^{-1}$; Dry gas composition = 10% CO/90% $N_2$; $CO:H_2O$ = 1:22.5; Catalyst Volume = 2 ± 0.1 ml

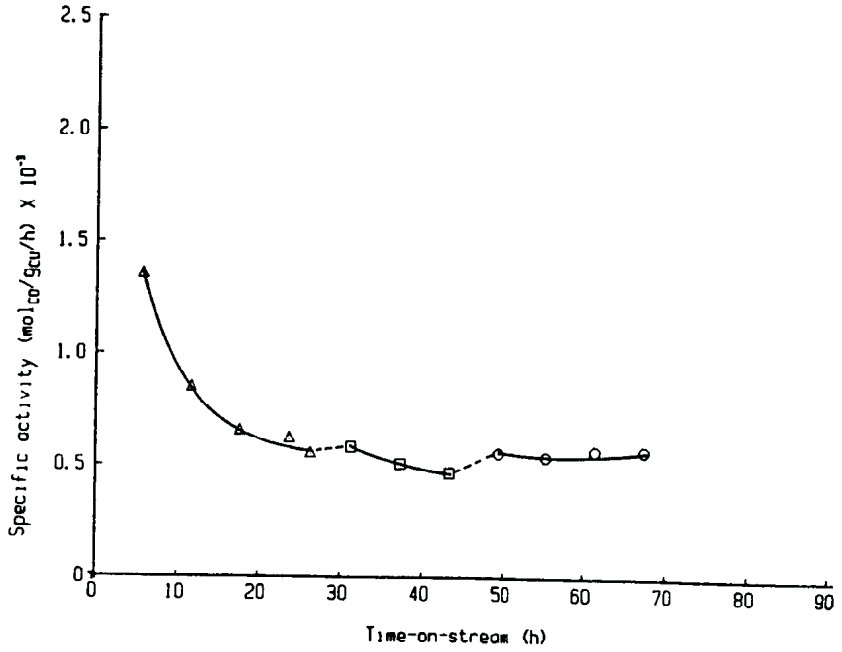


**Figure 5.7** **Stability of a perchloric acid leached Raney copper catalyst [P(8)] at various temperatures[a]**

△ = 200°C; ⊡ = 250°C; ⊙ = 300°C

[a] Total GHSV = 1000 $h^{-1}$; Dry gas composition = 10% CO/90% $N_2$; CO:$H_2O$ = 1:22.5; Catalyst Volume = 2 ± 0.1 ml

For both representative catalysts (Figures 5.6 and 5.7) it is evident that the evenly dispersed rim zinc contents could not effectively stabilize the very low copper surface areas (see Table 5.10) and consequently rapid sintering resulted in decreases in catalyst activity at all temperatures evaluated.

## 5.4 SUMMARY

The caustic leaching of precursor alloys rich in zinc proved to be an effective method for increasing the content of zinc in the Raney copper rim without compromising the formation of high copper surface areas, shown to result in high WGS activity. The residual zinc had a stabilizing influence on the catalyst surface area, and a quantitative relationship was observed between the amount of zinc dispersed in the catalyst rim, and long-term stability. Caustic leached Raney copper catalysts exhibited a high degree of WGS activity in the low temperature region (i.e. 175 - 300°C) under a variety of reaction conditions. Alloys leached in nitric and perchloric acids resulted in catalysts with low surface areas and low WGS activities. On this criteria alone, Raney copper catalysts prepared in this manner are regarded as unsuitable for commercial operation.

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# CHAPTER SIX

# THE STATISTICAL OPTIMISATION OF RANEY COPPER CATALYST PREPARATION VARIABLES

## 6.1 INTRODUCTION

Raney copper catalysts have been shown to be very active for catalysing the WGSR. Previous studies (Chapter 5) demonstrated that the chemical and physical properties of the resultant catalysts are dependent on the phase constitution of the precursor alloys and the liquid phase diffusion kinetics of the leach reaction - which is in turn dependent on the preparative **experimental conditions** (1). In this chapter, an optimal Raney copper catalyst has been formulated by considering the large number of variables which may have contributed towards catalytic activity and stability. Identification of the important factors in this system is a task which could involve extensive experimentation. An approach which has been shown (1, 2) to have considerable merit in similar situations involves the use of statistically designed experiments. The "statistical design of experiments" refers to the selection of suitable mathematically based experiments which enable *appropriate* data to be collected and subsequently analysed by statistical methods in order to obtain valid and objective conclusions (2).

The earliest designed experiments (2) were conducted in the agricultural field at the Rothamsted Research Station in 1843, where Sir Ronald Fisher developed and first used the *analysis of variance* as the primary method of statistical analysis in experimental design. Today, such experiments are widely employed for multi-disciplinary tasks.

Initially, a **factorial design** was employed to screen the large number of predictor variables with the purpose of

obtaining the most information from the least number of necessary runs. Factorial experiments permit more than one variable (factor) to be investigated **simultaneously** in a single experiment whilst, in a complete trial, all possible combinations of the levels of the variables are investigated (2). The statistical design for the general $2^k$ factorial design (k variables, each considered at two *chemically meaningful* levels designated as the *low value* or "-" and the *high value* or "+" in the matrix design) enables $2^k-1$ effects to be calculated. The effect of a variable is defined to be the change in response produced by a change in the level of the variable (2). This is frequently called a **main effect** because it refers to the primary variables of interest in the experiment (2). Box *et al.* (3) define 'main effect' as the measurement of the *average* effect of a variable under consideration, over all conditions of the other variables. Also, 1/2k(k-1) two-factor interactions, 1/6k(k-1)(k-2) three factor interactions...one k interaction may be evaluated from the design. A measure of **interaction** (3) is supplied by the difference between the average effect of say, variable A and both levels of a variable B. By convention, half the difference is called the "variable A" by "variable B" interaction or, in symbols, the A x B 2 factor/variable interaction. **Interaction(s)** between factors occur when the difference in response between the levels of one factor are not the same at all levels of the other factor(s) (2). Main effects and interactions, can be represented geometrically. Figure 6.1 shows the **possible** main effects and interactions of a $2^3$ design for 3 factors (namely T, C and K).

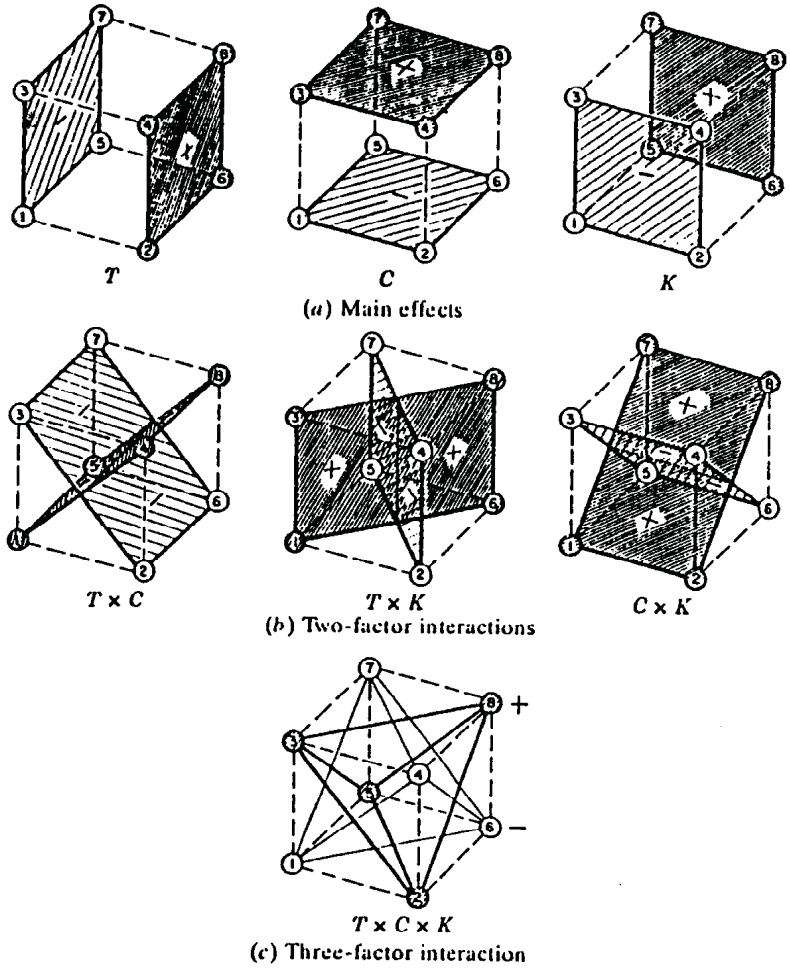



**Figure 6.1** **Geometric representation of contrasts corresponding to main effects and interactions (3)**

Main effects may be viewed as a *contrast* between observations on parallel faces of the cube (Figure 6.1), whereas interactions are a contrast between results on two diagonal planes. Factorial designs are necessary when interactions between variables may be present, as correct interpretation avoids misleading conclusions (2) which may arise from 'traditional' one-variable-at-a-time experiments. Specifically, if variables act additively, the factorial results in better precision (3), and if the variables do not act additively, the factorial, unlike the one-factor-at-a-time approach, can detect and estimate interactions that measure the nonadditivity (3).

Once the important variables have been established, then further information about their effects can be obtained from a more detailed experiment involving only this *reduced* set of variables (1). Typically, a **central composite** factorial design in conjunction with **response surface** methodology was used to optimise our selected variables with respect to high catalyst activity and stability. Central composite designs are an arrangement of a two-level factorial design together with a star design including the central point (4), as geometrically shown in Figure 6.2. The points in Figure 6.2 represent the chosen values of variables. Points of the square (joined by continuous lines) indicate the factorial design, whilst those intersecting the six faces of the square at right angles (joined by broken lines) form the star design. The open circle is the central point.

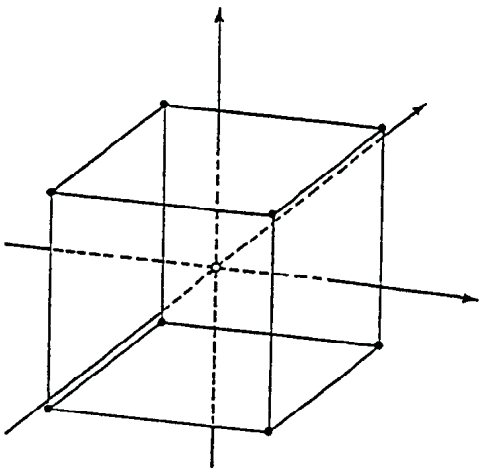


**Figure 6.2** **Geometric representation of a central composite design (4)**

From Figure 6.2 the most complete evaluation of the response surface, using a given number of experiments can be made. The central and star points make it possible to accurately describe any *curvature* in the system by use of a second order mathematical model if necessary. Response surfaces are usually graphically presented as plotted

contours of constant expected response, or translated into three-dimensional curves. The computer packages, 'Design Base', 'Design Expert' and 'Stat. Graphics' were used to facilitate the analysis of statistical data. Composite factorial designs are more efficient than one-variable-at-a-time experiments (5), particularly because the latter approach often fails to locate true optimums, since the strategy tacitly assumes that the maximized value of one variable is independent of the level of the other variable(s), which is usually not true (3).

## 6.2 SCREENING STUDY

This phase of the work involved the evaluation of the effect of 7 Raney copper catalyst preparation variables and 4 reactor condition variables on the responses: (i) initial activity, (ii) final activity and (iii) change in activity using a *fractional* factorial design. The number of experimental runs required by a full $2^k$ factorial design increases exponentially as k is increased (3). In this case, the factorial design for 11 variables each at 2 levels is a $2^{11}$ design and consists of 2048 experimental runs. Fortunately, the desired information can often be obtained by performing only a fraction of the full factorial design (3). A 1/128 fraction of this design consisting of 16 runs was chosen, and is called a resolution III design. The $2_{III}^{11-7}$ design has no main effects inextricably linked (aliased) with any other main effects, but main effects are aliased with two-factor interactions, and two-factor interactions are aliased with each other. Thus, only if the two-factor and higher order interactions are assumed to be negligible, can main effects be estimated. The $2_{III}^{11-7}$ design matrix is presented in Table 6.1

Table 6.1 The $2_{III}^{11-7}$ fractional factorial design matrix for determining the effects of 11 variables at two levels using 16 experiments

| Standard Order | Run Order | Variable* | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | A | B | C | D | E | F | G | H | I | J | K |
| 1 | 1 | − | − | − | − | − | − | − | − | + | + | + |
| 2 | 10 | + | − | − | − | + | − | + | + | − | − | − |
| 3 | 4 | − | + | − | − | + | + | − | + | − | − | + |
| 4 | 15 | + | + | − | − | − | + | + | − | + | + | − |
| 5 | 7 | − | − | + | − | + | + | + | − | − | + | − |
| 6 | 16 | + | − | + | − | − | + | − | + | + | − | + |
| 7 | 2 | − | + | + | − | − | − | + | + | + | − | − |
| 8 | 11 | + | + | + | − | + | − | − | − | − | + | + |
| 9 | 12 | − | − | − | + | − | + | + | + | − | + | + |
| 10 | 3 | + | − | − | + | + | + | − | − | + | − | − |
| 11 | 6 | − | + | − | + | + | − | + | − | + | − | + |
| 12 | 8 | + | + | − | + | − | − | − | + | − | + | − |
| 13 | 13 | − | − | + | + | + | − | − | + | + | + | − |
| 14 | 9 | + | − | + | + | − | − | + | − | − | − | + |
| 15 | 5 | − | + | + | + | − | + | − | − | − | − | − |
| 16 | 14 | + | + | + | + | + | + | + | + | + | + | + |

* "−" = Low Level
"+" = High Level

The *standard order* (Table 6.1) denotes the original fractional design, whilst the *run order* denotes the randomized order in which the experiment was performed. Statistical methods require that observations and errors must be independently distributed, random variables. Thus

by properly randomizing an experiment this requirement is validated and consequently results in the reduction of experimental error (2, 3). The $2_{III}^{11-7}$ design permits 11 variables to be assessed in 16 runs thereby allowing for the determination of experimental variability or error. The fractional factorial design is in essence the same as the "classical" Plackett and Burman design of similar magnitude, except that fewer two factor interactions are aliased with main effects. Thus by careful choice in the combination of *predicted* aliased effects, the optimum information from the least possible runs can be obtained. The higher order, three-factor interactions are considered to be redundant. In summary, the low resolution fractional factorial design may only be used for screening purposes. These designs do not permit *the separate* estimation of main effects, two factor and higher order interactions. Table 6.2 lists the low and high levels of the 11 variables screened.

**Table 6.2** **Low and high levels of the 11 variables screened using the $2_{III}^{11-7}$ fractional factorial design**

| Variable | Description | Level | |
|---|---|---|---|
| | | Low (-) | High (+) |
| A | Alloy particle size | 0.3 - 0.5 mm | 1.0 - 1.18 mm |
| B | Final caustic concentration | 10% | 30% |
| C | Leach reaction temperature | 30°C | 80°C |
| D | Reduction | 240°C/3.5 h | 240°C/16 h |
| E | Passivation | NO | YES |
| F | Caustic/soluble metal ratio | 1/1 | 3/1 |
| G | Leach time | 10 min | 2 h |
| H | Zincate solution | NO | YES |
| I | $CO/H_2O$ ratio | 1/20 | 1/30 |
| J | Reaction temperature | 200°C | 300°C |
| k | GHSV | 1000 $h^{-1}$ | 4600 $h^{-1}$ |

### 6.2.1 Experimental

Alloy B of nominal composition 25wt% Cu, 25wt% Zn and 50wt% Aℓ (see Chapter 2, Table 2.1) was used to prepare the Raney catalysts by leaching 20g of the alloy with aqueous sodium hydroxide. The catalysts were prepared and tested for selected responses in random order according to the conditions of the variables listed in Tables 6.1 and 6.2. If required, (see Table 6.1) leaching took place in caustic solutions containing 0.5M zincate (variable H) whilst passivation was conducted according to the procedure outlined in Appendix 1 (Variable E). The reduction (variable D) was similar at both levels, (see Chapter 2, Section 2.2.1) except for the total reduction time at 240°C. Responses chosen were (i) **initial activity:** taken after steady-state conditions had been achieved, up to a maximum of 20 hours-on-stream, (ii) **final activity:** taken after 168 hours on-stream, and (iii) **change in activity:** which is a measure of stability of the Raney copper catalyst, calculated from Equation 6.1.

$$\textit{Change in Activity} = |\textit{final activity} - \textit{initial activity}| \quad (6.1)$$

The WGS activity is expressed as percent CO conversion for $2 \pm 0.1$ml of catalyst tested in each case. CO conversion enabled easy and efficient recognition of chemically meaningful data predicted from mathematical models derived from the central composite design (see Section 6.3).
In all cases, after the leaching reaction was complete, the Raney catalyst was washed with distilled water (until the pH of the wash solution was approximately 7) and subsequently air dried or passivated. Catalyst was loaded into the fixed bed, stainless steel microreactors described in Chapter 2, and a gas mixture of $CO/N_2$ = 10/90 vol% was passed over the catalyst at the operating temperature at atmospheric pressure (0.825kPa).

## 6.2.2 Results and discussion of screening experiment

Responses (i) - (iii) presented as percent CO conversion for each run of the $2_{III}^{11-7}$ fractional factorial design are reported in Table 6.3.

Table 6.3 **Fractional factorial responses for initial activity, final activity and change in activity**

| Run Order | Initial Activity (%) | Final Activity (%) | Change in Activity (%) |
|---|---|---|---|
| 1 | 92.0 | 39.0 | 53.0 |
| 2 | 58.8 | 44.5 | 14.3 |
| 3 | 87.2 | 71.8 | 15.4 |
| 4 | 99.9 | 94.8 | 5.1 |
| 5 | 56.7 | 45.8 | 10.9 |
| 6 | 90.1 | 40.9 | 49.2 |
| 7 | 94.7 | 71.3 | 23.4 |
| 8 | 89.1 | 86.1 | 3.0 |
| 9 | 78.5 | 63.6 | 14.9 |
| 10 | 84.6 | 82.3 | 2.3 |
| 11 | 99.9 | 89.2 | 10.7 |
| 12 | 99.9 | 99.9 | 0 |
| 13 | 88.2 | 52.8 | 35.4 |
| 14 | 99.9 | 99.9 | 0 |
| 15 | 78.6 | 77.7 | 0.9 |
| 16 | 84.9 | 60.8 | 24.1 |

The *effect* of a variable on each response (known as the estimate) is simply the difference between the average value of the response for the eight runs at the high level and the average value of the response at the low level, according to Equation 6.2 (1).

$$E_A = \frac{\Sigma R \text{ at } (+)}{8} - \frac{\Sigma R \text{ at } (-)}{8} \qquad - (6.2)$$

where: $E_A$ = estimate of the effect of variable "A"
R = response or result (see Table 6.4)

The results of the $2_{III}^{11-7}$ fractional factorial analysis are presented in Table 6.4. Only "real" main effects with *significant* estimates are included, together with the standard error of determination. Estimates of the main effects of variables on chosen responses were considered significant if they were approximately three times the magnitude of the calculated error (5).

**Table 6.4** **Main effects which significantly influence initial activity, final activity and change in activity**

| Main Effect | Estimate ± S.T.D. Error |
|---|---|
| **INITIAL ACTIVITY** | |
| Passivation | 13.3 ± 2.5 |
| Leach temperature | -7.5 ± 2.5 |
| GHSV | 13.5 ± 2.5 |
| Reaction temperature | 12.7 ± 2.5 |
| **FINAL ACTIVITY** | |
| $CO:H_2O$ ratio | -18.2 ± 4.7 |
| Alloy particle size | 17.8 ± 4.7 |
| Caustic/soluble metal ratio | 15.5 ± 4.7 |
| Zincate solution | 15.3 ± 4.7 |
| **CHANGE IN ACTIVITY** | |
| $CO:H_2O$ ratio | 15.2 ± 4.3 |
| Alloy particle size | -17.8 ± 4.3 |
| Caustic/soluble metal ratio | -12.9 ± 4.3 |
| Zincate solution | -11.8 ± 4.3 |

From Table 6.4 it can be seen that "initial WGS activity" is influenced by *catalyst* passivation and leach temperature. Passivation controls the oxidation of Raney copper after leaching whilst, leach temperature *directly* affects the rate of the leaching process which is known to determine the Raney copper catalyst morphology (see Chapter 4). Using a Plackett-Burman design to screen predictor variables, Friedrich *et al.* (1) found leach temperature to be the most important preparation variable in the

determination of Raney copper methanol synthesis activity. It has been shown in Chapter 5 and confirmed by the low resolution statistical screening experiment (see Table 6.4) that GHSV and reaction temperature affect the (initial) WGS activity of Raney copper. In the case of "final activity" and "change in activity" the same four variables are significant. The extent of the forward WGS reaction is known to depend on the proportion of CO and steam ($CO:H_2O$ ratio) in the feed gas, (see Chapter 1, Section 1.2.2) as highlighted by the results of the fractional factorial design, whilst **long term catalytic performance** (assessed by responses ii and iii) was influenced by the alloy particle size distribution, caustic/soluble metal ratio and zincate solution (see Table 6.4). Raney copper stability was shown to be enhanced by the addition of zinc to the catalyst during the extraction of precursor ternary Cu-Zn-Aℓ alloys in caustic/zincate solutions (Chapter 4, Section 4.3.4).

The low resolution $2_{IIII}^{11-7}$ screening experiment confirmed the significance of a number of variables to affect the appropriate responses, thus demonstrating the applicability of selecting statistical methods to optimise the Raney copper catalyst system. Although *high* initial Raney copper WGS activity was easily achieved by the straightforward caustic leaching procedure over a large extraction time range (see Chapter 4, Section 4.3.2), rapid deactivation took place with time-on-stream. Therefore, the optimisation of a Raney copper catalyst for the WGSR required more detailed knowledge of the variables specifically affecting long term activity which have been identified from the screening experiment as alloy particle size distribution, caustic/soluble metal ratio and zincate concentration.

## 6.3 CENTRAL COMPOSITE DESIGN FOR CATALYST OPTIMISATION STUDY

The central composite design matrix for the three variables selected for further analysis is shown in Table 6.5.

Table 6.5 **The central composite design matrix for estimating the effects of particle size distribution, caustic/soluble metal ratio and zincate concentration on catalyst stability**

| Standard Order | Run Order | Alloy particle size (A) | Caustic/ soluble metal ratio (F) | Zincate solution (H) |
|---|---|---|---|---|
| 1 | 2 | -1 | -1 | -1 |
| 2 | 3 | +1 | 1 | 1 |
| 3 | 1 | -1 | -1 | 1 |
| 4 | 13 | +1 | 1 | -1 |
| 5 | 14 | +1 | -1 | 1 |
| 6 | 7 | -1 | 1 | -1 |
| 7 | 8 | +1 | -1 | -1 |
| 8 | 9 | -1 | 1 | 1 |
| 9 | 4 | 0 | 0 | 0 |
| 10 | 5 | 0 | 0 | 0 |
| 11 | 6 | 0 | 0 | 0 |
| 12 | 10 | 0 | 0 | 0 |
| 13 | 11 | 0 | 0 | 0 |
| 14 | 12 | 0 | 0 | 0 |
| i | i | -a | 0 | 0 |
| ii | ii | 0 | 0 | -a |
| iii | iii | 0 | 0 | a |
| iv | iv | 0 | -a | 0 |
| v | v | 0 | a | 0 |
| vi | vi | a | 0 | 0 |

This phase of the work was carried out in two steps. Initially runs 1-14 constituting a high resolution $2^3$ factorial experiment with six repeated determinations of the central point (from which experimental error could be accurately assessed) was conducted. From the $2^3$ factorial design, the seven "degrees of freedom" between the eight treatment combinations are associated with the main effects

of each of the 3 variables together with each 2-factor combination of the possible variables and the three factor interaction (2). Thus from these results an understanding of the *chemical nature* of the selected variables on the responses was obtained. Completion of the star points (runs i - vi in Table 6.5) in the second step enabled response surfaces to be generated from mathematical equations fitted to "final" and "change in" activity data obtained from a consideration of each variable at 5 distinct levels. The strategy for the optimisation of Raney copper involved selecting the alloy particle size distribution, caustic/soluble metal ratio and zincate concentration which resulted in the maximization of final activity and the minimization of change in activity. Intersection plots were used to help identify the required conditions. Table 6.6 lists the levels of variables A, F and H selected for the central composite design, whilst Table 6.7 shows the "standard conditions" of all other factors.

**Table 6.6** **Levels of the three Raney catalyst preparation variables selected for optimisation**

| Variable | Description | Level | | | | |
|---|---|---|---|---|---|---|
| | | -a | -1 | 0 | 1 | +a |
| A | Alloy particle size (mm) | 0.3-0.5 | 0.5-0.85 | 0.85-1.0 | 1.0-1.18 | 1.18-1.4 |
| F | Caustic/soluble metal ratio | 0.1/1 | 1/1 | 2/1 | 3/1 | 4/1 |
| H | Zincate concentration (M) | 0.25 | 0.4 | 0.5 | 0.6 | 0.75 |

Table 6.7 **Constant levels of all non-optimisation variables**

| Variable | Description | Level |
|---|---|---|
| A | Alloy particle size | VARIABLE[a] |
| B | Final caustic concentration | 20% |
| C | Leach reaction temperature | 50°C |
| D | Reduction | 240°C/16h |
| E | Passivation | YES |
| F | Caustic/soluble metal ratio | VARIABLE[a] |
| G | Leach time | 1h |
| H | Zincate solution | VARIABLE[a] |
| I | $CO:H_2O$ ratio | 1:22.5 |
| J | Reaction temperature | 200°C |
| K | GHSV | $1000\,h^{-1}$ |

[a] See Table 6.6

### 6.3.1 Experimental

The experimental procedure was similar to that reported for the screening experiment in Section 6.2.1. In each case 20g of Alloy B was leached in caustic solution according to the conditions set out in Tables 6.5, 6.6 and 6.7. The experimental runs were carried out randomly according to the order stipulated in Table 6.5.

### 6.3.2 Results and discussion of central composite design

The final and change in activity (expressed in percent CO conversion) for all runs was determined after 168 hours-on-stream, and the results are presented in Table 6.8.

Table 6.8 Composite design responses for final activity and change in activity

| Run Order | Final Activity (%) | Change in Activity (%) |
|---|---|---|
| 1 | 81.2 | 1.6 |
| 2 | 84.4 | 6.4 |
| 3 | 80.5 | 10.5 |
| 4 | 78.6 | 11.4 |
| 5 | 59.3 | 17 |
| 6 | 76 | 24 |
| 7 | 73.8 | 2.3 |
| 8 | 82.3 | 0 |
| 9 | 69.2 | 11.2 |
| 10 | 71.6 | 14.7 |
| 11 | 70 | 13.5 |
| 12 | 69.7 | 9.8 |
| 13 | 76.8 | 12.7 |
| 14 | 74.4 | 6.3 |
| i | 58.1 | 0 |
| ii | 80.9 | 6.8 |
| iii | 89.1 | 8.1 |
| iv | 73.8 | 3.6 |
| v | 76.8 | 4.9 |
| vi | 66.4 | 6.6 |

(a) *Effects*

The estimates (and standard error) of the main effects and two factor interactions on final activity and change in activity are presented in Tables 6.9 and 6.10 respectively.

**Table 6.9** **Estimates of the main effects and two factor interactions on final activity**

| Main Effect | Estimate ± S.T.D. Error |
|---|---|
| Alloy particle size | -5.9 ± 3.0 |
| Caustic/Soluble metal ratio | 6.6 ± 3.0 |
| Zincate solution | -0.8 ± 3.0 |
| **Two Factor Interactions** | **Estimate ± S.T.D. Error** |
| Alloy particle size X C/S ratio | 8.3 ± 3.0 |
| C/S ratio x Zincate solution | -3.6 ± 3.0 |
| Alloy particle size x Zincate solution | 6.8 ± 3.0 |

**Table 6.10** **Estimates of the main effects and two factor interactions on change in activity**

| Main Effect | Estimate ± S.T.D. Error |
|---|---|
| Alloy particle size | 0.3 ± 3.1 |
| Caustic/Soluble metal ratio | 2.6 ± 3.1 |
| Zincate solution | -1.4 ± 3.1 |
| **Two Factor Interactions** | **Estimate ± S.T.D. Error** |
| Alloy particle size X C/S ratio | -3.4 ± 3.1 |
| C/S ratio x Zincate solution | -13.5 ± 3.1 |
| Alloy particle size x Zincate solution | 6.2 ± 3.1 |

From Tables 6.9 and 6.10 it can be seen that none of the three variables (alloy size distribution, caustic/soluble metal ratio and zincate concentration) have a *singular* main effect on either response, but rather the interaction of alloy size and caustic/soluble metal ratio significantly

influences the final activity, whilst the change in activity is significantly affected by the interaction of caustic/soluble metal ratio and zincate concentration. To check the significant effects, normal probability plots for each response were constructed according to the method described by Box *et al.* (3). Curves were obtained by plotting the percentage normal distribution $P_i$ (where $P_i = 100\ (i - 1/2)/m$ for i = 1.2 ...m and i = order number of effect i) against the appropriate estimate of each respective response, and are presented in Figures 6.3 and 6.4.

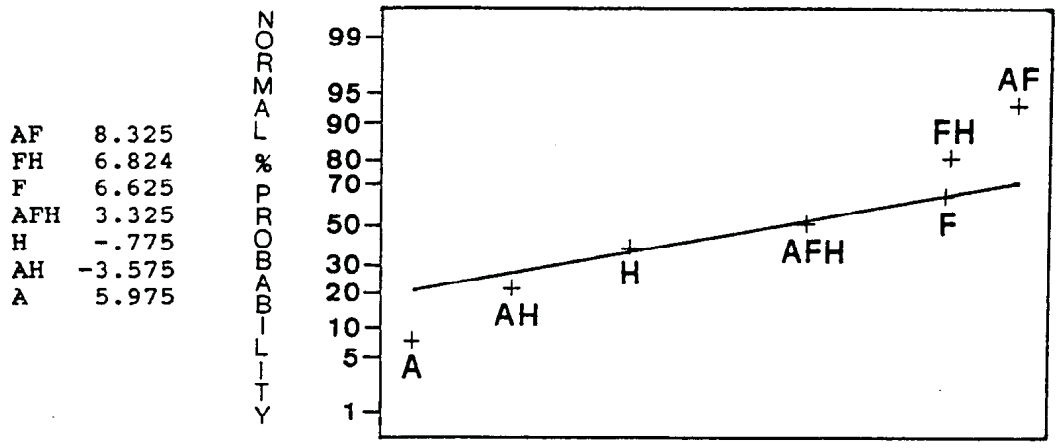



**Figure 6.3** **Normal probability plot for final activity**

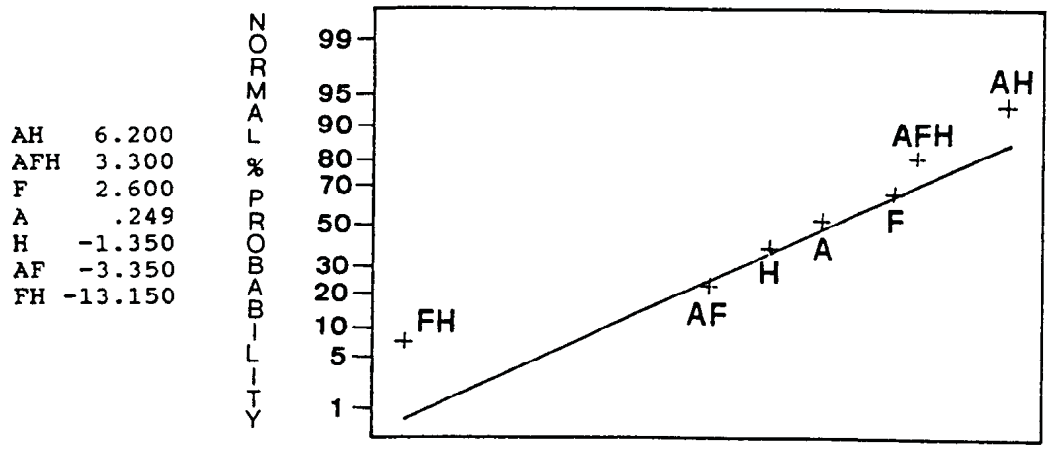
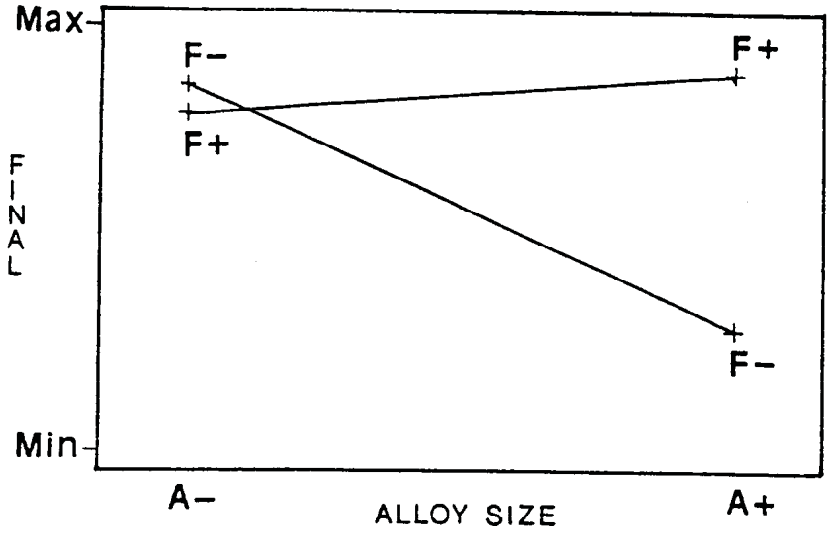



**Figure 6.4** **Normal probability plot for change in activity**

The vertical axes (see Figures 6.3 and 6.4) are altered to represent the sigmoidal cumulative normal curve as a straight line (3). The effects that are negligible will tend to fall along a straight line on this graph, while significant effects will be far from the line. Consequently, it can be seen from Figure 6.3 (graph of "final activity") that the interaction AF (or alloy size x caustic/soluble metal ratio) lies furthest from the line. Similarly, the interaction FH (or caustic/soluble metal ratio x zincate concentration) is well displaced from the normal probability straight line of Figure 6.4 (graph of "change in activity"). The normal probability plots therefore confirm the significant interactions calculated from the estimates (see Tables 6.9 and 6.10).

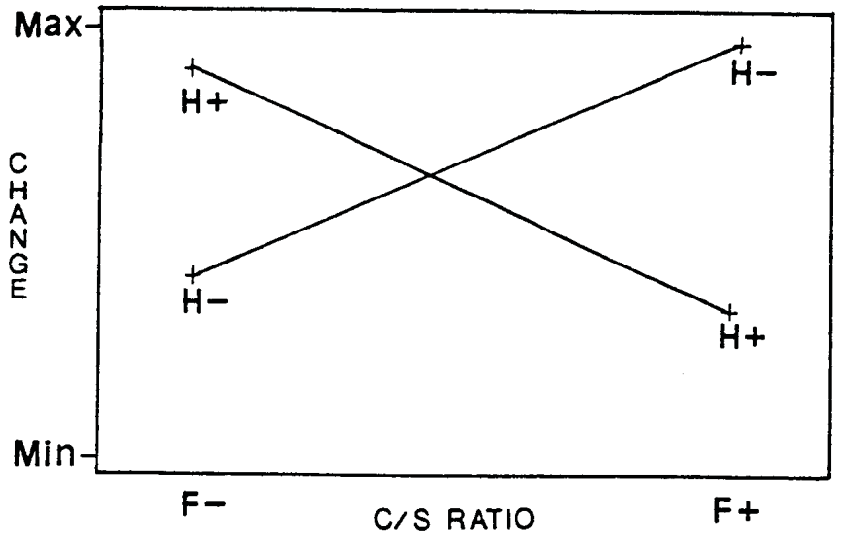
(b) *Interaction plots*

The interactions with respect to final activity (AxF) and change in activity (F x H) are graphically illustrated in Figures 6.5 and 6.6 respectively. The calculated BET and copper surface area responses for each interaction *point* are also included.




| Variable A | Variable F | Final (%) | $S_{BET}$ ($m^2.g^{-1}$) | $S_{Cu}$ ($m^2.g^{-1}$) |
|---|---|---|---|---|
| − | − | 80.9 | 19 | 2.5 |
| + | − | 66.6 | 13.5 | 1.9 |
| − | + | 79.2 | 16.5 | 2.5 |
| + | + | 81.5 | 14.5 | 2.2 |

**Figure 6.5** **Interaction of alloy particle size (A) and caustic/soluble metal ratio (F) with respect to final activity**




| Variable F | Variable H | Change (%) | $S_{BET}$ ($m^2.g^{-1}$) | $S_{Cu}$ ($m^2.g^{-1}$) |
|---|---|---|---|---|
| - | - | 1.9 | 19.0 | 2.4 |
| + | - | 17.7 | 17.5 | 3.2 |
| - | + | 13.8 | 13.5 | 1.9 |
| + | + | 3.2 | 13.5 | 2.0 |

**Figure 6.6** **Interaction of zincate concentration (H) and caustic/soluble metal ratio (F) with respect to change in activity**

Plots of this nature show the appropriate activity response from the interaction of the two variables involved at all extreme combinations. The final activity in Figure 6.5 is observed to be at a minimum for high alloy particle size distribution and low C/S metal ratio (A+F-). The A+F- combination also represents a minimum in BET and copper surface area (see Figure 6.5). Clearly, if limited caustic is used to leach *large* alloy particles, "*insufficient*" extraction fails to produce the surface area required for high activity. Combination A-F+ may represent the onset of the opposite situation in which "*extensive*" extraction (possibly due to large excesses of caustic solution required to leach smaller alloy particles) results in smaller surface areas. A similar trend was reported in Chapter 4 for Raney copper surface area and extent of leach

reaction.

From Figure 6.6 it can be seen that change in activity is minimized at extreme combinations of both caustic/soluble metal ratio (F) and zincate concentration (H). At the high level of caustic solution (F+), a high zincate concentration (combination F+H+) decreased the leach rate (see Chapter 4, Section 4.3.4) and consequently surface area (as compared to combination F+H-) but as expected, the additional zinc deposit from the increased zincate concentration (F+H+) minimized the change in activity with time-on-stream. At the low level of caustic solution (F-), the addition of a low zincate concentration (combination F-H-) resulted in a faster extraction rate which produced a Raney copper catalyst with high BET and copper surface area (as compared to combination F-H+) after one hour of leaching (see Figure 6.6). A higher zincate concentration (combination F-H+) slowed the leach rate to such an extent that a catalyst with much smaller comparative surface area resulted from the preparation. It was predicted that the Raney copper catalyst produced from the F-H+ combination would be unsuitable, and the large change in activity confirmed that excessive sintering of the small copper area resulted with time-on-stream.

(c) *Cubic plots*

From each set of response data presented for runs 1-8 ($2^3$ factorials) in Table 6.8, three dimensional cubic plots can be constructed (3) to combine all the information from the eight "treatment" combinations together. Figure 6.7 represents the cubic plot for the "final activity" response, whilst the cubic plot for the "change in activity" response is displayed in Figure 6.8.

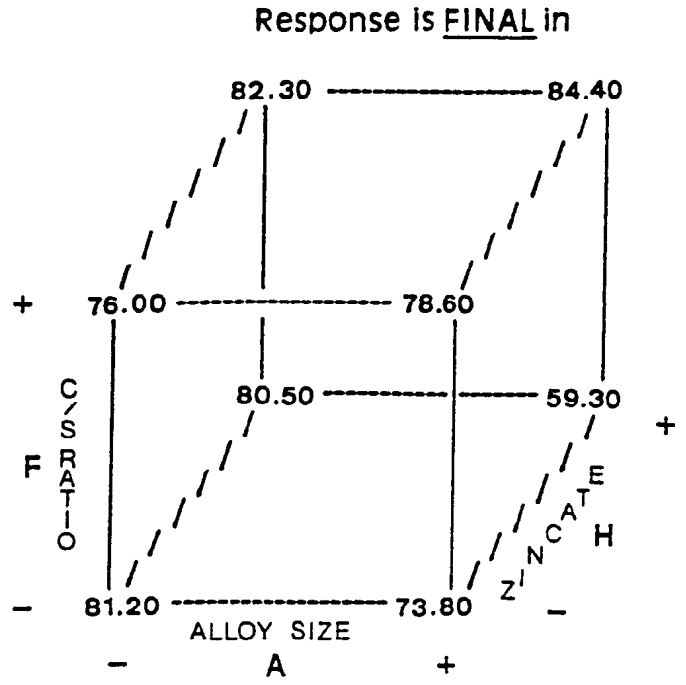



Figure 6.7 Cubic plot of final activity response

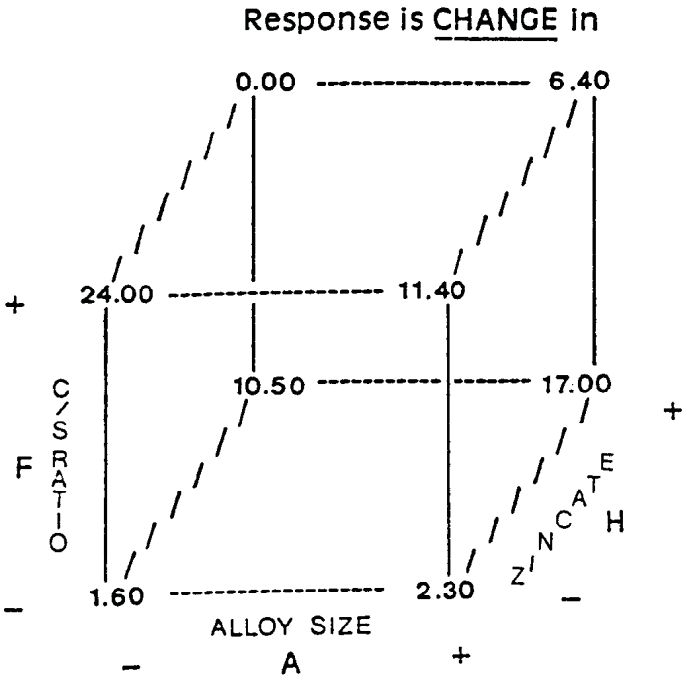



Figure 6.8 Cubic plot of change in activity response