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Selective Extraction of Copper from Brass Ash by Segregation Roasting

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Abstract - This paper describes a study on extraction of copper from brass ash by segregation roasting. The segregation roasting reactions were carried out using the principle of design of experiments. All experiments were carried out at two levels for four parameters i.e. temperature, time, leco char and sodium chloride percentage. Results were analyzed by the method known as ANOVA (Analysis of variance) and a regression equation was developed using coded forms :

$$Y = 53.72 - 3.74\ X_1 - 2.52\ X_2 + 4.87\ X_3 + 2.58\ X_4 - 4.31\ X_2X_4 + 1.972X_1X_3 + 1.886\ X_3X_4$$

Where Y represents the percent of copper recovery and X_1, X_2, X_3, X_4 are in coded form for temperature, time, % leco char and % sodium chloride addition respectively. The process was further optimized by a method known as Simplex Sequential Design (SSD). Using SSD method it was possible to arrive at 98 pct of copper recovery where the experiment was carried out using temperature 655^0C, time 9 min, leco char addition 4.48 pct and sodium chloride addition 4.01 pct.

INTRODUCTION

Segregation roasting process is considered to be one of the promising pyro-metallurgical process applied for extraction of copper from various oxidic sources (1-4).The process involves heating the oxidic material in presence of small quantity of a reducing agent like coal, coke or char coal and a chloride salt like sodium chloride, calcium chloride etc. to segregate the metal in its elemental stage, much below of its melting point on a reductant surface. The copper segregation process is extremely complex and involves many competing reactions. The successful operation of the process depends on a delicate balance of these reactions and the proper selection of various roasting parameters. The scheme of copper segregation reactions can be divide in three major steps, (i) the production of chloridizing gases, (ii) the chloridization of the copper content of the ore, and (iii) the precipitation of the copper on the carbon surface.

The reaction cycle is initiated with the production of hydrogen chloride by

hydrolysis of sodium chloride in the presence of certain gangue minerals.

$$2NaCl_{(s)} + H_2O_{(g)} + SiO_{2(g)} \text{---------}\rightarrow Na_2SiO_{3(s)} + 2HCl_{(g)} \qquad (1)$$

This reaction is extremely fast and can yield adequate quantities of hydrogen chloride in the presence of bound or vapor phase water. Reduction of cupric copper by removal of lattice oxygen to form a lower oxide can occur rapidly as follows :

$$2CuO + H_2 \text{----}\rightarrow Cu_2O + H_20 \qquad (2)$$

$$2CuO + CO \text{-----}\rightarrow Cu_2O + CO_2 \qquad (3)$$

Chloridization of the lower oxide occur according to reaction (4)

$$Cu_2O+2HCl = 2CuCl + H_2O \quad (4)$$

Volatilization of the cuprous chloride to form a gaseous trimmer is a rapid process.

$$3CuCl_{(l)} \text{---------}\rightarrow Cu_3Cl_{3(g)} \quad (5)$$

Reduction of cuprous chloride to form segregated copper is very fast and thermodynamically favorable reaction is represented as below,

$$Cu_3Cl_{3(g)} + 3/2H_2 = 3Cu + 3HCl \quad (6)$$

This basic mechanism has been accepted and the process has been adequately demonstrated for wide ranging of ores. This paper describes the application of segregation roasting process for selective extraction of copper from brass ash.

The segregation roasting process was carried out using principle of design of experiments. For a two level experiment of four parameters, i.e., temperature, time, sodium chloride addition and Leco char addition, a total number of sixteen experiments were conducted. A regression equation is developed from the results of the experiments and process is further optimized based on simplex sequential design method.

EXPERIMENTAL

The brass ash contains about 5.9% copper, 30% zinc, 6% iron, 5.6% silicon and 10% insoluble and 6% moisture. Experiments were carried out in a horizontal tube furnace with temperature accuracy of $\pm 2^oC$. Segregation roasting reactions were carried out for a specific amount of brass ash (10 g). The brass ash was mixed with required proportion of charcoal and sodium chloride and kept in a mullite boat. The boat was inserted in the hot zone of horizontal furnace under a stream of nitrogen. The furnace was heated to pre-designated temperature. The brass ash was allowed to react for a specific period of time as per experimental requirement. After the reaction was over, the mullite boat was removed from the hot zone of the furnace and allowed to cool in the relatively cold position in the furnace. After a certain interval of time, the boat was removed from the muffle furnace and kept outside. Whole reacted mass containing copper on char coal surface was leached in potassium persulphate. The filtrate is analyzed for copper recovery.

RESULTS AND DISCUSSION

A full factorial design of experiments were conducted using the principle of design of experiments. The four main parameters i.e., temperature (X_1), time (X_2), Leco char addition (X_3) and sodium chloride addition (X_4) were varied simultaneously at two levels, higher level (+) and lower level (-). The base level and range of parameters were selected as follows,

temperature, 720^oC, (700^0C-740^oC)

time, 30 min, (15-45 min)

Leco char addition, 3%, (2-4%)

sodium chloride addition 2%, (1-3%)

During the study, the temperature, time, char and sodium chloride additions were increased in steps size (ΔZ) of 20^0C, 15 min, 1% and 1% respectively. Sixteen experiments were conducted based on design of experiments at two levels with four parameters.

$$N = n^k \quad (7)$$

Where, N = the number of all possible combination of experiments, n = number of level, 2 (two level), and k= number of factors, 4. The following type of regression equation was applied to estimate various coefficients for independent and interaction parameter.

$$Y= bo + b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{23}X_2X_3 + b_{24}X_2X_4 + b_{34}X_3X_4 + b_{123}X_1X_2X_3 + b_{234}X_2X_3X_4 + b_{124}X_1X_2X_4 + b_{134}X_1X_3X_4 + b_{1234}X_1X_2X_3X_4 \quad (8)$$

Where, X_1 X_2 X_3 and X_4 represent temperature, time, percentage of char addition and sodium chloride addition in their coded form respectively and Y represents percentage metal recovery. The relationship between the coded and actual values are given as :

$X_1 = (X_1\text{-}720)/20$, $X_2=(X_2\text{-}30)/15$, $X_3=(X_3\text{-}3)/2$, $X_4\text{-}(X_4\text{-}2)/1$

The regression coefficients were estimated as :

$$bo = \frac{\sum Y}{N} ; \quad bi = \frac{\sum Xi \; Y_i}{N} ; \quad b_{12} = \frac{\sum (X_1X_2) \, Y_1}{N} \text{ etc.}$$

Coefficients, $b_{1,}$ b_2, b_3 and b_4 show respectively, the effect of temperature, time, char and sodium chloride addition, coefficients b_{12}, b_{13} etc. are the interacting effects of two parameters like temperature and time, temperature and percentage of char addition. Where as, coefficients b_{123}, b_{234} etc. are the interacting effect of three parameters. Coefficient b_{1234} is the interacting effect of all the four parameters. Table-1 lists the actual and coded values of parameters. Table 2 shows the complete design matrix based on the coded scale. It also gives the actual percentage yield of copper, Y which is response variable. Based on the results shown in Table 2, a regression equation similar to eq (7) was developed. The regression equation was subjected statistical test procedures. The test of significance was carried out for each coefficients of the regression equation using student 't' test at 99.95% ($\alpha = 0.05$) level of significance. The modified regression equation is as fellows:

$$Y = 53.72 - 3.74X_1 - 2.52X_2 + 4.87X_3 + 2.58X_4 - 4.31 X_2X_4 + 1.972X_1X_3 + 1.886X_3X_4 \quad (9)$$

Table-1

Actual and coded values of the variables for brass ash segregation roasting

Level	X_1 (temp In ^{0}C)	X_1 (Coded value)	X_2 (time min.)	X_2 (Coded value)	X_3 (char %)	X_3 (Coded value)	X_4 (Nacl %)	X_4 (Coded value)
Upper	740	+	45	+	4	+	3	+
Base	730	0	30	0	3	0	2	0
Lower	720	-	15	-	2	-	1	-

Table-2

Design matrix based on coded scale and copper recovery

Trial	Temp.	Time	Leco char Addition	Sodium Chloride Addition	Percentage of Copper recovery
1	+	+	+	+	54.92
2	-	+	+	+	61.38
3	+	-	+	+	66.23
4	-	-	+	+	66.77
5	+	+	-	+	33.15
6	-	+	-	+	48.46
7	+	-	-	+	52.23
8	-	-	-	+	64.61
9	+	+	+	-	53.84
10	-	+	+	-	58.15
11	+	-	+	-	49.53
12	-	-	+	-	55.92
13	+	+	-	-	44.15
14	-	+	-	-	52.80
15	+	-	-	-	43.07
16	-	-	-	-	49.64
17	0	0	0	0	51.69
18	0	0	0	0	52.77
19	0	0	0	0	52.25
20	0	0	0	0	53.15
21	0	0	0	0	51.23
22	0	0	0	0	51.80

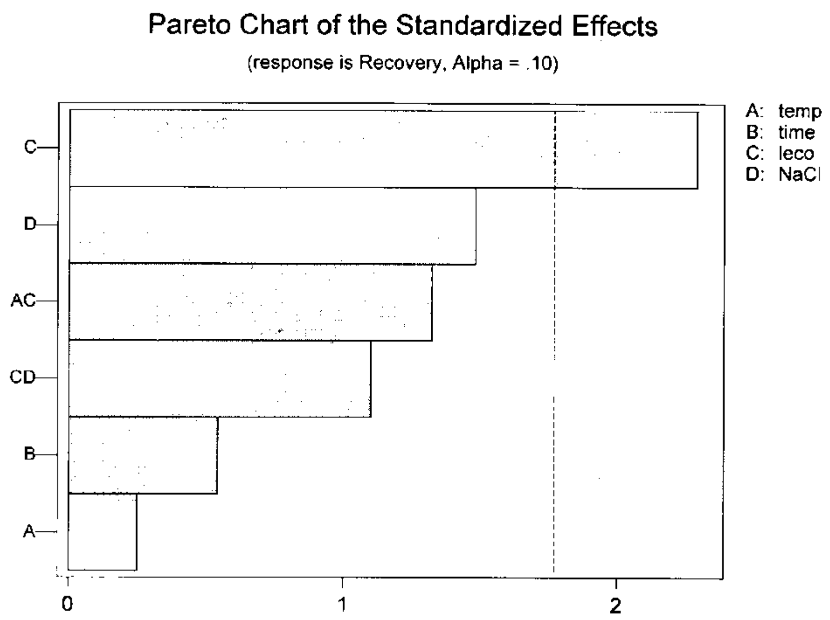

Fig-1 Pareto Chart presenting standardized effects

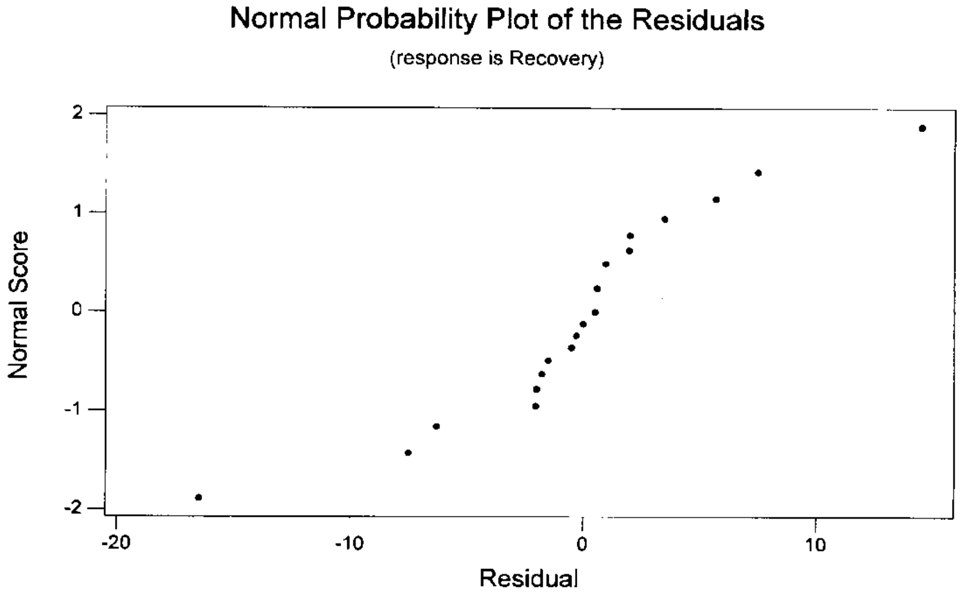

Fig-2 Normal probability plot for the statistical design

In the regression equation 9, Y is pct of metal recovery and X_1, X_2, X_3, X_4 are the operating parameters in coded form. The above regression equation clearly shows that temperature and time have negative influence on copper recovery where as pct of Leco char and sodium chloride addition have positive influence. The pareto chart for the above factorial design shows the various interacting parameters to effect the copper segregation (fig-1). This chart gives both the magnitude and importance of the most significant parameter. The chart also constitute a line of reference and any effect that expands past this reference line has got high potentiality. Thus, as the chart reveals leco-char addition seems to be the most active parameter for copper recovery followed by NaCl, time and temperature. The interacting parameters x_3x_4 and x_1x_3 seem to be the most active. The normal probability plots of the statistically designed experiments shows standardized effects of these experiments as shown in fig-2, indicating that the experimental parameters and levels chosen under observation are valid for the above segregation reaction.

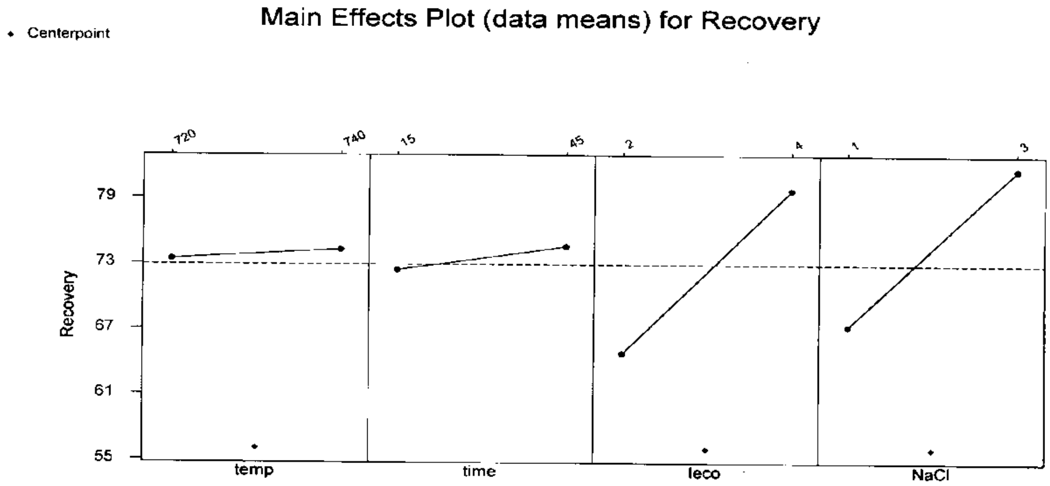

Fig-3 Main effect plot representing the mean of each parameter

Figure-3 shows the main effects plot representing the mean of each parameter at each level. This is used to compare the magnitudes of various main effects. The main effect occurs when the main response changes across the levels of a factor. Here the plot implies, even at lower level, temperature has a negative effect on recovery i.e., the temperature has to be still decreased in order to obtain a higher recovery. Similarly, time factor shifts towards lower side for better segregation of copper. The less addition of char seems to be optimized at the center point where as NaCl addition seeks the lower level to give better copper recovery.

Optimisation

i) Response optimization:

Response optimisation is carried out to identify the combination of input variable settings that jointly optimise a single response. It also provides a global solution for the input variables through an optimization plot. The optimization plot is interactive, which can adjust input variable setting on the plot to get a more desirable solution. The above regression equation (8) can be utilized for the response optimisation. During the optimization, the overall desirability of the response is obtained to be zero at a maximum recovery of 90% (fig-4). The above test concludes, the composite desirability for the above input variable is obtained to be zero, where the global solution is considerable i.e., temperature 730 C, time 30 mins with 2% NaCl and 3% char. In order to obtain a desirability of one, the global solution has to be shifted accordingly. It has been verified that with a decreasing trend the global solution can give a maximum desirability at about 650 C with 15 mins retention time where the other variables remain constant. From the above solution, the Overlaid Contour plots can be drawn which provides information to correlate response variable with factorial variables.

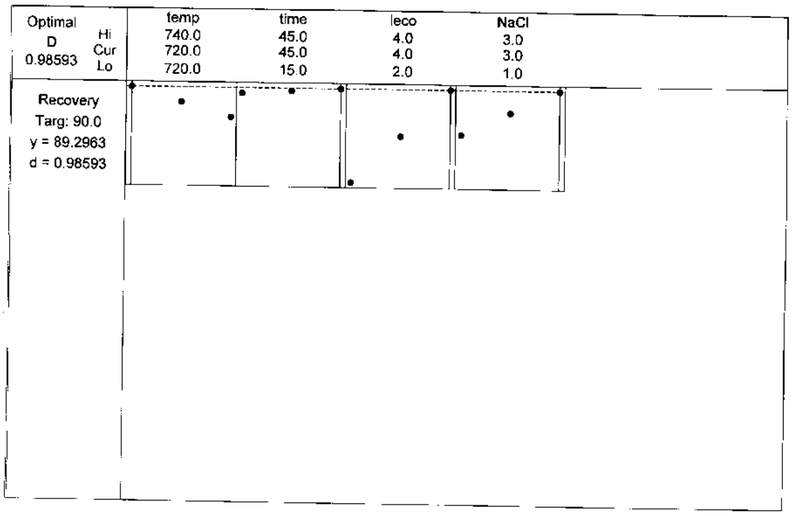

Fig-4 Response optimization plot

ii) Overlaid Contour Plots:

Overlaid contour plot shows how the response variable relates to two major factorial variables. In a contour plot the fitted values are connected to produce the contour lines of constants. These plots are used for establishing operating conditions that produce desirable response values. It also visualise an area of compromise where the maximum recovery can be obtained. In the present study, two factors temperature and time, are used as the two axes in the plot, the other two factors leco-char and NaCl addition are taken as the hold values (Constant Values). The white area inside the plot (fig-5) shows the range of time and temperature, where the criteria for the response variable is satisfied. This area equally serves as the best operating condition for a maximum recovery of 80-99%. From the above data the final optimisation can be obtained as below:

Traditionally optimisation is carried out by calculating the partial derivation and employing the gradient to find the maximum. Although efficient, gradient methods have several limitations, such as, obtaining the analytical form of the partials can be tedious for complex functions and rather than a maximum, a saddle point may be found since the gradient is also zero at this point.

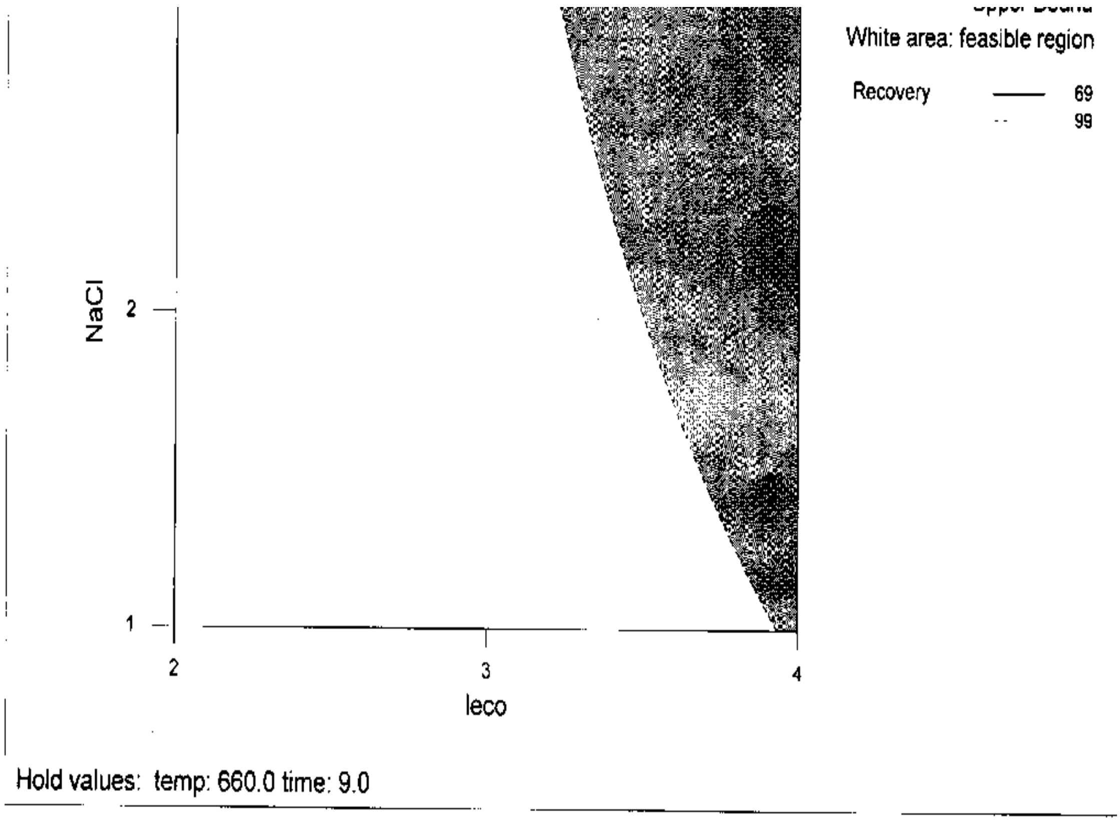

Fig-5 Overlaid contour plot with hold values temp= 660^{0}C, Time = 9 mins.

In 1962, W, Spendley, C.R. Hext and F.R. Himsworth proposed a method of optimisation that sequentially projected the worst point in a simplex through the centroid of remaining points (5) in 1965, J.A. Welder and R. Mead published a more flexible version of the simplex procedure in that it adapted itself to the local landscape (6).

There are three methods of changing the simplex : reflection, contraction and expansion. A new point is generated during reflection of the worst point, through the centroid of all other points. If the reflection point is better than current best point, it replaces the current worst point. In order to get an optimum recovery, an expansion step is tried using the data obtained at the reflection best point, the expansion step is by passed and the contraction step is tried where the reflection point is compared with all other points except the worst one. If any other reflection point is better, it replaces the worst point and further studied to get the maximum recovery. The statistical data obtained from the above experiments, represented in table-2, are subjected to simplex method analysis. The trial run with the lowest recovery is taken as the worst point and also, some other points with lower recovery are taken into consideration. The simplex method analysis reveals some new experimental points with variable parameters, which are generated through mirror reflection study of the worst and worse points. The mirror reflection of each point has been represented in Table-3. Further experiments were carried out with the parameters obtained from the mirror reflection study for each experiment and the results are represented in Table-4.

Table-3

Representation of mirror reflection data for each worse point along with their experimental parameters

Old expt no.	New expt no.	Temp., ⁰C	Time	% Leco-char	% NaCl
5	23	700	13	4.12	0.85
15	24	692	73	4.41	2.85
13	25	685	12.43	4.73	3.10
11	26	678	41.28	2.83	3.36
16	27	710	42.23	4.91	3.66
6	28	710	13.59	5.29	1.75
7	29	665	43.4	5.46	1.60
9	30	665	8.97	4.48	4.00

Table-4

Segregation roasting parameters are in natural scale and corresponding copper recovery for optimisation study

New expt. No.	Old expt No.	Temp. ⁰C	Time	% Leco Char	% Sodium Choride	% Copper Recovery
23	5	700	13	4.12	0.85	81.84
24	15	692	73	4.41	2.85	87.23
25	13	685	12.43	4.73	3.10	86.15
26	11	678	41.28	2.83	3.36	84.00
27	16	710	42.23	4.91	3.66	84.50
28	6	710	13.59	5.29	1.75	73.70
29	7	665	43.40	5.46	1.60	80.15
30	9	665	8.97	4.48	4.00	98.00

CONCLUSIONS

The above segregation process has been explained under various factorial studies. The possible range of parameters , their rate of influence, activity and percentage addition to reveal maximum recovery of copper has been verified thoroughly. Response optimization and contour plots could able to find the input factorial limits for maximum recovery. The segregation process was further optimised by simplex sequential design and it was possible to arrive at conditions where at bast 98 percent of copper could be recovered, with the following parametric conditions: temperature, 655ºC, time, 9 minutes, Leco char addition, 4.48 pct and sodium chloride addition, 4 pct.

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