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SHORT COMMUNICATION

Anodic leaching of tungsten alloy swarf: a statistical approach

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1. Introduction

Tungsten finds extensive use in the preparation of special alloys owing to its favourable mechanical properties and high melting point. Considerable quantities of swarf are generated during the production of these special alloy components. Many methods are employed for the recovery of tungsten from the swarf. Apart from physical methods [1, 2] like melting, crushing, cold-stream process etc., electrolytic processes have also been attempted [3–12]. In the electrolytic method both acidic and alkaline electrolytes are used. In the case of acidic electrolyte, strong oxidizing conditions [3, 4] are maintained to convert tungsten into tungstic acid. In order to prevent the passivation of the anode, chloride is sometimes added and the use of a.c. electrolysis has also been suggested [4, 12]. In the case of alkaline electrolyte, the tungsten in the alloy is anodically dissolved as sodium tungstate [8] from which pure tungstic oxide is obtainable. This method is selective as it prevents the other metallic impurities like Fe, Co, Ni etc. from dissolving.

1.1. *Statistical design*

It is well known that the use of statistical design enables identification of the optimum conditions with fewer experiments. A regression equation is obtained from which the effect of an individual variable and its relative effect on the total process can be assessed. The synergistic effect of two or more variables can also be obtained which is not possible with the classical type of experiments. This technique is currently used for optimization [13–15] in many fields, including extractive metallurgy.

In the present investigation, a simple factorial experiment was used where the parameters were varied at two levels. The parameters were current density (X_1), sodium hydroxide concentration (X_2) and sodium chloride concentration (X_3). The number of experiments required for the two level experiments having three variables d is given by the equation

$$N = p^k$$

$$N = 2^3 = 8 \text{ trials}$$

where N is the total number of trials required, p the number of levels and k the factors affecting the anodic dissolution.

Base level experiments were also to be carried out to test the significance of the coefficients and adequacy of the model.

2. Experimental details

Anodic leaching was carried out in a PVC vessel of 1 dm^3 capacity. The anode was a tungsten alloy cylinder of 2.7 cm diameter and 9 cm length. The cathode was a perforated stainless steel sheet (15 cm × 38 cm) placed concentric to the anode. The temperature of the cell was maintained around 30 ± 1°C.

A regulated power supply was used as d.c. source. The actual (natural scale) and coded (dimensionless scale) values are given in Table 1.

After each experiment the electrolyte was filtered, the residue washed and washings were added to the filtrate. The tungsten in the solution was estimated with lead nitrate using 4-(2-pyridylazo)-resorcinol indicator [16] and the current efficiency for tungsten dissolution was computed. The tungsten alloy contained 3% iron and 1% nickel.

3. Results and discussion

The design matrix and the results obtained are shown in Table 2.

The regression equation is given by

$$y = Q_0 + Q_1X_1 + Q_2X_2 + Q_3X_3 + Q_{12}X_1X_2 + Q_{13}X_1X_3 + Q_{23}X_2X_3 + Q_{123}X_1X_2X_3 \quad (1)$$

where $Q_j = \sum_{i=1}^{N}(X_{ji}Y_i/N)$ and $j = 0, 1, 2, 3, \ldots, k$.

After inserting the values of the coefficients, the regression equation becomes

$$\hat{Y} = 61.45 - 17.62X_1 + 15.30X_2 - 11.83X_3 + 4.53X_1X_2 - 0.40X_2X_3 - 6.72X_1X_3 - 6.7X_1X_2X_3 \quad (2)$$

For a significant level of $\alpha = 0.05$ and $\gamma = 2$ degrees of freedom, the tabulated value of the Student t-distribution $t\alpha(\nu) = 4.3$ (see Appendix 1). Thus, the coefficient Q_{23} is insignificant and this must be deleted from the equation; the regression equation then takes the form,

$$\hat{y} = 61.45 - 17.62X_1 + 15.30X_2 - 11.83X_3 + 4.53X_1X_2 - 6.72X_1X_3 - 6.7X_1X_2X_3 \quad (3)$$

where $\hat{Y}$ is the predicted value of the response variable.

A Fischer test indicates that the model is adequate at 95% confidence. (see Appendix 2).

3.1. *Effect of current density*

The regression equation shows that the current

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Table 1. Actual and coded values of variables

Levels	*Current density*		*[NaOH]*		*[NaCl]*	
	Actual $X_1/\mathrm{A\,m^{-2}}$	*Coded* X_{1i}	*Actual* $X_2/\mathrm{g\,dm^{-3}}$	*Coded* X_{2i}	*Actual* $X_3/\mathrm{g\,dm^{-3}}$	*Coded* X_{3i}
Upper	415.0	+1	100	+1	80	+1
Lower	250.0	−1	30	−1	20	−1
Base	332.5	0	65	0	50	0

X_1 = current density; X_2 = sodium hydroxide concentration; X_3 = sodium chloride concentration.

density has the maximum effect on the dissolution of tungsten in the electrolyte chosen and its effect is negative indicating a fall in the current efficiency with increase in current density. The decrease in current efficiency is probably due to the formation of slimy hydroxides of iron and nickel adhering to the surface and hindering the tungsten dissolution.

3.2. *Effect of sodium hydroxide*

The regression equation shows that sodium hydroxide concentration has a strong positive effect on the dissolution of tungsten. It has been shown by Faizullin and Levira [17] that the plateau current is directly proportional to hydroxyl ion concentration when a pure tungsten rod is dissolved in potassium hydroxide solution. This view is also supported by Heumann and Stolica [18]. It has been observed that the limiting current density also depends on the OH^- concentration. The effect is so strong that the interactive effect of current density and sodium hydroxide concentration is positive, though current density individually has a negative effect.

3.3. *Effect of sodium chloride*

Chlorides are generally added to the electrolytes to reduce passivation of the dissolving anodes. Here the concentration of sodium chloride was varied from 20 to 80 g dm^{-3}. It is seen from the regression equation that its effect is negative. Chloride ions in the concentration range used probably give rise to high rate of corrosion leading to pitted surfaces [19]. Electrolyte penetrates the pits and causes interior dissolution. This results in the formation of layers whereby hydroxides of nickel and iron occur between the layer of undissolved tungsten surface and that formed on the outer surface. This causes a rise in the cell voltage. Thus chloride, which normally aids anodic dissolution, shows a negative effect in the range 20–80 g dm^{-3}. The interactive effect of current density and sodium chloride is negative.

The interaction of all the three parameters is again found to be negative. This indicates that at higher current density and higher chloride concentration the increase in concentration of alkali is unable to improve the current efficiency of tungsten dissolution.

3.4. *Verification of the regression equation*

To verify the regression equation obtained two trials were carried out under different conditions. The value of the parameters and the current efficiency obtained through the experiments and the regression equation are tabulated in Table 3.

In the case of the first experiment of Table 3, the efficiency of tungsten dissolution is expected to be high, as low anodic current density, high concentration of alkali and low concentration of sodium chloride were employed. In the case of the second experiment, high anodic current density, moderate concentration of sodium hydroxide and high concentration of chloride were used and hence the efficiency is expected to be low.

4. Conclusion

The regression equation obtained from the experiments

Table 2 The design matrix for anodic tungsten dissolution in alkali

Si	X_0	X_1	X_2	X_3	X_1X_2	X_2X_3	X_3X_1	$X_1X_2X_3$	*Current eff. /%*
1	+1	+1	+1	+1	+1	+1	+1	+1	37.71
2	+1	+1	+1	−1	+1	−1	−1	−1	89.60
3	+1	+1	−1	+1	−1	−1	+1	−1	12.83
4	+1	−1	+1	+1	−1	+1	−1	−1	91.30
5	+1	−1	−1	+1	+1	−1	−1	+1	56.60
6	+1	−1	+1	−1	−1	−1	+1	+1	88.37
7	+1	+1	−1	−1	−1	+1	−1	+1	35.17
8	+1	−1	−1	−1	+1	+1	+1	−1	80.00
9	–	0	0	0					96.60
10	–	0	0	0					95.52
11	–	0	0	0					94.40

Table 3. Experimental parameters and current efficiency

Sl	*Parameters*						*Current efficiency*	
	Anodic current density X_1		*[NaOH]* X_2		*[NaCl]* X_3		*Experiment*	*Regression eqn.*
	Actual value $/\mathrm{Am}^{-2}$	*Relative coded value**	*Actual value* $/\mathrm{g\,dm}^{-3}$	*Relative coded value*	*Actual value* $/\mathrm{g\,dm}^{-3}$	*Relative coded value*		
1	282	−0.88	80	+0.80	35	−0.570	87.80	86.66
2	387	+0.93	50	−0.60	70	+0.875	28.65	20.81

* The relative coded value is calculated as follows:
X_1, $250\,\mathrm{A\,m}^{-2} = -1$ for $282\,\mathrm{A\,m}^{-2}$, $250/282\,x - 1 = -0.88$
X_2, $100\,\mathrm{g\,dm}^{-3} = +1$ for $80\,\mathrm{g\,dm}^{-3}$, $80/100\,x + 1 = +0.80$
X_3, $20\,\mathrm{g\,dm}^{-3} = -1$ for $35\,\mathrm{g\,dm}^{-3}$, $20/35\,x - 1 = -0.57$

carried out on the statistical design shows that within the region investigated (anodic current density between 250 and 450A m^{-2}, sodium hydroxide concentration between 30 and 100 g dm^{-3} and sodium chloride concentration between 20 and 80 g dm^{-3}) the higher current density and high sodium chloride concentration have a negative effect on tungsten dissolution, whereas sodium hydroxide concentration plays a positive role. A current density of 350 A m^{-2} with 100 g dm^{-3} of sodium hydroxide and 20 g dm^{-3} of sodium chloride are found to be optimum and resulted in efficiency of more than 90% for tungsten dissolution.

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Appendix 1

$$Y = \frac{Y_0}{3} = \frac{96.9 + 95.52 + 94.40}{3} = 95.60$$

$$\text{Error mean square, } Se^2 = \frac{(Y_0 - Y_0)^2}{3 - 1}$$

$$= 1.56$$

$$\text{Variance regression coeff., } S_{\mathrm{bj}} = \frac{Se}{N}$$

$$= \frac{1.249}{2.828} = 0.44$$

where N is the number of trials.

For $\alpha = 0.05$, $\gamma = 2$ degrees of freedom, $t_{\mathrm{p}}(f) = 4.303$.

Appendix 2

$$\text{Variance ratio, } F = Sr^2/Se^2 = 1.879/4$$

where $Sr^2 = (Y_i - \hat{Y}_i)^2/N - (K+1)$, Y_i is the experimental value and $\hat{Y}_i$ the calculated value from regression equation.

$$F = 0.4697/1.56$$

$$= 0.3010$$

$$F \text{ tabulated } (4,\,2) = 19.3$$

$$F < F \text{ Tab } (4,\,2)$$

Hence the model is adequate.