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Molybdenum recovery from molybdenum waste catalyst: Modeling of alkaline leaching

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ABSTRACT

Dissolution of molybdenum from molybdenum waste catalyst (MWC) that contain wt %: 42.79 Mo, 9.54 Fe, 4.9 Al, 8.68 SiO_2, 6 Na, and 1.5 Cr using different leaching agents such as H_2SO_4, HCl, and NaOH was carried out. It was found that, NaOH is the best leaching agent because it has the highest Mo recovery in combined with the lower Fe and Al dissolution than the HCl. Factorial design of experiments and application of statistical analysis on the results of leaching studies using NaOH were carried out. A regression equation for the dissolution of Mo was developed as a function of NaOH stoichiometric (S), L/S ratio (C, ml/g), and temperature (T, °C). All parameters were varied at two levels for designing experiments to estimate error.

KEYWORDS

Molybdenum;
Hydrometallurgy, Waste catalyst;
NaOH leaching;
Factorial design.

INTRODUCTION

Molybdenum is an element with an extremely rich and interesting chemistry having very versatile application in various fields of human activity. It is used extensively in metallurgical applications. Because of there anti–wear properties, molybdenum compound find wide application as lubricates particularly in extreme or hostile environmental situation. Many molybdates and heteropoly molybdates are white and therefore, used as pigments. In addition, they are non-toxic and act as efficient corrosion inhibitors and smoke suppressants. Hydro processing of petroleum is one of the largest industries employing heterogeneous molybdenum catalysts. Molybdenum catalysts have shown great promise in the liquefaction of coal and this may develop into one of its most important catalytic uses. The use of molybdenum compounds in homogeneous catalysis is also significant. Sahu et. el.[1] reported that the Recovery of valuable metals such as Mo, V, Ni, Al from spent hydroprocessing catalys using acid leaching of spent hydro-processing catalyst followed by separation of molybdenum and vanadium Both molybdenum and vanadium were selectively extracted with a suitable organic solvent leaving nickel and dissolved aluminum in the raffinate. In previous work, Seham et. el.[2-5] discuss the recovery of metal values from hydrodesulphurization catalyst using different techniques.

Every year large amount of waste catalyst rich in Mo is wasted and has no uses. This molybdenum catalyst used for oxidation of alcohol to formaldehyde, after a number of activation–deactivation cycles, the activity of the catalyst is eventually reduced to the extent that the catalyst has to be renewed. In Egypt, Mansoura for Resin & chemical materials Co. and Delta for Fertilizers companies are using this catalyst.

The aim of this work is to investigate Mo recovery from this waste catalyst using different leach agents such as NaOH, H_2SO_4 & HCl. The alkaline leaching by NaOH has been carried out using a statistical design.

EXPERIMENTAL

Source and analysis of molybdenum waste catalyst (MVC)

The sample of waste catalyst employed in this study was collected and kindly donated by Mansoura for Resin & chemical materials Co., Egypt. Metal content e.g. Mo, Fe, SiO_2, Al, Na and Cr were determined using Pereken Elmer atomic absorption as follow:

0.5 g dry sample was fused with fusion mixture (sodium and potassium carbonate) then quenched in 0.1 L sulfuric acid 70wt% in addition to 12.5 g Ammonium sulfate. The solution was placed on the hotplate magnetic stirrer and continues boiling until white gas (So_3 gas) evolved for five min.

Filtration followed by drying and burning the solid precipitate is conducted. The undissolved solids are silica and acid insoluble matter. The silica percentage calculated by precipitate weight difference before and after HF evaporation[6]. The filtrate was completed to 500 ml and the all above-mentioned elements are calculated.

Characterization of molybdenum waste Catalyst (MWC)

For preparation of a sample for technological testing, the 50 kg original was thoroughly mixed by the ring and cone method, quartered three times. Since the material was hygroscopic the sample was dried in oven at 110 °C overnight before the leaching test. Percentages of the metals were calculated on dry basis.

The dried sample of MWC was ground up to 100 % - 200 mesh. X –ray diffraction (XRD) and X-ray fluorescent (XRF) were performed on the powder sample of as received MWC, alkaline leaching residue and acid leaching residue using Philips – PW 1730 (XRD) and Sequential XRF – ARL 9400.

(a) Leaching

Dried sample was leached using different kinds of leach liquors such as NaOH, H_2SO_4, and HCl. In this study, the calculated amount of the leach liquor was heated in a flask to the required temperature in thermo stated water bath or Oil bath in the case of temperature 115 °C. 30 g of MWC was gradually added to the leach liquor while stirring using a mechanical stirrer. The flask was removed from the thermo-stated bath after the reaction time and the slurry was immediately filtered. The main factors affecting the leaching process, namely the effects of temperature, concentration and solid liquid ratio were examined using factorial design.

RESULTS AND DISCUSSION

X-ray diffraction

It was found that the as received MWC containing $MoO_3.2H_2O$ as the main compound, followed by Mo_9O_{26} and $Fe_2(MoO_4)_3$ while MoO_3 is trace. To calculate the organic content and loss on igination, two samples of MWC were heated at 350 °C and 1000 °C for 120 min. The XRD of the first one shows that there is no difference between the original sample and the sample heated up to 350 °C. The weight loss is 0.348 %. In the second case (ignition at 1000 °C), the XRD shows that the main compounds are Mo_9O_{26} and $Fe_2(MoO_4)_3$, followed by SiO_2 while Fe_2SiO_4 is trace. Which mean that the most of $MoO_3.2H_2O$ was converted to Mo_9O_{26} due to ignition at 1000 °C. That confirmed by the result of weight loss on ignition = 7.796 %.

X-ray Fluorescent (XRF)

The results listed in TABLE 1 reveal that the original MWC mainly containing Mo, Si, Fe, Al and Cr. On the other hand, the solid residue after sulfuric acid leaching containing mainly Mo, Si, Al, Fe and Cr, respectively, which means that the dissolution of Mo in this case is not complete, In contrast, the solid residue after alkaline leaching mainly containing Fe, Si, Cr, Al, and Mo, respectively. This indicates that the Mo dissolution using NaOH is better than H2SO4 as will shown latter.

TABLE 1 : XRF results

Element	Original MWC, %	Sulfuric acid leaching residue, %	Alkaline leaching residue, %
Mo	29.34	18.94	2.20
Si	8.53	17.7	8.72
Fe	9.54	4.51	37.8
Al	4.90	7.14	3.01
Cr	1.73	1.21	6.15

TABLE 2 : Chemical analysis of waste catalyst

Metal	Wt. %
Mo	42.79
Fe	9.54
Al	4.90
Sio_2	8.68
Na	6.00
Cr	1.5
A.I.*	4.64
Moisture,110 °C	0.5679
LOI **at 350 °C	0.3477
LOI** at 1000°C	7.796

*A.I.: Acid insoluble; **LOI: Loss on Ignition

Complete chemical analysis of mwc

The results of chemical analysis on dry basis of the as received sample are listed in TABLE 2.

Leaching

To evaluate the leaching behavior of Mo form MWC, different acids and alkaline leach liquors were tested.

(a) Effect of time

Effect of leaching time was conducted using 10% NaOH or 50 % H_2SO_4 at different time under the conditions listed in TABLE 3.

It is clear from the results listed in TABLE 3 that the time of leaching has no effect on the recovery percentage of (Mo) from the MWC in the two cases. These results suggesting that 30-min is quite enough. On the other hand, the (Mo) recovery with 10% NaOH is much higher than Mo recovery with 50% H_2SO_4 that confirmed by XRF results of the residue which mean that the leaching agent has strong effect on the recovery percentage. Therefore, effect of leaching agent was studied.

(b) Leaching agent effect

TABLE 3 : Effect of time

Time, min	Mo Rec. %	
	10% NaOH	50% H_2SO_4
15	90.7	45.03
30	89.0	44.67
45	89.5	43.93
60	90.6	45.10
90	89.9	44.53
120	90.5	46.00

Conditions of leaching: Temp: 95 °C, Stirring speed: 450 rpm, and L/S ratio 10 ml/g

TABLE 4 : Effect of leaching agent type

Leaching agent type	Recovery, %	
	Mo	Al
30% HCl	68.79	3.56
30% H_2SO_4	19.24	0.45
10 % NaOH	85.19	0.24

Conditions: Time 30 min., Temp: 90°C, L/S ratio: 3.33 ml/g & Stirring speed: 450 rpm

In this study, three different leaching agents were used under the conditions listed in TABLE 4.

It is clear from results listed in TABLE 4 that NaOH is the best leaching agent because it has the highest Mo recovery percentage and lower Al recovery; in addition, the iron is insoluble in NaOH. Which mean that NaOH is selective leaching agent for Mo only that makes the separation of Mo from the leaching solution is easy. Therefore, conditions that controlling the leaching process using NaOH were studied using statistical factorial design as follow.

(c) Factorial Design of sodium hydroxide leaching

Leaching experiments were carried out according to the factorial design of experiments[7-13].

To make the mathematical factorial design we should define the factors controlling the leaching process and depend on the number of these variables, the

TABLE 5 : Data from 2^3 factorial design

Test No.	NaOH (S)		L/S ratio		Temperature, °C		Observation Mo Rec. %
1	1.5	-	3.33	-	40	-	78.5
2	2	+	3.33	-	40	-	85.19
3	1.5	-	5	+	40	-	77.3
4	2	+	5	+	40	-	74.8
5	1.5	-	3.33	-	90	+	71.9
6	2	+	3.33	-	90	+	83.5
7	1.5	-	5	+	90	+	81.6
8	2	+	5	+	90	+	82.6

number of experiments will define. It was found that leaching time (t, min.), temperature (T, °C), NaOH stoichiometric (S), and Liquid /Solid ratio (C, ml/g) are the controlling factors of leaching process. Depend on the above results it was found that the leaching time has no effect on the Mo recovery. Therefore, a central composition design was used with several levels for the variables S, C and T. The reduced form of the variables is as follows.

$$X_1 = \frac{S - Sm}{\Delta S}, \qquad X_2 \frac{C - Cm}{\Delta C}, \qquad X_3 \frac{T - Tm}{\Delta T}$$

Where

$$Sm = \frac{S_+ + S_-}{2}, \qquad \Delta S = \frac{S_+ - S_-}{2}$$

$$Cm = \frac{C_+ + C_-}{2}, \qquad \Delta C = \frac{C_+ - C_-}{2}$$

$$T_m = \frac{T_+ + T_-}{2}, \qquad \Delta T = \frac{T_+ - T_-}{2}$$

Where:

$S_+ = 2.0$, $S_- = 1.5$, $C_+ = 5.0$, $C_- = 3.33$ ml/g, $T_+ = 90$, and $T_- = 40$ °C are the maximum and minimum values of the three variables in the range studied. The matrix for the three variables and the corresponding Mo recovery yield (y) is listed in TABLE 5.

NaOH stoichiometric was calculated according to the following equation:

$$2\,NaOH + Mo \rightarrow Na_2MoO_4 \qquad (1)$$

The regression equation for the above matrix may be represented as :

$$Y = b_o + b_1X_1 + b_2X_2 + b_3X_3 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 + b_{123}X_1X_2X_3 \qquad (2)$$

Where Y = the percentage of metal extracted; b = empirical model coefficients; X_1, X_2, X_3 = dimensionless coded factors for NaOH stoichiometric (S), L/S ratio (C, ml/g), and temperature (T, °C), respectively. The relations between the coded and actual values are given as:

$$X_1 = (S - 1.75)/\,0.25 \qquad (3)$$

$$X_2 = (C - 4.16)/\,0.83 \qquad (4)$$

$$X_3 = (T - 65)/\,25 \qquad (5)$$

Where 1.75, 4.16 and 65 are S_m, C_m and T_m, respectively. And 0.25, 0.83, and 25 are “S, “C, and “T, respectively. The regression coefficients were estimated by:

$$b_o = \frac{\sum Y_i}{N} \qquad (6)$$

$$b_j = \frac{\sum X_j Y_i}{N} \qquad (7)$$

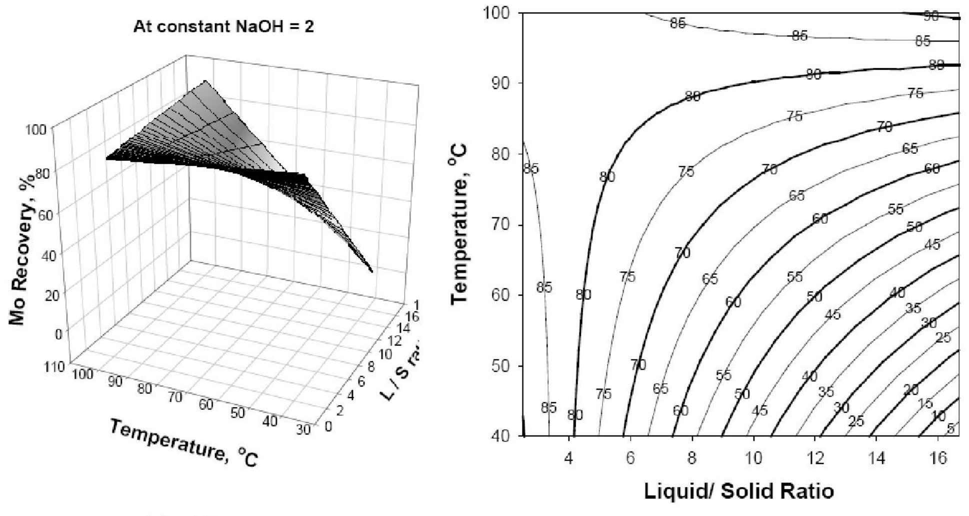
$$b_{nj} = \frac{\sum (X_{ni} X_{ji}) Y_i}{N} \qquad (8)$$

Where X_j, X_{ni} and X_{ji} are the coded singes (+ or -).

The regression equation for extraction of Mo was developed and the main interaction coefficients were tested for significance by Student’s t –test method at 95 % confidence level. The regression equation (2) becomes:

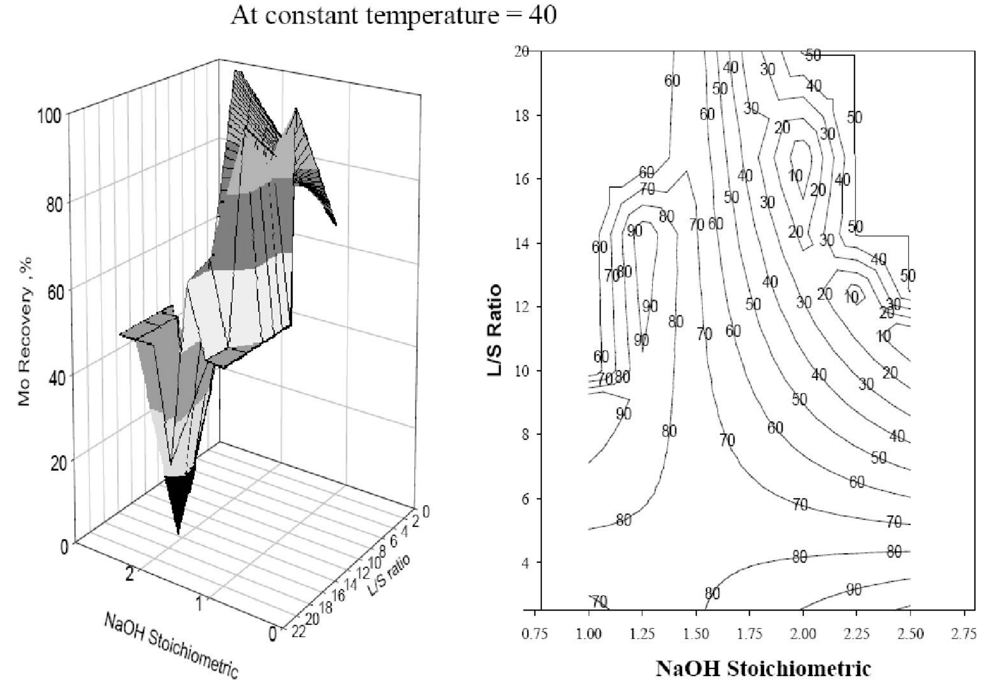
$$Y_{Mo} = 79.42 + 2.1\,X_1 - 0.348\,X_2 + 0.47\,X_3 - 2.47\,X_1X_2 + 1.05\,X_1X_3 + 2.54\,X_2X_3 - 0.176\,X_1X_2X_3 \qquad (9)$$

It is clear from this equation that X_1 (NaOH, S) and interaction of X_2X_3 (L/S ratio: temp) are the significant while the increase in these variables increasing the Mo Rec. On the other hand, the interaction be-



(a): 3D (b):

Figure 1 : Relation between Mo recovery percentage against L/S ratio and temperature



(a): 3D (b): Contour

Figure 2 : Relation between Mo recovery percentage against L/S ratio and NaOH stoichiometry

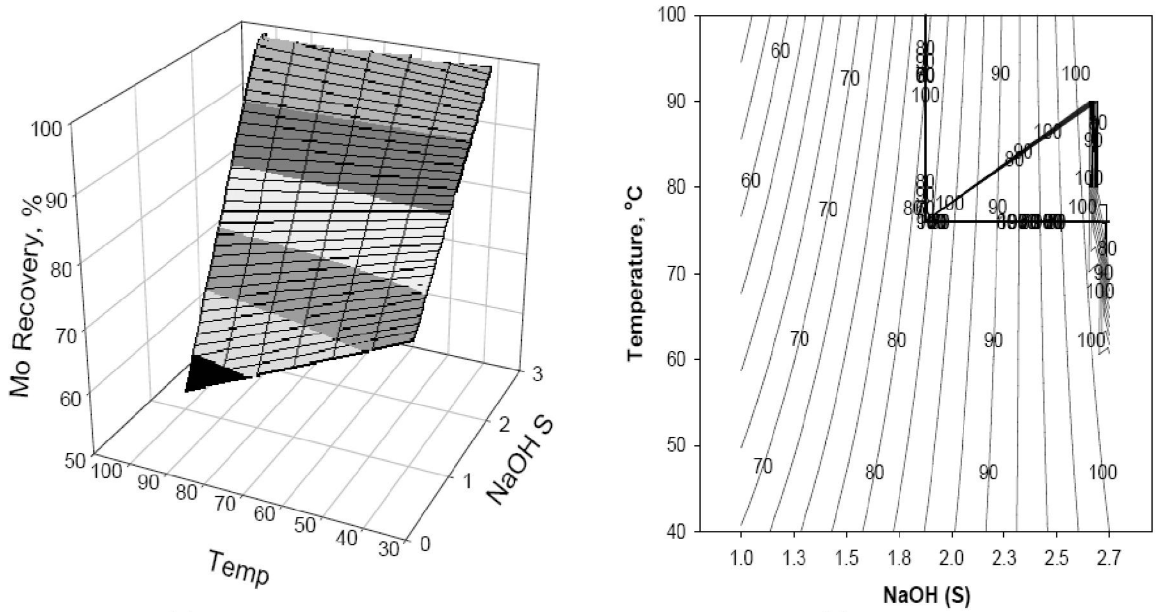
tween X_1X_2 (NaOH S: L/S ratio) is negatively significant, which means that increasing this effect decreasing the Mo Recovery. This is logic because of at constant NaOH S the increasing L/S ratio, decreasing the NaOH concentration of the leaching solution, which negatively affect Mo recovery.

Using equation (9) the predicted profiles are calculated and shown in Figures 1,2, and 3.

It is clear from Figure 1(a and b) that at low temperature, that Mo recovery increases with decreasing L/S ratio. This may be due to increase of NaOH concentration with decreasing liquid /solid ratio at constant NaOH S = 2. On the other, at high L/S ratio, increasing the temperature increases the recovery. While at low L/S ratio, increasing temperature has no effect on the recovery.

Figure 2(a and b) shows the relation between L/S ratio, NaOH stoichiometric against Mo recovery at constant temperature 40 °C. It is clear Mo recovery has two optimum peaks, at high NaOH S with low L/S

At constant L/S ratio = 3



(a) 3D (b) Contour

Figure 3 : Relation between Mo recovery percentage against temperature and NaOH stoichiometry

TABLE 6 : Matrix of effects

No	Observation Mo Rec.%	X1 NaOH, S	X2 L/s ratio	X3 Temp, °C	X1X2	X1X3	X2X3	X1X2X3
1	78.5	-	-	+	+	+	+	-
2	85.19	+	-	-	-	-	+	+
3	77.3	-	+	-	-	+	-	+
4	74.8	+	+	+	+	-	-	-
5	71.9	-	-	+	+	-	-	+
6	83.5	+	-	-	-	+	-	-
7	81.6	-	+	-	-	-	+	-
8	82.6	+	+	+	+	+	+	+
	635.39	+16.79	-2.79	+ 3.81	-19.79	+8.41	+20.39	-1.41

ratio. This may be attributed to that this area has the highest NaOH concentration. The second peak is around (1.2-1.25) NaOH S against (10-15) L/S ratio ml/g. In contrast; the lowest recovery was reached at high L/S ratio (15-17) against (1.9-2) NaOH S.

Figure 3 (a and b) shows the relation between NaOH S, temperature against Mo recovery at constant L/S ratio = 3. It is clear that at constant NaOH S the temperature has no effect on the recovery. While at constant temperature the increasing of NaOH S increasing the recovery.

(d) Analysis of variance

To estimate the main effects and interactions, matrix of effects was constructed as listed in TABLE 6. To estimate Mo recovery mean value (Y^o) =

$$\frac{635.39}{8} = 79.42$$

The main effect of NaOH S = $\frac{16.79}{4} = 4.197$

The main effect of L/S ratio = $\frac{-2.79}{4} = -0.6975$

The main effect of temperature = $\frac{3.81}{4} = 0.9525$

The effect of NaOH S * L/S ratio = $\frac{-19.79}{4} = -4.947$

Effect of NaOH S * Temperature, °C = $\frac{8.41}{4} = 2.102$

Effect of L/S ratio * Temp., °C = $\frac{20.39}{4} = 5.097$

Effect of NaOH S * L/S ratio * Temp., °C = $\frac{-1.41}{4} = -0.35$

To estimate the variance (σ^2) by ANOVA:

$$\sum Y^2 = Y_1^2 + Y_2^2 + ...Y^2{}_8 = 50613$$

$$\sum Y = Y_1 + Y_2 + ...Y_8 = 635.39$$

SY^2 = Corrected sum squares = (ΣY^2)– CF

Where CF = Correction factor = $\left(\frac{\sum Y}{N}\right)^2 \times N = \frac{\left(\sum Y\right)^2}{N}$

CF = $(635.39)^2 / 8 = 403720.45 / 8 = 50465.05$ (degree of freedom (df) = 1)

ANOVA table is as follows:

Source	ssq	df	
ΣY^2	50613	8	
CF	50465	1	
SY^2	148	7	$S^2 = \frac{148}{7} = 21.14$

Standard deviation is S = $\sqrt{s^2} = \sqrt{21.14} = 4.598$

The standard error of (Y^o) is

$$SE\left(Y^o\right) = \sqrt{S^2/n} = \sqrt{\frac{21.14}{8}} = 1.625$$

95% interval statement for mean efficiency (η) are given by:

$$Y^o \pm t_{7,\,0.025} = \sqrt{S^2/n}$$

From student's t-test tables:

$\mathbf{t_{7,\,0.025} = \pm\ 2.36}$

In comparison with the (t) ratio, the main effect NaOH S is the most significant factor affecting the recovery (the higher the ratio the higher the recovery).

On the other hand, the main effect of L/S ratio or temperature is not statistically significant.

In addition, the results indicate that the most significant interaction is NaOH S * L/S ratio that is statistically significant but this interaction has adverse effect on the recovery of the process. Which mean that the higher of such interaction, the lower the recovery. These results are confirmed the results in Figure 3 (a and b).

On the other hand, the interaction of LS ratio * Temp is statistically significant where the higher the interaction the higher the recovery. In other words, the increase in temperature can compensate for the adverse effect of L/S ratio and these results are confirmed Figure 2 (a and b).

In comparison (t) value with the interaction ($X_1 X_2 X_3$), it is not statistically significant and usually it can be taken as estimation for the experimental error.

CONCLUSION

Leaching of molybdenum waste catalyst (MWC) using different leaching agents such as H_2SO_4, HCl and NaOH was curried out. And it was found that NaOH is the best leaching agents. Factorial design of experiments has been applied in the study of MWC leaching with NaOH. It is concluded after calculation that the main effect of NaOH S is the most significant factor. While, the main effect of L/S ratio or temperature is not significant.

In addition the interaction NaOH S * L/S ratio adversely affect Mo recovery. While, the interaction L/S ratio * Temperature is significant, in comparison with (t) value.

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