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OPTIMIZATION OF PURE BORAX PENTAHYDRATE EXTRACTION FROM CALCINED TINCAL

Yuksel ABALI[*], Salih Ugur BAYCA[**], Gokhan EDGUNLU[*]

[*] Celal Bayar University, Science and Arts Faculty, Chemistry Department, 45030 Muradiye, Manisa
[**] Celal Bayar University, Soma Vocational School, Soma, 45500 Manisa, Turkey, salihbayca@gmail.com

Abstract: In this study, conditions for the calcination process of tincal were investigated and the optimum calcination conditions for boron extraction from tincal were determined. The experimental parameters were dissolution temperature, solid-to-liquid ratio, dissolution time and stirring speed. The optimum dissolution parameter levels were determined to be temperature 80 °C, solid-to-liquid ratio 10 g/dm^3, stirring speed 250 rpm and dissolution time 5 min.

Keywords: *optimization, calcined tincal, borax, dissolution, leaching, Taguchi method*

Introduction

The optimization of dolomite ore dissolution in hydrochloric acid solutions was studied by Abali et al. (2011). The dissolution of roasted zinc sulphide concentrate in sulphuric acid solutions was investigated in an optimization study by Copur et al. (2004). Behnajady et al. (2012) found the optimum conditions for the dissolution of lead from zinc plant residues in NaCl–H_2SO_4–$Ca(OH)_2$ media by the Taguchi method. Ekinci et al. (2007) studied optimization and modeling of boric acid extraction from colemanite in water saturated with carbon dioxide and sulfur dioxide gases. Yesilyurt (2004) found that the boric acid extraction efficiency from colemanite ore was 99.66%. Kucuk (2006) found that the dissolution percentage of ulexite in NH_4Cl solution was 98.37%. In the study of Bese et al. (2010) the Taguchi method was applied to determine the optimum conditions of dissolution of metals in the Waelz sintering waste in HCl solutions. The orthogonal array (OA) experimental design was chosen as the most suitable method to determine the experimental plan, L_{25} (5^5), five parameters, each with five values. Keles et al. (2009) reported that silver cementation from nitrate containing solution using the Taguchi method was studied to understand and optimize silver cementation yield by considering design and rotation rate of the impeller, temperature and pH of the solution.

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Tincal is best represented by formula $Na_2B_4O_5(OH)_4 \cdot 8H_2O$, with 2 moles of water existing as hydroxyl groups and 8 moles as crystal water (Gerhartz, 1985). The largest known tincal deposit in the world is in Kirka, some 220 km to the west of Ankara, Turkey (Abali et al., 2006; Smith and Mcbroom, 1992). The commercially produced calcined tincal has 52% B_2O_3 with particle size of -6 mm and borax pentahydrate which has 47.76 % B_2O_3 with particle size of -1 mm (Etimaden, 2013).

A robust design method was developed in order to reduce cost and improve the dissolution of calcined tincal in water. In the experiments, an L_{16} orthogonal array was employed to determine the effect of four process parameters on the dissolution efficiency of calcined tincal. For each factor, four levels were chosen to cover the wide region of variation. The parameters selected in this study, dissolution temperature, solid-to-liquid ratio, stirring speed and dissolution time, can potentially affect the dissolution efficiency of calcined tincal in water. The experimental factors and their levels, were determined by preliminary tests. Since four parameters were investigated in the research, four levels of each parameter were considered. Therefore, an L_{16} orthogonal array (L_{16} 4^4) was selected for this study. The total of 16x4 = 64 data values in the layout of this L_{16} OA were collected for analysis in the study.

The quantitative design is used in the Taguchi method to optimize the process with multiple performance characteristics. The orthogonal array (OA) experimental design was chosen as the most suitable method to determine the experimental plan, L_{16} (4^4), with four parameters for each of four values. In order to observe the effects of noise sources on the dissolution process, each experiment was repeated twice under the same conditions at different times. The performance characteristics were chosen as the optimization criteria. There are three categories of performance characteristics, the larger-the-better, the smaller-the-better and the nominal-the-best. The performance statistics was evaluated by using Eq. 1 (Phadke, 1989; Pignatiello, 1988).

For the larger-the-better approach

$$SN = -10\log\left(\frac{1}{n\Sigma}\frac{1}{Y^2}\right) \tag{1}$$

where the larger-the-better is performance characteristics, n is the number of repetitions performed for a given experimental combination, and Y is the performance value of the i^{th} experiment. Detailed information on the Taguchi method is given by Abali et al. (2011).

The aim of the present study was to investigate the optimization of the dissolution of tincal dissolved in large amounts in hot water in order to obtain pure borax pentahydrate, using the Taguchi method. The each experiment was repeated twice under the same conditions at different times to observe the effect of noise sources on the dissolution process. After optimum calcination conditions for the extraction of boron from tincal were determined, the optimum water dissolution conditions for maximizing the boron oxide contents of the dissolution solution were determined by the Taguchi experimental design method, and then the dissolution experiments were carried out according to this design method. An *F* test was carried out on the dissolution results to determine the most effective and least effective parameters. Signal-Noise (*SN*) graphs were drawn for each of the parameters to determine the optimum conditions. The maximum dissolution performance of calcined tincal was predicted by calculation at the optimum conditions.

Materials and methods

The tincal used in the present experiments was obtained from Kirka, Eskisehir, Turkey. The ore was initially crushed by jaw crusher, and then the sample was placed in a porcelain crucible. Calcination of tincal was carried out using a muffle furnace. The solubility of borax decahydrate and borax pentahydrate in water is shown in Table 1.

Table 1. Solubility of borax decahydrate and borax pentahydrate in water (Jansen, 1999)

Temperature °C	Solubility, wt % in water	
	Borax decahydrate $Na_2O{\cdot}5B_2O_3{\cdot}10H_2O$	Borax pentahydrate $Na_2O{\cdot}5B_2O_3{\cdot}5H_2O$
0	1.18	
10	1.76	
20	2.58	
25	3.13	
30	3.85	
40	6.00	
50	9.55	
60	15.90	16.40
70		19.49
80		23.38
90		28.37
100		34.63

Particle size in the sample was -1.25 mm after crushing and screening. The boron oxide content of the tincal sample was determined as 23.2% B_2O_3, whereas tincal theoretically contains 36.5% B_2O_3. This can be explained by the fact that the ore used in the experiment contained 63.38% tincal mineral and 36.62 % impurities. Alp et al., (2004) reported that the impurities in tincal ore were calcite, dolomite, montmorillonite minerals.

The dissolution experiments were carried out in a 250 cm^3 three necked glass reactor equipped with a mechanical stirrer with a digital controller unit and timer, a thermostat and a cooler. The experimental parameters and their levels are given in Table 2.

Table 2. Parameters and their values corresponding to their levels

	Parameters	Parameter levels			
		1	2	3	4
A	Dissolution temperature, °C	20	40	60	80
B	Solid-to-liquid ratio, g/dm^3	10	20	50	100
C	Stirring speed, rpm	250	350	450	600
D	Dissolution time, minutes	5	10	20	45

The temperature of the reaction medium could be controlled to within ±0.5 °C. In the dissolution process, 100 cm^3 of water was introduced into the reactor. After the desired dissolution temperature was reached, a predetermined amount of the sample was added to the solution while the content of the vessel was stirred at a certain speed. At the end of the experiment, the contents of the vessel were filtered using a blue filter paper and the filtrate solution was analyzed volumetrically for B_2O_3 (Koklu et al, 2003). The chemical composition of the calcined tincal was determined by volumetric and gravimetric methods.

The dissolution efficiency of B_2O_3 was Y percent

$$Y = \frac{M_1}{M_o} \cdot 100 \tag{2}$$

where M_o is the amount of B_2O_3 in the original sample (g) and M_1 is the amount of B_2O_3 in the solution after dissolution (g).

Results and discussion

Calcination of tincal

Results obtained from tincal calcination showed that the percentage of boron oxide increased with increasing calcination temperatures and with increasing calcination times.

The calcination reaction of tincal is given in Eq. 3.

$$Na_2B_4O_5(OH)_4 \cdot 8H_2O_{(s)} \xrightarrow{\text{Heat}} Na_2O \cdot 2B_2O_{3(s)} + 10H_2O. \tag{3}$$

When tincal is completely calcined, anhydrous borax is formed. Anhydrous tincal theoretically contains 69.19% B_2O_3. The results are given in Fig. 1.

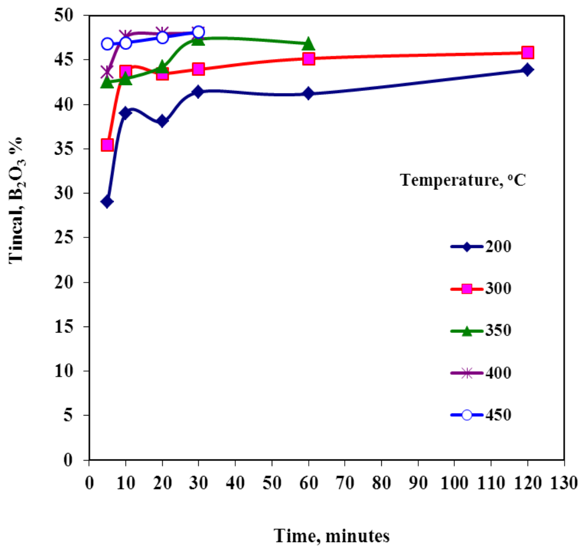

Fig. 1. The effects of calcination temperature and time on boron oxide

Calcination at 450 °C for 30 minutes was selected. The boron oxide content of calcined tincal was found to be 48.19% B_2O_3. Tincal calcination at 400 °C and 450 °C gave similar results. However, 450 °C was selected in order that the calcination should be homogeneous. The boron oxide value (48.19% B_2O_3) was much lower than the theoretical boron oxide value for anhydrous borax (69.19% B_2O_3). This can be explained by the tincal not being completely calcined. This boron oxide value is very close to the boron oxide value (47.8% B_2O_3) of borax pentahydrate. The calcination reaction is given by

$$Na_2B_4O_5(OH)_4 \cdot 8H_2O \longrightarrow Na_2O \cdot 2B_2O_3 \cdot 5H_2O + 5H_2O. \quad (4)$$

Thus, the product resulting from the calcination of tincal in this study may be called borax pentahydrate.

Dissolution of calcined tincal

The dissolution of calcined tincal in water was investigated to determine the optimum conditions. The dissolution reaction of calcined tincal in water can be described by the following equation

$$Na_2O \cdot 2B_2O_3 \cdot 5H_2O_{(s)} + H_2O_{(l)} \longrightarrow 2Na^{+}{}_{(aq)} + B_4O_5(OH)_4{}^{2-}{}_{(aq)} + 4H_2O_{(l)}. \quad (5)$$

The reaction between calcined tincal and pure water results in sodium ions and tetraborate ions. Kotz et al. (2006) reported that tetraborate anions [$B_4O_5(OH)_4{}^{2-}$] occur in borax in solution in water. This pregnant leach solution was crystallized at room temperature and borax decahydrate crystals were obtained. Tincal was completely dissolved in hot water (95 ^{o}C) and this solution contained maximum 36.5% B_2O_3.

Statistical analysis

An L_{16} orthogonal array with five columns and 16 rows was used in this study. Each dissolution parameter was assigned to a column, and 16 dissolution-parameter combinations were possible. Therefore, only 16 experiments were required to study the entire parameter space using the L_{16} orthogonal array. The experimental layout for the five dissolution parameters using the L_{16} orthogonal array is shown in Table 3.

Table 3. The experimental plan, parameters and results

Exp. No.	Temperature (^{o}C)	Solid-liquid ratio (g/dm^3)	Stirring speed (rpm)	dissolution time (min)	Experimental results		
					Y_1	Y_2	$Y_{average}$
1	20	10	250	5	65.98	66.18	66.08
2	20	20	350	10	43.96	43.93	43.95
3	20	50	450	20	30.29	25.79	28.04
4	20	100	600	45	4.98	6.17	5.57
5	40	10	350	10	70.77	74.23	72.50
6	40	20	250	20	63.01	52.63	57.82
7	40	50	600	45	41.36	24.11	32.74
8	40	100	450	5	8.14	10.57	9.36
9	60	10	250	20	91.54	81.15	86.34
10	60	20	350	45	64.69	65.58	65.14
11	60	50	450	5	43.78	45.17	44.48
12	60	100	600	10	10.22	11.60	10.91
13	80	10	450	45	94.75	95.54	95.14
14	80	20	600	5	88.08	100.00	94.04
15	80	50	250	10	37.90	52.43	45.17
16	80	100	350	20	12.89	13.48	13.19

F-ratios of the factors were calculated and are given in Table 4. The *F* test is a tool to determine which process parameters have a significant effect on the dissolution value. The results show that solid-to-liquid ratio parameters were significant on the calcined tincal dissolution rate.

The *F*-value for each process parameter is simply the ratio of the mean of the squared deviations to the mean of the squared error. Usually, the larger the *F*-value, the greater the effect on the dissolution value due to the change of the process parameter. The optimum combination of process parameters can be predicted using the dissolution efficiency characteristics and ANOVA analyses.

Table 4. The results of variance analysis (ANOVA) and F tests

	Parameters	Degree of freedom DOF	Sum of Squares SS	Mean Squares MS	Test Statistic F
A	Temperature	3	1506.587	502.196	0.922
B	Solid/liquid ratio	3	11569.957	3856.652	7.084
C	Stirring speed	3	1997.544	665.848	0.145
D	Dissolution time	3	236.729	78.910	1.223
	Error	3	1633.203	544.401	
	Total	16	13677.614		

In order to determine the optimum dissolution rate, the larger-the-better dissolution efficiency characteristic in Eq. (1) was taken for the dissolution efficiency of B_2O_3, and the SN ratios for the larger-the-better dissolution efficiency were calculated. The level which had the higher value determined the maximum level of each factor. For example, level five for temperature had the highest *SN* ratio value.

The effects of dissolution temperature on the performance statistics for calcined tincal are given in Figure 2. The results showed that the dissolution efficiency of B_2O_3 increased with increasing dissolution temperature. Abali et al. (2007) reported that the dissolution rate of tincal in phosphoric acid solution increased with increasing temperature. Dissolution efficiency was 51.72% at a temperature of 60 ^{o}C, but reached 61.88% efficiency at 80 ^{o}C. Therefore a dissolution temperature of 80 ^{o}C was chosen.

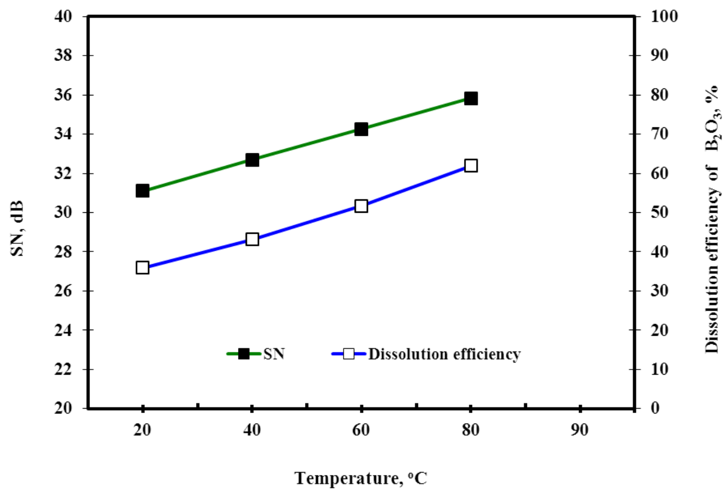

Fig. 2. The effect of dissolution temperature on the performance statistics for calcined tincal

As seen in Figure 3, the dissolution efficiency decreased with an increasing dissolution solid-to-liquid ratio. As the amount of reagent (water) per unit of solid (tincal) in the suspension increased at low solid to liquid ratio, the reaction rate increased. This might be attributed to the fact that the amount of reagent compensation to every particle decreases with increasing amounts of solid in the suspension. Similar results were found by Abali et al. (2006) for tincal in oxalic acid solutions. Maximum dissolution efficiency was achieved with 10 g/dm^3 solids and the dissolution efficiency was 80.02%. Therefore, a solid-to-liquid ratio of 10 g/dm^3 was chosen.

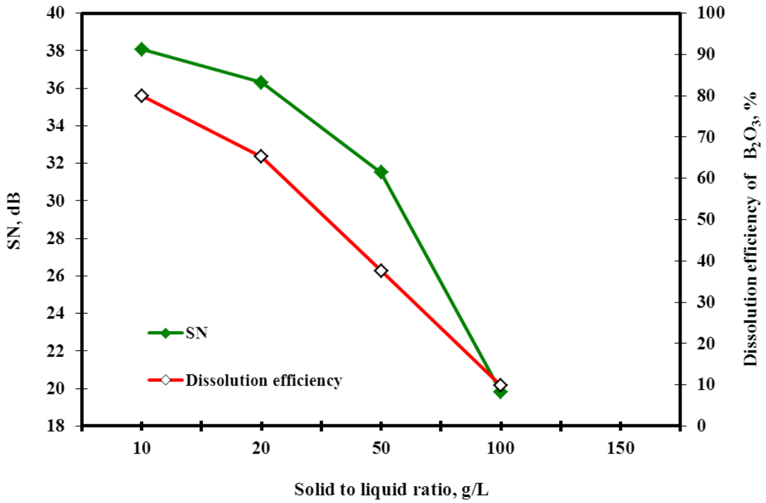

Fig. 3. The effect of solid-to-liquid ratio on the performance statistics for calcined tincal

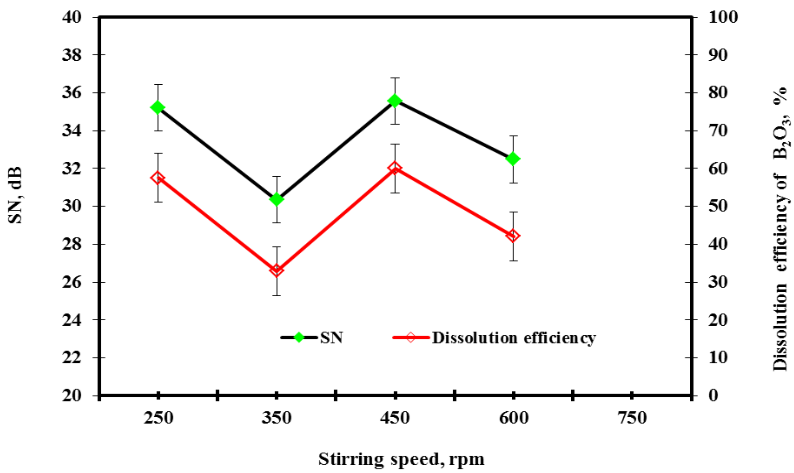

Fig. 4. The effect of stirring speed on the performance statistics for calcined tincal

The effect of stirring speed on the performance statistics for calcined tincal is shown in Fig. 4. Dissolution efficiency was 57.58%, 32.91%, 60.04% and 42.08% at stirring speeds of 250, 350, 450 and 600 rpm, respectively. There was a fluctuations of the results. This fluctuating behaviour was observed in previous studies by Copur et al. (2004) in studying the effect of sulphuric acid solutions on zinc sulphide. A stirring speed of 250 rpm was chosen.

Figure 5 shows that the dissolution efficiency fell within 5-10 minutes of reaction time, but rose slowly after 20-45 minutes. The maximum dissolution efficiency was reached at 5 minutes of leaching time. Therefore, a leaching time of 5 minutes was chosen.

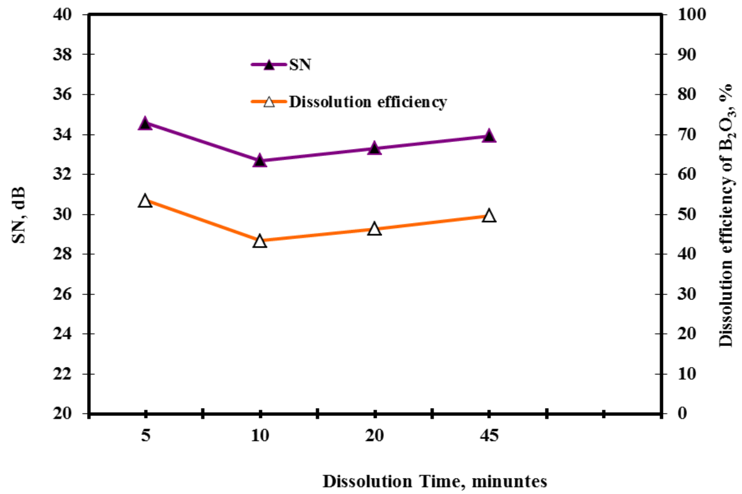

Fig. 5. The effect of dissolution time on the performance statistics for calcined tincal

The optimum dissolution conditions for B_2O_3 production were selected according to conditions of maximum amount, as shown in Table 5.

Table 5. Optimum working conditions predicted dissolution of tincal

Parameters	Case 1	Level	Case 2	Level
Temperature, ^{o}C	60	3	80	4
Solid/liquid ratio, g/dm^3	10	1	10	1
Stirring speed, rpm	250	1	250	1
Dissolution time, min	5	1	5	1
Predicted dissolution efficiency of B_2O_3, %	98.35		100	

The optimum process conditions were selected as A_4, B_1, C_1, and D_1. The predicted dissolution efficiency using optimum *SN* conditions was calculated.

Conclusions

Calcination of tincal at 450 ^{o}C for 30 minutes resulted in a product of borax pentahydrate.

The optimum conditions for borax extraction from calcined tincal by water dissolution can be determined by using the Taguchi experimental design method with a small number of experiments. In the optimization study, sixteen experiments were carried out and each experiment was repeated twice. A total of 32 experiments were performed.

It was found that the dissolution efficiency increased with decreasing solid-to-liquid ratio and increasing temperature, and that the most significant parameter affecting the dissolution of calcined tincal was the solid-to-liquid ratio. The least significant parameter affecting the dissolution of calcined tincal was the stirring speed. The optimum reaction conditions were determined as A_4, B_1, C_1, D_1 and a dissolution temperature of 80°C, a solid-to-liquid ratio of 10g/dm^3, a stirring speed of 250 rpm, and 5 minutes for dissolution time. The dissolution efficiency of calcined tincal in water was estimated to be 100% under optimum conditions with 95% confidence level.

Pure borax pentahydrate crystals were obtained by dissolving tincal in hot water at these optimum conditions.

Borax pentahydrate is highly soluble in hot water. Borax pentahydrate solution can be divided by solid-liquid separation insoluble material. When the solution is cooled, borax pentahydrate crystals precipitated. The Taguchi method can be applied to produce the compounds of borax on a large scale.

The optimum conditions of this laboratory-scale study were determined by the statistical analysis method. This statistical method permits scientists observing more than one independent variable at a time.

In the dissolution study discussed in the paper, researchers working in this field helped to interpret the scientific data. The results of this study can be very useful for designing plant operating on an industrial scale.

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