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Research article

The determination of the optimum conditions upon the leaching performance of calcined magnesite

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ABSTRACT

The aim of the study is to examine the reaction of calcined magnesite in the citric acid media, and after that it is determination of optimal conditions about the leaching performance of calcined magnesite by an experimental plan of Taguchi Statistical Method with L_{16} (4^5). The parameters such as particle size, reaction temperature, acid concentration, solid–liquid ratio and reaction period are tested. In this work, the optimal combination of the parameters that achieves robustness against noise factors is found as: 50 °C, 45 min, -319 μm, 0.125 g/mL, and 2M, respectively. Extraction efficiency of the magnesium from calcined magnesite is 98.86 %.

1. Introduction

For the production of magnesium compounds such as magnesium carbonate, oxide, hydroxide, citrate, magnesite ore is generally utilized as the raw material. Magnesium and its compounds play an important role in daily life and the production of magnesium salts open large fields for future applications such as disease treatment (Dasu et al., 2003; Noronha and Matuschak, 2002; Vandamme et al., 2012). There are several forms of magnesium (e.i., magnesium citrate) easily absorbed by human body. Hydrometallurgical techniques are usually processed for the producing of magnesium citrate.

Taguchi statistical method is improved by Genichi Taguchi to develop the quality of manufactured goods, and more recently is also realized to marketing, biotechnology and engineering (Ashraf et al., 2005; Demir et al., 2003b; Fredd and Fogler, 1998; Glaser et al., 1988). There are many ways to design a test and one of them is a full factorial experiment. But, it is very time-consuming when there are many factors. In order to minimize the number of tests required, fractional factorial experiments (FFEs) are developed. FFEs use only a portion of the total possible combinations to estimate the effects of main factors and the effects of some of the interactions. Taguchi has developed a family of FFE matrices which can be utilized in various situations. These matrices reduce the experimental number but still give reasonably rich information. Taguchi system on the traditional experimental design techniques, in addition to keeping the experimental cost at a minimum level, minimizes the variation in product response while keeping the mean response on target. Its other advantage is that the optimum working conditions obtained from the laboratory study it also is applicable for the actual productions (Kackar, 1985; Logothetis, 1992; Phadke et al., 1983).

Taguchi method is a technique to lay out experimental plan in most economical, logical and statistical way. It can be of significant benefit from it when one wants to study the effects of multiple factors (i.e. variables, parameters, ingredients, etc.) on the performance and to determine the best parameters combination for process. This technique is highly effective when one wish to examine influence of each factors about the performance and appoint which factor has more effective, which ones have less. The information from the experiment allows also us: how we can determine which factor is causing most variations in the result, how we can set up our process such that it is insensitive to the uncontrollable factors, which factors have more influence on the mean performance, what we need to do to reduce performance variation around the target, how we can adjust factors for a system whose response varies proportional to signal factor, how to combine multiple criteria of evaluation into a single index, how the uncontrollable factors affect the performance etc.

Different works are carried out on leaching of magnesite/magnesia with varied reagents for determining the optimum conditions by Taguchi methods (Demir and Donmez, 2008; Donmez et al., 1999; Ersahan et al., 1994; Lacin et al., 2005). Good comprehending of the mechanisms encountered is important not only for an efficient operation of leaching reactors but also for design.

In a study by Abali et al. (2006) the optimum conditions on the leaching of magnesite in H_2SO_4 media were found as acid concentration of 2M, solid-liquid ratio of 0.05 g mL^{-1}, reaction temperature of 65 °C,

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stirring speed of 300 rpm and reaction time of 60 min. Demir et al., 2003a, 2006 worked the mechanisms of the dissolution processes of natural and calcined magnesite by citric acid solutions. For both processes, reaction rates were identified to be chemically reaction-controlled.

In this study, we wanted to find out how the reaction temperature, particle size, reaction period, solid to liquid ratio and acid concentration effected the extraction of magnesium from calcined magnesite by citric acid and we compared results with natural magnesite ore (Demir and Donmez, 2008).

2. Experimental

The calcined magnesite used for this study was supplied from calcinations of magnesite located in Oltu region Erzurum, Turkey. The magnesite ore was calcined according to results obtained in a comparative study of Coats-Redfern and Suzuki methods (Demir et al., 2003b). Calcined magnesite was prepared by the calcination of natural magnesite in a furnace under nitrogen atmosphere at 700 °C for 2 h. After crushing, the sample was ground, and sieved for particle diameter fractions of as -319, -519, -1019, and -2819 μm. Its chemical analysis was carried out by standard gravimetric and volumetric methods. SiO_2 and ignition loss analyzes were made gravimetrically. The Ca, Fe and Mg analyses in the solids were determined with volumetric method by 0.01 M EDTA. Mg content of the solution was analyzed in medium of Eriochromschwartz T indicator by adjusting pH = 10 and Ca with murexide indicator by pH = 12. Conversion values for Mg are calculated by the following formula:

$$x_{Mg} = \frac{Mg^{2+}\ content\ in\ solution}{Mg\ content\ in\ original\ sample}$$

The analytical results were given in Table 1. X-ray diffractogram of the calcined magnesite and SEM micrograph for magnesium citrate product were seen in Fig. 1 and Fig. 2, respectively. The citric acid having a formula $C_6H_8O_7$ (citric acid) was purchased from Merck Chemical Corp. and used as received.

Leaching tests for calcined magnesite were done in a glass reactor heated by a constant temperature bath and equipped with a mechanical stirrer having a digital controller unit, a thermometer and a back cooler. After adding 200 mL of citric acid solution to the reaction vessel and when the temperature reached the desired value, a sample weighted according to the appropriate solid-to-liquid ratio was then added to the reactor while stirring the content of the reactor at 600 rpm. After each test, the slurry was filtered immediately, and the Mg^{+2} content of the solution was determined by complexometric method.

Experimental parameters and their levels (Table 2) were determined in the light of preliminary tests. The reason being it was the most adequate of the conditions five parameters for four levels, L_{16} (4^5) orthogonal array (OA) design was decided on test plan (Tables 3 and 4). In order to observe the noise effects, each experiment was repeated twice under the same conditions at different times. Taguchi's "The larger the better" performance statistic formula (Z_B) was chosen as the optimization criterion (Eq.1) (Demir et al., 2003b):

$$Z_B = -10Log\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{Y_i^2}\right) \quad (1)$$

Where n was the number of repetitions done for an experimental

Table 1
The chemical composition of calcined magnesite.

Component	(%, w/w)
MgO	92.14
CaO	2.82
Fe_2O_3	1.05
SiO_2	3.99

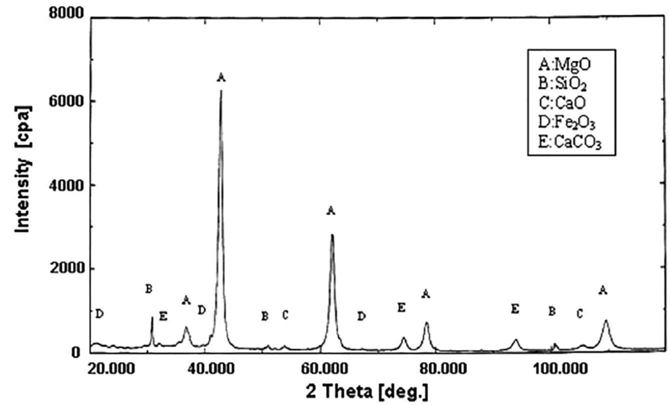

Fig. 1. Graph of XRD for calcined magnesite.

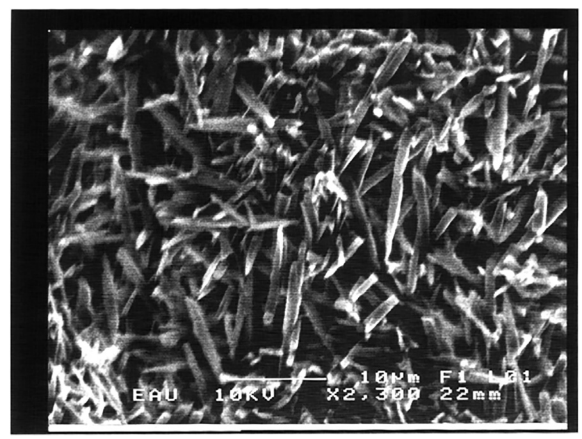

Fig. 2. SEM micrograph for magnesium citrate.

Table 2
Parameters and values for levels to be examined in tests.

	Parameters	Levels			
		1	2	3	4
A	Acid concentration (M)	2.0	2.5	3.0	3.5
B	Reaction period (min)	10	20	30	45
C	Reaction temperature (°C)	20	30	40	50
D	Solid-to-liquid ratio (g.mL^{-1})	0.0500	0.0625	0.0833	0.1250
E	Particle size (μm)	-319	-519	-1019	-2819

Table 3
L_{16} (4^5) experimental plan.

Experiment No	A	B	C	D	E
1	1	1	1	1	1
2	1	2	2	2	2
3	1	3	3	3	3
4	1	4	4	4	4
5	2	1	2	3	4
6	2	2	1	4	3
7	2	3	4	1	2
8	2	4	3	2	1
9	3	1	3	4	2
10	3	2	4	3	1
11	3	3	1	2	4
12	3	4	2	1	3
13	4	1	4	2	3
14	4	2	3	1	4
15	4	3	2	4	1
16	4	4	1	3	2

Table 4
Dissolution percentage (%) for Mg in L_{16} (4^5) experimental plan.

Experiment No	A	B	C	D	E	% Mg 1St Trial	% Mg 2nd Trial	% Mg (Average)
1	2	10	20	0.05	-319	83.83	80,43	82.13
2	2	20	30	0.0625	-519	87.13	83.44	85.28
3	2	30	40	0.083	-1019	85.17	86.56	85.86
4	2	45	50	0.125	-2819	82.37	76.94	79.65
5	2.5	10	30	0.083	-2819	15.88	19.42	17.65
6	2.5	20	20	0.125	-1019	63.44	70.16	66.80
7	2.5	30	50	0.05	-519	97.45	95.59	96.52
8	2.5	45	40	0.0625	-319	93.02	92.72	92.87
9	3	10	40	0.125	-519	72.37	72.98	72.67
10	3	20	50	0.083	-319	84.79	85.95	85.37
11	3	30	20	0.0625	-2819	32.64	33.88	33.26
12	3	45	30	0.05	-1019	82.55	74.52	78.54
13	3.5	10	50	0.0625	-1019	62.67	54.73	58.70
14	3.5	20	40	0.05	-2819	32.25	40.80	36.52
15	3.5	30	30	0.125	-319	79.10	80.32	79.71
16	3.5	45	20	0.083	-519	77.68	78.83	78.25

combination, and Y_i performance value of *i*th experiment. In Taguchi method, the experiment corresponding to optimum working conditions might have not been done during the whole period of the experimental stage. In such cases, Taguchi suggested an estimation formula based on individual differences between the average of chosen factor levels and the overall mean (Logothetis, 1992; Phadke et al., 1983):

$$Y_i = \mu + \sum (average\ of\ selected\ source\ level\ -\ \mu) \quad (2)$$

Where Y_i and μ were the average yield and overall mean of performance value, respectively. Because Eq. (2) was a point guess, which was found by using experimental data in order to define whether results of the confirmation test were significant or not, the confidence interval must have been evaluated. The confidence interval at chosen error level could be calculated by Eq. (3) (Taguchi, 1987):

$$Y_i \pm \sqrt{F_{\alpha;1,df_e} * MSSe * \left(\frac{1+\sum ED}{N}\right)} \quad (3)$$

Where *F* was the value of F table, α; error level, df_e; degrees of freedom of mean square error, MSSe; mean sum of squares for the residual variance, ED; total effectual number of degrees of freedom and *N*; number of total experiments. At the end of the calculations, we checked the validity of the result by confirmation experiments.

3. Results and discussion

3.1. Dissolution reactions

When the magnesium oxide is chemically reacted with the citric acid solutions, the following reactions take place:

$$C_6H_8O_{7(s)} + 2H_2O_{(l)} \leftrightarrow 2H_3O^+_{(aq)} + C_6H_6O_7{}^{-2}{}_{(aq)} \quad (4)$$

$$MgO_{(s)} + 2H_3O^+_{(aq)} \leftrightarrow Mg^{+2}_{(aq)} + 3H_2O_{(l)} \quad (5)$$

$$Mg^{+2}_{(aq)} + C_6H_6O_7{}^{-2}{}_{(aq)} \leftrightarrow MgC_6H_6O_7(aq) \quad (6)$$

3.2. Definitation of the optimum conditions

The obtained data for the leaching process are analyzed by Taguchi method for valuation of the influence of each parameter on the optimization process. The results are exhibited in Table 4 and graphs which show the variation of the performance statistics with parameters examined in the Figs. 3, 4, 5, 6, and 7. First we explain with an example how these graphs are constructed. Let us take Fig. 5 which shows the variation of the performance statistics with reaction temperature. Now let us try to determine experimental conditions for the first data point. The reaction temperature for this point is 20 °C which is level 1 for this parameter. Now let us go to Table 3 and find the experiments for which reaction temperature level (column C) is 1. It is seen in Table 3 that experiments for which column C is 1 are experiments with experiment no 1, 6, 11 and 16. Thus, the performance statistics value of the first data point is the average of those obtained from experiments with experiment numbers 1, 6, 11 and 16. Experimental conditions for the second data point are the conditions of the experiments for which column C is 2 (i.e. experiments with experiment no 2, 5, 12, 15), and so on. The numerical value of the maximum point in each graph marks the best value of that particular parameter. If Figs. 3, 4, 5, 6, and 7 are studied carefully, it can be seen that levels of the experiment corresponding to optimum conditions are A: 1, B: 4, C: 4, D: 1, E: 1. But, as there is no significant difference between level 1 and 4 of performance statistics for D parameter, 4th level of solid-to-liquid ratio is chosen because of the economic factor. Consequently, we define the optimum conditions from the leaching experiments as A: 1,

Table 5
Optimum working conditions, predicted and observed amounts of Mg^{+2}.

Parameters		Optimum levels	Optimum values
A	Acid concentration (M)	1	2
B	Reaction period (min)	4	45
C	Reaction temperature (°C)	4	50
D	Solid to liquid ratio ($g.mL^{-1}$)	4	0.125
E	particle size (μm)	1	-319
Observed amount of magnesium dissolved (%)		98.86	
Predicted amount of magnesium dissolved (%)		97.05	
Predicted confidence interval (%)		92.29–100	

Table 6
Effect of each parameter for the performance statistics (ANOVA Table).

	Parameters	df	SS	MSS	F-ratio	Effectiveness
A	Acid concentration (M)	3	1818.69	606.23	59.92	Effectual
B	Reaction period (min)	3	2534.06	844.68	83.49	Effectual
C	Solid to liquid ratio (gmL^{-1})	3	391.26	130.42	12.89	Effectual
D	Reaction temperature (°C)	3	1197.05	399.01	39.44	Effectual
E	Particle size (μm)	3	9606.80	3202.26	316.54	Effectual
Error		16	161.86	10.11		
Total		31	15709.75	506.76		

F(3.16)0.95 = 3.24.

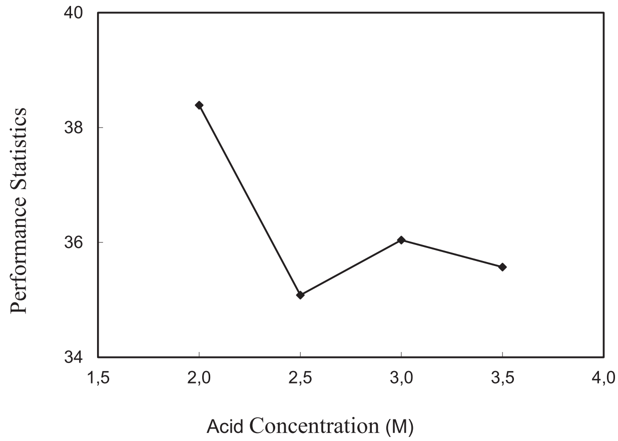

Fig. 3. The effect of acid concentration on the optimization.

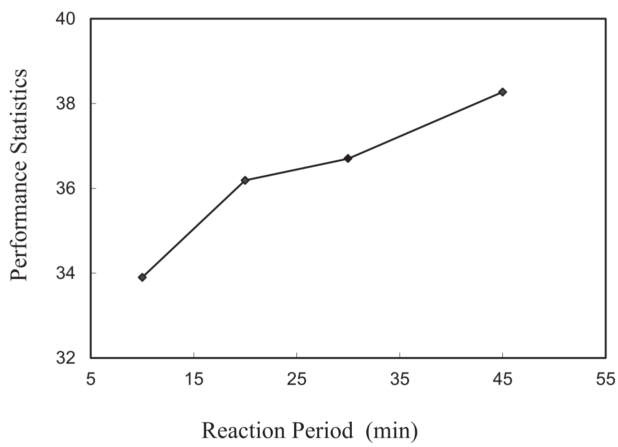

Fig. 4. The effect of reaction period on the optimization.

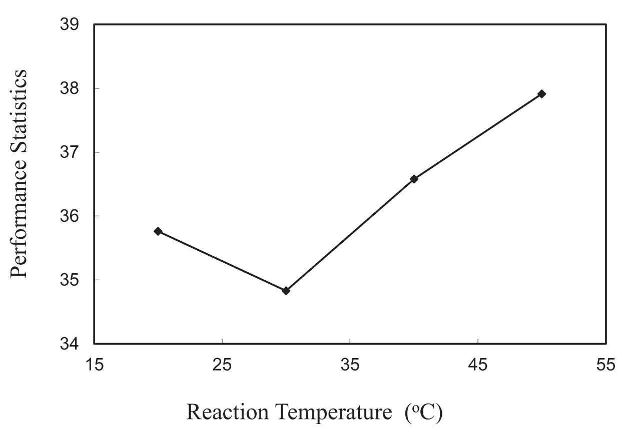

Fig. 5. The effect of reaction temperature on the optimization.

B: 4, C: 4, D: 4, E: 1 (Table 5). As test plan about Table 3 is scrutinized together with Table 2, it is possible to observe that test concerning optimum conditions (A: 1, B: 4, C: 4, D: 4, E: 1) is not done out during the experimental work. So, we predict the dissolution percentage at the optimum condition for % 95 confidence interval by using Eqs. (2) and (3). It is calculated as 97.05 ± 4.76, that is, from 92.29% to 100%. In order to test the predicted result, confirmation experiments are carried out two times at optimum working conditions. From the fact that the dissolution percentages obtained from confirmation experiments (98.86 %) are within the calculated confidence interval (see Table 5), it can be said that experimental results are within ±5 % in error. In addition, F-ratio and the effectiveness of each parameter on the performance statistic are given in Table 6.

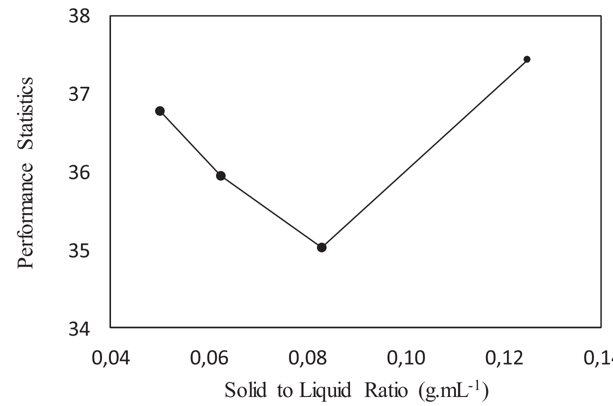

Fig. 6. The effect of solid to liquid ratio on the optimization.

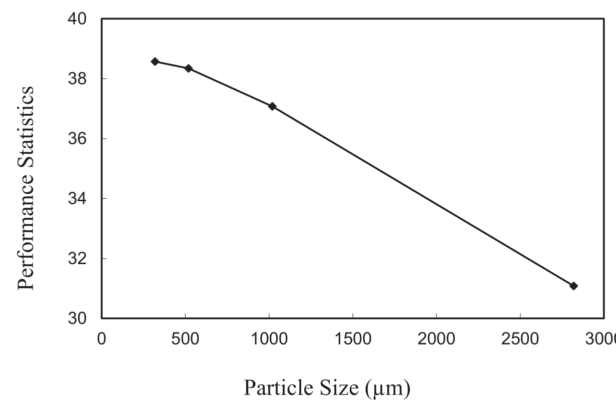

Fig. 7. The particle size effect on the optimization.

Consequently, the optimal conditions determined for the leaching of calcined magnesite in the citric acid media are given as follows: reaction temperature; 50 °C, reaction time; 45 min, acid concentration; 2 M, particle size; -319 μm, and solid to liquid ratio; 0.125 g mL^{-1}.

When the performance statistics graphs are examined, it is seen that the most effective parameter is particle size. In general, it can be said that dissolution rate increases with increasing reaction temperature and reaction period. According to the previous study (Demir et al., 2006), if the acid concentration values are above 1.0 M, this has a negative effect on the dissolution rate. Therefore, increasing the acid concentration and particle size reduces the dissolution rate. Again, as the solid-liquid ratio increased, the dissolution rate first decreased and then increased. This situation can be attributed to the adverse effect of acid concentration and the internal interactions.

4. Conclusions

The basic aim of this study is to evaluate the parameter effects on leaching in citric acid media of calcined magnesite and to define optimal leaching conditions of calcined magnesite by Taguchi technique. Dissolution process in the heterogeneous systems depends on both process conditions and surface properties of ore. The calcination of magnesite ore, which produce magnesium oxide, enhances the surface properties of the ore and also helps yield of reactivity. Therefore, calcined magnesite is used in this study. The parameters investigated are acid concentration, reaction period, reaction temperature, solid–liquid ratio and particle size. Because the desired characteristic for response is the maximum magnesium extraction, Taguchi's 'the larger the better' performance criterion is used. The conclusions obtained from the present study are presented as follows:

- For the leaching process, the extraction efficiency of magnesium from calcined magnesite with citric acid is rather sensitive in terms of particle size. The other parameters which are affecting the efficiency of extraction are reaction period, reaction temperature, solid-to-liquid ratio, and acid concentration, respectively.
- Optimum conditions found in laboratory medium by Taguchi technic are also applicable for actual productions. Therefore, on an industrial-scale, the data obtained for the laboratory-scale work can be beneficial for the process of calcined magnesite.
- Using a non–toxic organic solvent such as citric acid to dissolve the magnesia is useful for the conservation of environment.
- Because citric acid is weaker than inorganic acids, there is no need to use much more expensive equipments and devices because of device corrosion. This means low capital investment.
- Since citric acid as a solvent is a weak acid, gang minerals in the solid do not dissolve. So, this process leads the selective extraction for calcined magnesite.
- In the citric acid media, the process conditions and dissolution percentages corresponding to optimal dissolution of calcined magnesite are submitted and compared with natural magnesite ore work (Demir and Donmez, 2008). The results are as follows:

Parameters	Natural Magnesite work	Calcined Magnesite work
Acid concentration (M)	2	2
Reaction period (min)	120	45
Reaction temperature (°C)	75	50
Solid-to-liquid ratio ($g.mL^{-1}$)	0.125	0.125
Particle size (μm)	-319	-319
Dissolution percentage (%)	99.9	98.86

When the results of two studies are compared, dissolution percentages at the optimum conditions are observed to be very close. But, the reaction period decreases about three times and reaction temperature decreases from 75 to 50 degrees Celsius in the experiments performed with calcined magnesite. At first sight, calcined magnesite work may be more advantageous for citric acid production. But, this requires an appropriate cost analysis.

Additionally, there is no study of raw magnesite and calcined magnesite on the same parameters. But, according to the article (Demir and Donmez, 2008), the study results of Table 2 (level 2) represent experiment results close to the optimum values of calcined magnesite. With the evaluation of the results of this study, under almost the same working conditions, while the dissolution percentage of calcined magnesite is approximately 99 %, it is estimated that the dissolution percentage of the raw magnesite value is less than 70 %.

Declarations

Author Contribution Statement

Fatih Demir: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Bünyamin Dönmez: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing Interest Statement

The authors declare no conflict of interest.

Additional Information

No additional information is available for this paper.

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