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## PRODUCTION OF HIGH QUALITY MAGNESIUM CHLORIDE FROM RECYCLED WASTE MAGNESITE POWDER

Necmettin ERDOGAN<sup>\*</sup>, Erkan YERSEL<sup>\*\*</sup>, Cengiz CELEBI<sup>\*\*\*</sup>,  
Nevzat KAVAKLI<sup>\*\*\*\*</sup>, Turan BATAR<sup>\*\*\*\*</sup>

<sup>\*</sup> Aksaray University, Department of Mining Engineering, Aksaray, Turkey  
nerdogan@aksaray.edu.tr

<sup>\*\*</sup> Canakkale Onsekiz Mart University, Department of Mining Engineering, Canakkale, Turkey

<sup>\*\*\*</sup> Ministry of Energy and Natural Resources, Ankara, Turkey

<sup>\*\*\*\*</sup> Gediz University, Faculty of Engineering and Architecture, Izmir, Turkey

**Abstract:** This study investigates the production of high-quality  $MgCl_2$  from recycled waste magnesite powder with an average particle size of  $d_{50}$  0.079 mm using the HCl acid leaching method. The experimental parameters were, leaching temperature, leaching time, amount of the acid, liquid-to-solid ratio, scale-up factor, acid concentration, particle size and mixing speed. The experiments were performed under reproducible conditions. The results showed that optimum leaching parameters were: temperature of 70 °C, 180 min leaching time, 130 cm<sup>3</sup> acid consumption, 3.6 cm<sup>3</sup>/g liquid-to-solid ratio, scale-up factor of 1, 10.17 M acid concentration, 0.079 mm average particle size and a mixing speed 60 rpm. Under these optimum conditions, the leaching yield was 96.72%. The produced  $MgCl_2$  solution contained 0.04%  $SiO_2$ , 0.36%  $CaO$ , 0%  $Fe_2O_3$ , 0%  $Al_2O_3$ , 46.73%  $MgCl_2$ , 52.87% L.O.I. and 99.60%  $MgCl_2$ +L.O.I. (=  $MgCl_2 \cdot 6H_2O$ ). These results indicated that high-quality magnesium chloride can be produced from waste magnesite powder.

**Keywords:** waste magnesite powder, leaching hydrochloride acid, magnesium chloride,  $MgCl_2$

### Introduction

Magnesite ( $MgCO_3$ ) is a primary source for the production of magnesium and its compounds. Natural magnesite theoretically contains 47.6%  $MgO$  and impurities such as silicon dioxide, iron and calcium. It is the basic raw material for the manufacture of alkaline refractory products and used in iron-steel, cement, glass, sugar, lime and paper industries as well as the paint and ink industry, the pharmaceutical industry as an anti-acid, and in the production of many magnesium chemicals (Abali at al., 2006).

Shaped and unshaped magnesite refractories have been used for many years as high strength hot-face refractories in a wide range of furnaces.

They have important applications where high degrees of refractoriness or resistance to basic environments are required, such as steel making vessels and rotary cement kilns (Shikano, 1998; Palco et al., 2002).

Chou et al. (1989) investigated the dissolution of various carbonates (including calcite, magnesite and dolomite) in HCl solutions at 25 °C using a continuous fluidized bed reactor and samples of a relatively coarse particle size. Ozbek et al. (1999) investigated the dissolution kinetics of magnesite with Cl<sub>2</sub> gas in water. They found that the diffusion was controlled through the fluid layer. Harris et al. (1988) studied the production of magnesium from concentrated magnesium chloride solutions. In addition, Abali et al. (2006) investigated the optimum conditions for the dissolution of magnesite with H<sub>2</sub>SO<sub>4</sub> solutions. They reported that the optimum conditions were 65 °C, 5/100 g/cm<sup>3</sup>, 2M, 60 min and 300 rpm. Abdel-aal et al. (1996) analyzed Egyptian magnesite ore (43.32% MgO) from the Eastern Desert leached with aqueous hydrochloric acid. They reported that the optimum conditions of leaching were: ore particle size -0.5 mm, temperature 60 °C, leaching time 15 min, HCl-to-MgO molar ratio 1.06, and liquid/solid ratio of 2.5:1 cm<sup>3</sup>/g. These conditions led to a recovery of approximately 99.1% MgO. Abali et al. (2011) also investigated the Taguchi method to determine the optimum conditions for leaching dolomite ore in hydrochloric acid solutions. The experimental parameters were leaching temperature, solid-to-liquid ratio, acid initial concentration, leaching time and stirring speed. The optimum leaching parameter levels were found to be temperature 50 °C, solid-to-liquid ratio 2%, acid concentration 20 g/cm<sup>3</sup> (2 mol/dm<sup>3</sup>), stirring speed 450 rpm, leaching time 5 min. Under the optimum process conditions, the dolomite ore leaching efficiency was approximately 83%. Ozdemir et al. (2009) investigated the recovery of magnesium from magnesite tailings in aqueous hydrochloric acid solutions with acid leaching in a batch reactor using hydrochloric acid solutions. Subsequently, they also investigated production of magnesium chloride hexahydrate (MgCl<sub>2</sub>·6H<sub>2</sub>O) from leaching solution. The parameters were the effects of temperature, acid concentration, solid-to-liquid ratio, particle size and stirring speed on the leaching process. According to Ozdemir et al. (2009), the pseudo-second-order reaction model seems to be appropriate for the magnesium leaching.

The aims of this study are firstly to investigate the use of recycled waste magnesite powder to produce high-quality magnesium chloride. For this purpose, the acid leaching method was used to determine the optimum leaching conditions and parameters. The experimental plan was based on parameters and their levels to determine the leaching rate of waste magnesite powder in HCl solutions. To determine the optimum conditions the parameters of signal-noise graphics were drawn. The maximum leaching performance of the waste magnesite powder was predicted from the calculation of the optimum conditions. The produced MgCl<sub>2</sub> solution comprised: 0.04% SiO<sub>2</sub>, 0.36% CaO, 0% Fe<sub>2</sub>O<sub>3</sub>, 0% Al<sub>2</sub>O<sub>3</sub>, 46.73% MgCl<sub>2</sub>, 52.87% L.O.I. and

99.60%  $\text{MgCl}_2 + \text{L.O.I.}$  ( $= \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ). These results show that high-quality magnesium chloride was successfully produced from waste magnesite powder. Thus, waste magnesite powder produced in the electrofilter installation of the ore processing plants can be recycled thus saving money. In addition, the waste powder is prevented from damaging the environment.

## Experiment

### Material

For the experiments the waste magnesite powder was obtained from the electrofilter output of the ore processing plant of the Kütahya Magnesite Enterprises Company, Turkey. In order to determine the properties of waste magnesite powder sample the chemical, physical and mineralogical tests were carried out. A wet chemical analysis method was used according to the ASTM C574-78 standard and the results were given in Table 1. In order to determine the particle size distribution of the waste magnesite powder, sieve analysis was carried out. Of the material 80% was of  $d_{80}$  size and the average grain size was considered to  $d_{50}$ . The results are given in Table 2. In order to determine the  $d_{80}$  and  $d_{50}$ , a cumulative undersize graph was drawn to analyze sieving results. The cumulative undersize chart is presented in Fig. 1,  $d_{80}$  and  $d_{50}$  are equal to 0.165 mm and 0.079 mm, respectively. In order to determine the mineralogical structure of the sample, X-Ray Diffraction (XRD) analysis was carried out and analysis of the results is given in Fig. 2. The leaching agent, purchased from Detsan, was 32% acid grade hydrochloric acid (10.17 M) having  $1.159 \text{ g/cm}^3$  density.

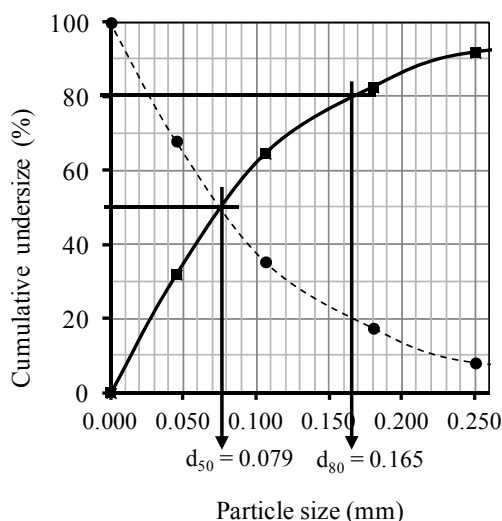


Fig. 1.  $d_{80}$  and  $d_{50}$  of the waste magnesite powder

Table 1. Chemical analysis of the waste magnesite powder

Compounds	Weights %
MgO	43.80
SiO <sub>2</sub>	13.32
CaO	2.13
Fe <sub>2</sub> O <sub>3</sub>	2.35
Al <sub>2</sub> O <sub>3</sub>	0.65
L.O.I	37.75
Total	100.00

Table 2. Sieve analysis of waste magnesite powder

Size fraction (mm)	Weights (%)	Cumulative undersize (%) $\Sigma\uparrow$	Cumulative oversize (%) $\Sigma\downarrow$
-1+0.5	1.97	100.00	1.97
-0.5+0.250	6.15	98.03	8.12
-0.250+0.180	9.38	91.88	17.50
-0.180+0.106	17.92	82.50	35.42
-0.106+0.045	32.60	64.58	68.02
-0.045+0	31.98	31.98	100.00
Total	100.00		

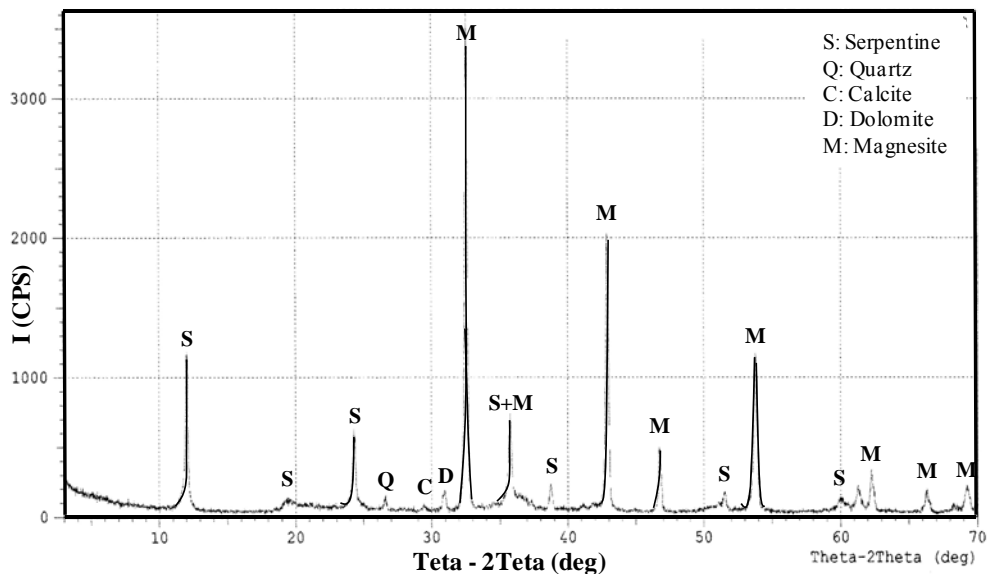


Fig. 2. XRD of the waste magnesite powder

## Method

The HCl acid leaching method was used for the production of high-purity  $\text{MgCl}_2$ . The leaching experimental setup is shown in Fig. 3, and the leaching flow-chart is presented in Figure 4. The experimental parameters are leaching temperature, leaching time, amount of the acid, liquid-to-solid ratio, scale-up factor, acid concentration, particle size and mixing speed as shown in Table 3. The variable leaching parameters are: leaching temperature 30–40–50–60–70 °C, leaching time 60–120–180–240–300 min, amount of acid 100–110–120–130–140  $\text{cm}^3$ , liquid–solid ratio 3.0/1–3.3/1–3.6/1  $\text{g}/\text{cm}^3$ , and the scale–up factor 1–2–3–4–5. The acid concentration of 10.17 M, the average grain size 0.079 mm, the mixing rate of 60 rpm were determined and were applied as fixed leaching parameters. The required quantity of the waste magnesite powder and acid for leaching were calculated according to the stoichiometric formula and weighed. Water, waste magnesite powder and acid were fed sequentially into the leaching tank. The leaching tank was heated indirectly. At the end of the leaching process, the  $\text{MgCl}_2$  solution was produced by separating the soluble and insoluble minerals using a filter paper. The optimum leaching conditions were determined as a result of the experiment. In order to determine the quality of magnesium chloride in optimum leaching conditions, chemical analysis was performed by wet chemical analysis method according to the ASTM C574-78 standard.

## Results and discussion

Waste magnesite powder was received from the electro-filter of the ore processing plant in the Kütahya Magnesite Enterprises Company of Turkey. The results of chemical analysis of sample are given in Table 1. The amount of  $\text{SiO}_2$  was 13.32%. The particle size of the sample was analyzed and the results are given in Table 2. Exactly 80% of the material passed through the sieve was  $d_{80}$  and  $d_{50}$  was the average grain size. The  $d_{80}$  and  $d_{50}$  were measured as 0.165 mm and 0.079 mm, respectively, and the results are given in Fig. 1. In order to determine the mineralogical structure of the sample, X-Ray Diffraction (XRD) analysis was made, and the results of the analysis are given in Fig. 2. According to the XRD chart the major mineral in the waste magnesite powder is magnesite, and minor minerals are serpentine, calcite, dolomite and quartz. The experimental setup of the magnesium chloride production is given in Fig. 3, and the flow chart is given in Fig. 4. Variable and fixed leaching experiment parameter values are given in Table 3.

In order to determine the quality of the magnesium chloride, chemical analysis was undertaken using a wet chemical analysis method according to the ASTM C574-78 standard. According to the results of the chemical analysis given in Table 5, the solution of magnesium chloride contained 0.04%  $\text{SiO}_2$ , 0.36%  $\text{CaO}$ , 0%  $\text{Fe}_2\text{O}_3$ , 0%  $\text{Al}_2\text{O}_3$ , 46.73%  $\text{MgCl}_2$ , 52.87% L.O.I. and 99.60%  $\text{MgCl}_2 + \text{L.O.I.}$  (=  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ). Thus, the results show that high-purity magnesium chloride was produced from the waste magnesite sample.

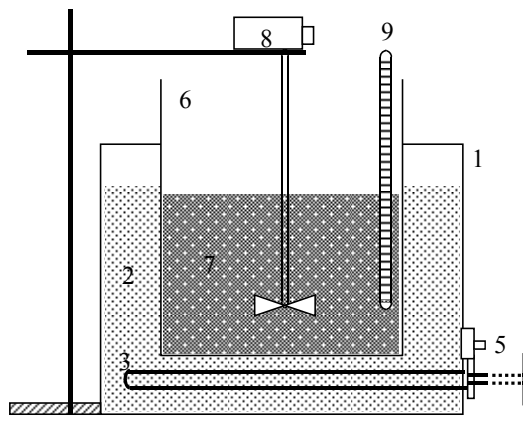


Fig. 3. Leaching experimental setup: 1 – water bath, 2 – water, 3 – heater, 4 – power supply, 5 – thermostat, 6 – glass beaker, 7 – solution, 8 – mixer, 9 – thermometer

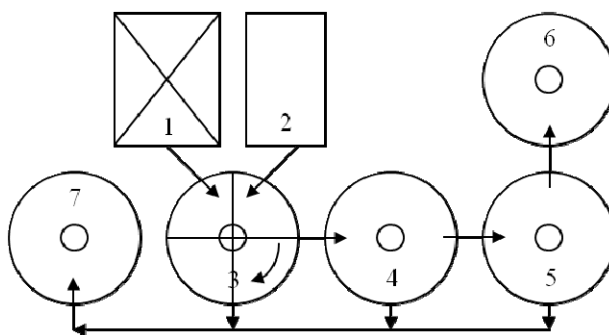


Fig. 4. Leaching flow sheet: 1 – waste magnesite powder tank, 2 – HCl acid tank, 3 – leaching tank, 4 – solution settling tank, 5 – solution settling tank, 6 – clean solution tank, 7 – waste (minerals) collection tank

Table 3. Parameters of leaching experiment

	Temperature change	Time change	Amount of acid change	Scale-up change
Leaching temperature (°C)	30-40-50-60-70	70	70	70
Leaching time (min)	180	60-120-180-240-300	180	180
The amount of acid (cm <sup>3</sup> )	130	130	100-110-120-130-140	130
Liquid-to-solid ratio (cm <sup>3</sup> /g)	3.6/1	3.6/1	3.0/1; 3.3/1; 3.6/1	3.6/1
Scale-up factor	1	1	1	1-2-3-4-5
Acid concentration (M)	10.17	10.17	10.17	10.17
The average particle size; d <sub>50</sub> (mm)	0.079	0.079	0.079	0.079
Mixing speed (rpm)	60	60	60	60

Table 4. Optimum leach parameters

Parameters	values
Leaching temperature (°C)	70
Leaching time (min)	180
The amount of acid (cm <sup>3</sup> )	130
Liquid-to-solid ratio (cm <sup>3</sup> /g)	3.6/1
Scale-up factor	1
Acid concentration (M)	10.17
The average particle size; d <sub>50</sub> (mm)	0.079
Mixing speed (rpm)	60
Leach yield (%)	96.72

Table 5. Chemical analysis results of the magnesium chloride solution

Compounds	Weights %
MgCl <sub>2</sub>	46.73
SiO <sub>2</sub>	0.04
CaO	0.36
Fe <sub>2</sub> O <sub>3</sub>	0
Al <sub>2</sub> O <sub>3</sub>	0
L.O.I.	52.87
Total	100.00
MgCl <sub>2</sub> +L.O.I. = MgCl <sub>2</sub> .6H <sub>2</sub> O	99.60

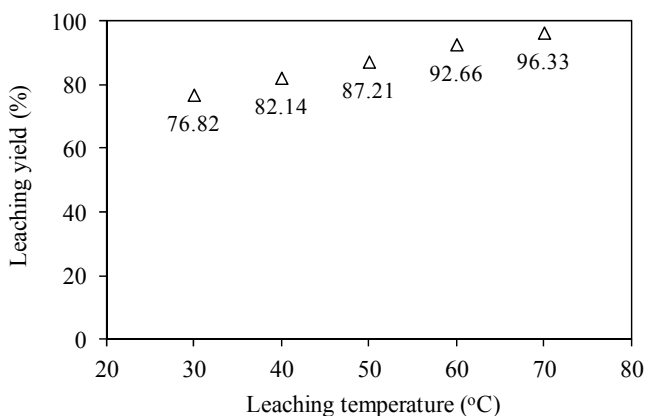


Fig. 5. Leaching yield in relation to leaching temperature

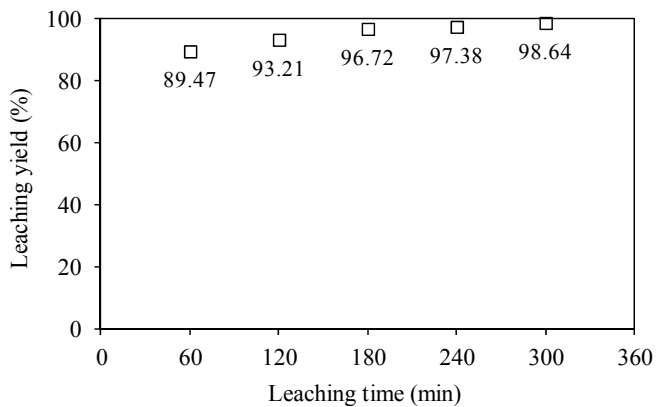


Fig. 6. Leaching yield in relation to leaching time

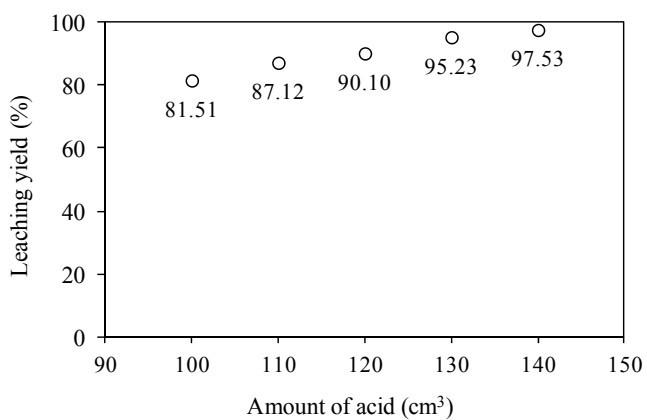


Fig. 7. Leaching yield in relation to amount of acid

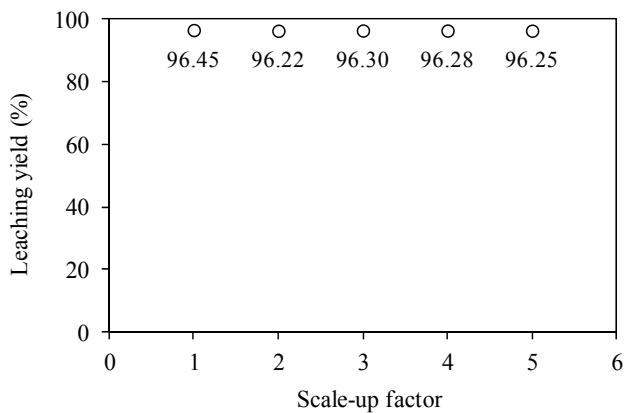


Fig. 8. Leaching yield in relation to the scale-up factor



Chou et al. (1989) investigated the dissolution of various carbonates (including calcite, magnesite and dolomite) in HCl solutions at 25 °C using coarse particle size samples. However, in this study a fine particle sample of waste magnesite was analyzed at 70 °C. Abali et al. (2006) investigated the optimum conditions for dissolution of magnesite with H<sub>2</sub>SO<sub>4</sub> solutions. They reported that the optimum conditions were found to be 65 °C, 5/100 g/cm<sup>3</sup>, 2M, 60 min and 300 rpm. In the current study the optimum conditions were; leaching temperature 70 °C, leaching time 180 min, the amount of acid 130 cm<sup>3</sup>, liquid-to-solid ratio 6.3 cm<sup>3</sup>/g, the acid concentration 10.17 M and a mixing speed of 60 rpm. Abdel-aal et al. (1996) analyzed Egyptian magnesite ore (43.32% MgO) from the Eastern Desert leached with aqueous hydrochloric acid. They reported that the optimum conditions of leaching were ore particle size -0.5 mm, temperature 60 °C, leaching time 15 min, HCl to MgO molar ratio 1.06, and liquid/solid ratio of 2.5:1 cm<sup>3</sup>/g, recovery 99.1% MgO. By contrast, in this study optimum conditions were; average particle size 0.079 mm, temperature 70 °C, leaching time 180 min, liquid-to-solid ratio 6.3 cm<sup>3</sup>/g, recovery 99.60% MgCl<sub>2</sub>+L.O.I (= MgCl<sub>2</sub>·6H<sub>2</sub>O).

In the current study from very fine waste material MgCl<sub>2</sub>·6H<sub>2</sub>O was produced with the yield of 99.60% containing no Al<sub>2</sub>O<sub>3</sub> and no Fe<sub>2</sub>O<sub>3</sub>.

## Conclusions

The aim of this study was to investigate the optimization of waste magnesite powder using leaching in hydrochloric acid solutions, to produce high-quality magnesium chloride, and thus, recycle waste magnesite powder. The experimental parameters were: leaching temperature, leaching time, amount of acid, liquid-to-solid ratio, scale-up factor, acid concentration, particle size and mixed speed. The experiments were carried out under reproducible conditions. On completion of the experiments, the optimum leaching parameter levels were found to be temperature 70 °C, leaching time 180 min, amount of acid 130 cm<sup>3</sup>, liquid-to-solid ratio 3.6 cm<sup>3</sup>/g, scale-up factor 1, acid concentration 10.17 M, average particle size 0.079 mm and mixing speed 60 rpm. Under the optimum leaching conditions, the yield was 96.72% and pH 8. The produced MgCl<sub>2</sub> solution consisted of 0.04% SiO<sub>2</sub>, 0.36% CaO, 0% Fe<sub>2</sub>O<sub>3</sub>, 0% Al<sub>2</sub>O<sub>3</sub>, 46.73% MgCl<sub>2</sub>, 52.87% L.O.I. and 99.60% MgCl<sub>2</sub>+L.O.I. (= MgCl<sub>2</sub>·6H<sub>2</sub>O). These results show that high-quality magnesium chloride can be successfully produced by recycling waste magnesite powder. In addition to protecting the environment by reducing the amount of waste this process has economic benefits.

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