

Chemical Exfoliation Characteristics of Karakoç Phlogopite in Hydrogen Peroxide Solution

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The chemical exfoliation characteristics of phlogopite samples taken from Sivas–Yıldızeli-Karakoç (Turkey) ore were investigated. H_2SO_4 , HCl , HNO_3 , H_3PO_4 and H_2O_2 solutions at varying concentrations were tested for chemical exfoliation and the best reagent for this purpose was determined to be hydrogen peroxide. In the exfoliation tests performed, hydrogen peroxide concentration, temperature and reaction time were observed to be important parameters, with solid/liquid ratio being of minor importance. The exfoliation characteristics of the material increased with increases in hydrogen peroxide concentration and depending on the reaction time (1-30 hours) a maximum value of a 49-fold increase in swelling was obtained in 30% hydrogen peroxide solution at room temperature with a change of the density from 2.75 g/cm^3 to 0.37 g/cm^3 . Although maximum swelling was reached in 30 hours at room temperature in 30% hydrogen peroxide solution, the reaction time was lowered to 70 minutes by an increase in temperature to 60°C . Above 60°C the material started to decompose into fine particles, with complete loss of its characteristics above 80°C . The experimental results were interpreted mathematically and a regression model was proposed to calculate the swelling ratio for any hydrogen peroxide concentration and reaction time at room temperature.

Key Words: chemical exfoliation, hydrogen peroxide, phlogopite, swelling, vermiculite

Introduction

Vermiculites are expandable 2:1 phyllosilicates formed mainly by the alteration of micas¹ (phlogopites or biotites). The expanded (exfoliated) material is low in density, chemically inert, and adsorbent, has excellent thermal and acoustic insulation properties, is fire resistant and is widely used as a lightweight aggregate, thermal insulator and in agricultural applications²⁻⁴.

Vermiculite exfoliates upon heating at temperatures between 870 and 1100°C and, although the individual flakes may expand as much as 30-fold, the bulk volume of the commercially prepared material increases

8-12-fold⁵. The highest expansion was shown by samples containing mica or mica-vermiculite interstratifications and the expansion was related to the sudden release of water⁶. In addition, the thermal behaviour of pure vermiculite and mica-vermiculite interstratifications showed that the presence of interstratification produced thermal effects at lower temperatures⁷. Motoharu and Katsutoshi⁸ showed that the rehydration properties of vermiculite were strongly affected by the hydration energies of the interlayer cations and the nature of the stacking of the minerals seemed to be the most important factor controlling the behaviour of interlayer cations in the thermal dehydration process. Üçgül and Girgin⁹ tested the thermal expansion characteristics of Karakoç (Turkey) phlogopite in flame and electric furnace conditions and maximum expansion ratios were determined to be 13- and 18-fold respectively.

Vermiculite and phlogopite also exfoliate by chemical processes utilizing hydrogen peroxide, weak acids and some electrolytes^{5,10}. When phlogopite from the Kovdor deposit was treated with 30% H₂O₂ solution, an increase in volume by factors of 150-200 was obtained¹¹ and the swelling was determined to be four times higher for the disordered crystals than for perfect crystals. Muromtsev et al.¹² investigated the reaction between vermiculite and hydrogen peroxide and suggested a mechanism based on the reactivity of the oxygen formed at the initial moments of peroxide decomposition. The effect of H₂O₂ concentration, temperature and solid/liquid ratio on the exfoliation characteristics of Karakoç phlogopite was determined¹³ and an exfoliation ratio of 49 was obtained.

Sivas-Yıldızeli-Karakoç (Turkey) ore body, with an approximate reserve of 2 750 000 tonnes, contains phlogopite as the main mineral. In this study, the chemical exfoliation characteristics of the samples taken from this ore body using hydrogen peroxide solution were investigated.

Experimental

Materials and Methods

Samples taken from the ore body were platy and blackish, with a rectangular shape of average size 3 cm and the thickness varying between 0.1 and 0.5 cm. The density and the bulk density¹⁴ of the samples were determined to be 2.75 g/cm³ and 0.85 g/cm³, respectively. The chemical composition of the sample was determined by X-ray fluorescence analysis (Philips PW 11480 spectrometer), the results of which are given in Table 1 in comparison with ideal phlogopite composition¹⁵.

Table 1. Chemical compositions of Karakoç ore and ideal phlogopite

%	SiO ₂	MgO	Al ₂ O ₃	K ₂ O	FeO	Fe ₂ O ₃	TiO ₂	CaO	Na ₂ O	F	L.O.I.
Karakoç Ore	36.28	16.99	16.37	7.98	6.63	4.69	2.90	1.68	0.38	1.39	4.30
Phlogopite	40.00	26.00	17.00	10.00	2.80	0.20	Trace	Trace	0.50	—	3.00

L.O.I.: Loss on ignition

Although the composition of Karakoç ore in terms of Si, Al, K and Na are in good agreement with the ideal phlogopite composition, deviations in Mg, Fe, Ti, Ca, F and H₂O contents are observed. It can be concluded that part of the ferrous iron was converted into ferric iron due to oxidation that in turn intensified the colour of the mineral. The presence of Ca can be attributed to ion exchange as the cation exchange capacity of the sample determined by Na⁺/NH₄⁺ exchange¹⁶ was 56.68 meq/100g. The mineralogical composition of the sample was determined by X-ray diffraction analysis (Philips PW 3710)

and the pattern, which is in agreement with ASTM Card No: 16-352 for phlogopite, is given in Figure 1. Although the main mineral seems to be phlogopite, extra scattering below about 9° (2θ) in Figure 1 is indicative of mixed layering effects and probably the occurrence of interstratified vermiculite. Ethylene glycolated XRD pattern shows the presence of minor amounts of smectite in the sample.

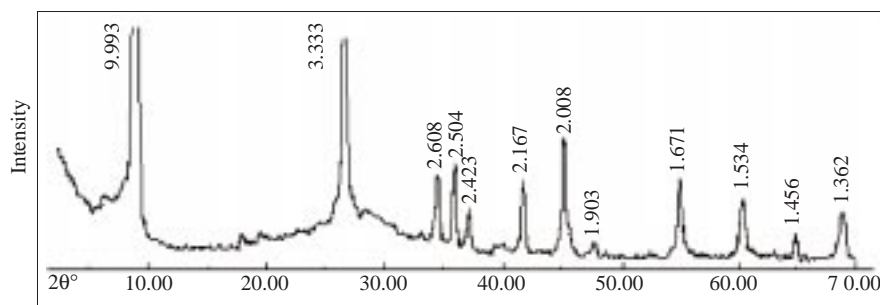


Figure 1. XRD pattern of Karakoç phlogopite ore

TGA and DTA analyses were carried out between 25 and 1100°C on the raw material using a Rigaku Model 2.22E2 analyser for determining the dehydration behaviour and any possible phase change related to thermal behaviour, and all the endothermic effects were related to loss of water (Table 2).

Table 2. Dehydration and dehydroxylation characteristics of the sample

Type of water	Temperature Range (°C)	Amount (%)
Free water	36.6 - 77.1	1.30
Crystal water	149.5 - 178.3	1.20
Dehydroxylation	659.6 - 699.5	1.80
	Total	4.30

Considering the analysis results, the mineralogical composition of the sample was determined to be $(K_{1.49} Na_{0.11} Ca_{0.26}) (Mg_{3.71} Fe(II)_{0.81} Al_{2.83} Fe(III)_{0.52}) (Si_{5.31} Ti_{0.18}) (O_{19.18} (OH)_{4.20} F_{0.61})$

In the experimental work, square-shaped samples with an average size of 2 cm and a thickness of 0.2 cm were used. The samples were placed in a 150 cm³ tube that was inserted in a water bath the temperature of which was maintained within $\pm 0.5^\circ\text{C}$ with a thermostatic control and 100 ml of hydrogen peroxide solution was added to the tube. After completion of the reaction, the swelling observed on the samples (thickness) was measured. The density and bulk density of the exfoliated samples were also determined.

Results

In the pre-tests performed, H₂SO₄, HCl, HNO₃, H₃PO₄ and H₂O₂ solutions at varying concentrations were used for chemical exfoliation and the only positive response was obtained with H₂O₂ solution. In addition, hydrogen peroxide concentration, temperature and reaction time were determined to be the main parameters that directly affect the chemical exfoliation characteristics of the sample, with solid/liquid ratio being of minor importance.

A series of swelling tests was performed to determine the effects of hydrogen peroxide concentration (1-30 wt.%) and reaction time (1-30 hours). The exfoliation characteristics of the sample related to hydrogen peroxide concentration and reaction time, in terms of increase in thickness and decrease in bulk density, are given in Figure 2.

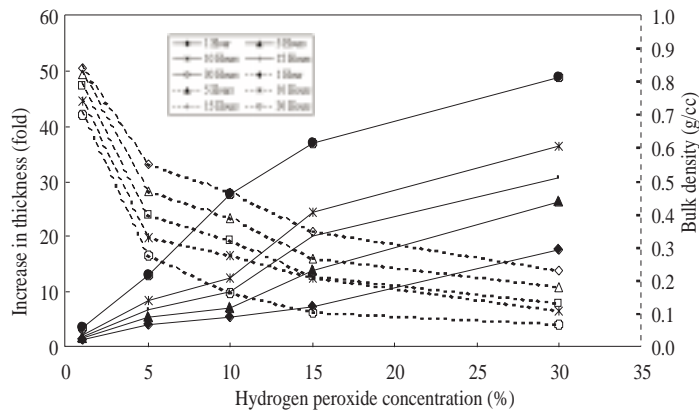


Figure 2. Change in exfoliation with hydrogen peroxide concentration and time

As the industrially accepted minimum value for swelling is 15-fold, this value was reached in hydrogen peroxide concentrations of 27%, 21%, 15%, 12% and 5.5% for reaction times of 1, 5, 10, 15, and 30 hours, respectively. A maximum swelling of 49-fold was obtained with 30% hydrogen peroxide solution and the swelling values reached were 17.6-, 26.2-, 30.7-, 36.5 and 49-fold for reaction times of 1, 5, 10, 15 and 30 hours, respectively.

Figures 3 to 7 give the results of the swelling tests performed between 40°C and 60°C and reaction times between 10 minutes and 30 hours.

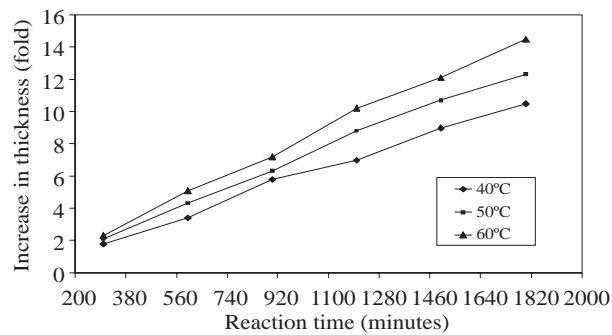


Figure 3. Change in exfoliation with temperature in 1% H₂O₂ solution

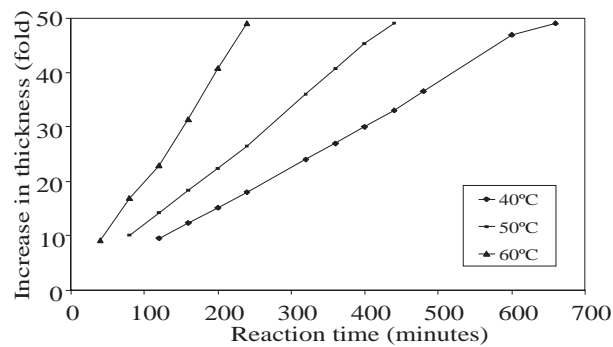


Figure 4. Change in exfoliation with temperature in 5% H₂O₂ solution

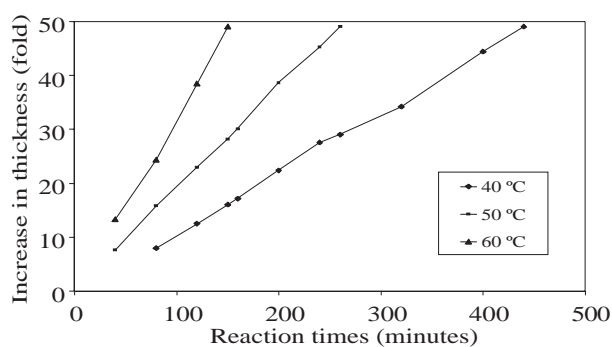


Figure 5. Change in exfoliation with temperature in 10% H₂O₂ solution

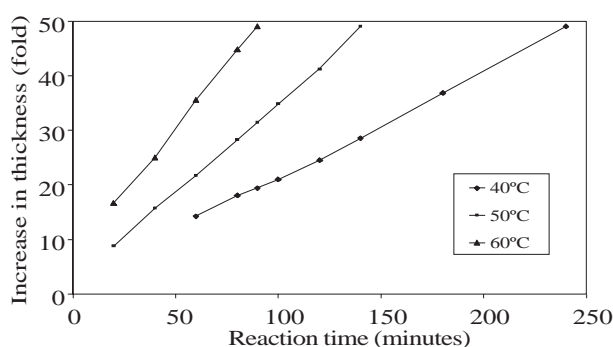


Figure 6. Change in exfoliation with temperature in 20% H₂O₂ solution

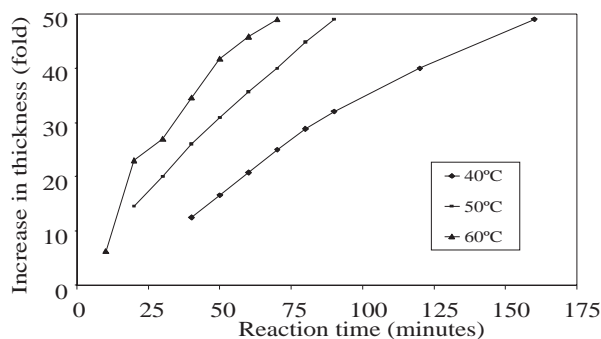


Figure 7. Change in exfoliation with temperature in 30% H₂O₂ solution

Figures 3 to 7 show that the increase in temperature from 40°C to 60°C increases the swelling property and shortens the reaction time substantially. Although 49-fold swelling is obtained at 40°C for a reaction time of 660 minutes in a 5% hydrogen peroxide concentration, the same value is reached at 60°C for a reaction time of only 240 minutes (Figure 4). Temperature seems to have a strong effect on exfoliation and lowers the reaction time, but, above 60°C, the material starts to decompose into fine particles with complete loss of its characteristics above 80°C.

Experiments were performed at 25°C using 30% hydrogen peroxide solution for a reaction time of 30 hours with a solid/liquid ratio between 1/40 and 1/1 and the results are presented in Table 3. The results show that the solid/liquid ratio is not an important parameter for swelling, and wetting of particles with hydrogen peroxide solution is the only requirement.

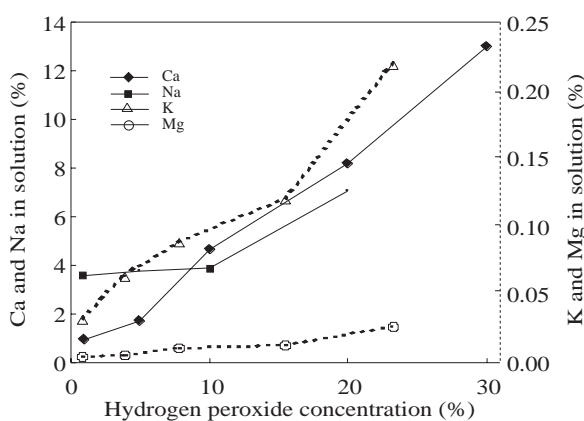
Table 3. Effect of solid/liquid ratio on exfoliation

Solid/liquid ratio	Increase in bulk density (fold)
1/40	49
1/20	48
1/10	48
1/8	49
1/6	47
1/4	49
1/2	49
1/1	49

Swelling tests were carried out in hydrogen peroxide concentrations between 1 and 30% with a solid/liquid ratio of 1/40 for 30 hours to determine the changes in the solid and the liquid phases. For this purpose, changes in the pH values of the solutions were determined (Table 4) and also sodium, potassium, calcium, magnesium and iron analyses were performed in these solutions (Figure 8) using atomic absorption spectrometry.

Table 4. Change in pH in solutions during exfoliation

H ₂ O ₂ concentration (%)	pH before exfoliation	pH after exfoliation
1	4.68	7.80
5	4.23	6.85
10	3.74	6.06
20	3.42	5.52
30	3.36	5.42


Figure 8. Change in dissolution of Na, Ca, K and Mg with H₂O₂ concentration

The amounts of sodium, potassium, calcium and magnesium in solution increases with increases in hydrogen peroxide concentration, the behaviour being Na>Ca>K>Mg for hydrogen peroxide concentrations of 1-5%. However, this behaviour changes to Ca>Na>K>Mg for hydrogen peroxide concentrations above 5%. No iron and aluminium were detected in the solutions.

The XRD pattern of the material after treatment with 30% hydrogen peroxide solution for 70 minutes at 60°C gives the same pattern as in Figure 1, showing that the swelling causes no phase changes in the material. The only change was that the blackish colour of the original material is observed to change into metallic silvery after swelling.

Mathematical Evaluation of the Experimental Results

Considering the non-systematic behaviour of exfoliation with temperature, a mathematical evaluation was performed taking hydrogen peroxide concentration and reaction time as independent variables and the exfoliation ratio as the dependent variable.

For the estimation of the aim function¹⁷, independent values should change systematically. As the solution of the optimisation problem is based on the change in exfoliation ratio with time for a known concentration of hydrogen peroxide, the exfoliation function can be expressed as f_1, f_2, f_3 etc. These functions can be obtained by regression analysis using the least square method¹⁸. This type of interpretation shows that there is a linear relationship between exfoliation ratio and reaction time as given by Eq. (1).

$$G_o = at + b \quad (1)$$

In this equation, G_o is exfoliation ratio (fold), t is reaction time (hours), and a and b are parametric coefficients. The changes in parametric constants with hydrogen peroxide concentration were determined using a non-linear regression method¹³ as given by Eq. (2) and Eq. (3) and the squares of the regression constants (R^2) for these equations were determined to be 0.9791 and 0.9828, respectively.

$$a = -0.0018[H_2O_2]^2 + 0.0893[H_2O_2] - 0.0245 \quad (2)$$

$$b = 0.0226[H_2O_2]^2 - 0.1131[H_2O_2] + 2.2235 \quad (3)$$

Considering the above-mentioned approach, the change in the exfoliation ratio with hydrogen peroxide concentration and reaction time can be expressed by Eq. (4).

$$G_o = (-0.0018[H_2O_2]^2 + 0.0893[H_2O_2] - 0.0245)t + (0.0226[H_2O_2]^2 - 0.1131[H_2O_2] + 2.2235) \quad (4)$$

Comparative results of the estimated values for G_o determined ($G_{o(est)}$) using Eq.(4) and those determined experimentally ($G_{o(exp)}$) are given in Table 5.

Table 5. Change in calculated and experimental values of exfoliation ratio with hydrogen peroxide concentration and reaction time

Reaction time (hours)	Hydrogen peroxide concentration (%)									
	1		5		10		20		30	
	$G_{o(exp)}$	$G_{o(est)}$	$G_{o(exp)}$	$G_{o(est)}$	$G_{o(exp)}$	$G_{o(est)}$	$G_{o(exp)}$	$G_{o(est)}$	$G_{o(exp)}$	$G_{o(est)}$
1	1.3	2.2	4.0	2.6	5.5	4.0	7.2	10.0	17.6	20.2
5	1.5	2.5	5.4	4.1	7.0	6.8	13.9	14.2	26.2	24.3
10	2.0	2.8	6.8	6.0	10.0	10.2	20.0	19.4	30.7	29.5
15	2.3	3.1	8.5	7.9	12.5	13.7	24.5	24.6	36.4	34.7
30	3.5	4.0	13.0	13.5	27.6	24.0	36.8	40.3	49.0	50.2

Discussion

Maximum thermal expansion ratios for Karakoç phlogopite ore were determined to be 13.2 for direct contact with flame and 18 for electrical furnace conditions respectively⁹. The results of this study show that the same material can better be exfoliated chemically with hydrogen peroxide solution and a maximum swelling of 49-fold in thickness can be achieved without any phase changes.

The mechanism of thermal exfoliation is explained by the conversion of contained water to steam upon rapid heating, which causes the layers to separate. The mechanism of chemical exfoliation is different and can be explained in terms of the decomposition of hydrogen peroxide upon reaction with the water molecules¹² in phlogopite. Thus, the hydrogen peroxide molecules that penetrated into the interlayer spaces of phlogopite upon exchanging with water molecules decompose with the evolution of atomic oxygen. The evolved oxygen atoms, having combined with oxygen molecules, separate the silicate layers from each other. Oxygen atoms also attack the hydroxide groups of the silicate structure causing vigorous release of the hydroxides from the silicate structure, which is verified by an increase in pH (Table 4) in the solution phase. These types of interactions disrupt the electrostatic equilibrium between the layers and cause appreciable dissolution of the interlayer cations (Ca, Na, and K) from the structure, causing separation of the layers.

Although no iron was detected in the solutions, iron present in the interlayers may cause catalytic decomposition of H₂O₂ in accordance with the fact that the decomposition of H₂O₂ is catalysed¹⁹ by traces of Fe⁺³.

The increase in pH values of H₂O₂ solutions is mainly caused by release of hydroxyls from the structure and the dissolved oxygen resulting from the decomposition of H₂O₂. Due to the high fluoride content of the sample, partial release of fluoride ions (salt of weak acid) into the solution phase also contributes to the increase in the pH values, which was verified by comparing the pH values of the hydrogen peroxide and sodium fluoride containing hydrogen peroxide solutions.

The results were evaluated mathematically and a regression model was proposed to calculate the swelling ratio for any hydrogen peroxide concentration and reaction time at 25°C that can be used to produce exfoliated material with the desired physical properties.

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