Enrichment of Magnesite and Usage to Obtain Magnesium Fluoride

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Abstract: Magnesium is the sixth most abundant element, constituting 2% of the total mass of the earth's crust. It is a metal that exists only in chemical compounds, and generally in carbonate and oxide forms. The most important mineral forms are magnesite ($MgCO_3$), dolomite ($MgCO_3.CaCO_3$), and carnallite ($KCl.MgCl_2$-$6H_2O$). Magnesium metal, which is obtained from different sources by various methods, has an important place in the industry. There are approximately 16 billion tons of dolomite and 110 million tons of magnesite reserves in Turkey. The aim of this study is to investigate the use of idle magnesium clay raw material (in Eskişehir) for the production of magnesium fluoride and thus to propose a chemical process for the relevant raw material to the industry. For the experiments, a 10 kg sample was taken and after the whole was ground to 75 µm size, XRF, XRD, and DTA analyzes were performed. As a result of XRF analysis, it contains 44.28% MgO. For XRD analysis, it was determined that it is magnesite with $MgCO_3$ structure, and that it also has dolomite and chlorite group mineral structures. MgF_2 was created by employing HF from the relevant raw material as a result of the study, and it was discovered that the efficiency was higher in the raw magnesite experiments.

Keywords: Enrichment of Magnesite, Calcination of Magnesite, Magnesite.

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INTRODUCTION

Magnesium is the third most commonly used structural metal after aluminum and iron. It has an important place in today's technology, both as a metal and as a compound. Due to its abundance, light weight, and easy alloying, magnesium metal has great potential for components in the automotive, aerospace, and military industries. While magnesium is expected to be more popular due to its important mechanical properties, it seems to be in the background due to the difficulties in obtaining it. There are six sources of raw materials for the production of magnesium: magnesite, dolomite, bischofite, carnallite, serpentine, and sea water. These sources differ in magnesium content, production methods, and their origin. Dolomite [$CaMg(CO_3)_2$] and magnesite [$Mg(CO_3)$] are the most widely used Mg metal ores. Magnesite has more Mg content than dolomite, but large magnesite deposits are geographically limited. Magnesite mineral theoretically contains 52.3% CO_2 and 47.7% MgO and it is the primary source for the production of magnesium and its compounds. On the other hand, this mineral almost never occurs pure enough to be used directly in any significant deposit. Its ores contain a variety of gangue minerals, mostly other carbonates, silicates, and oxides (1). World magnesite resources are estimated at over 12 billion tons and are primarily located in China, Russia, North Korea, Australia, Slovakia, Brazil, Turkey, India, and Canada (2).

Although there is a considerable amount of dolomite and magnesite reserves (3;4), magnesium metal was not being produced in Turkey (5) before 2016. Magnesite is generally used instead of its natural state by converting it to MgO by calcining. The calcination of magnesite and the degree of reactivity of the obtained product are technologically important (6). Magnesite that is to be used in the production of metallic magnesium must also be purified by calcining. Thus, the material is enriched in magnesium. Magnesite has a porous structure as it loses CO_2 and H_2O during the calcination process, and the specific gravity of calcined magnesite is between 1.3 and 1.9 g/cm^3 (1). Magnesite and magnesite products in the world are evaluated and priced in terms of chemical content, CaO/SiO_2 ratio, bulk density, and crystal structure. Ores containing more than 93.5% MgO on a calcined basis are considered valuable raw materials.

The methods used in the enrichment of magnesite ore can be listed as follows; manual sorting and optical sorting, enrichment with size reduction, heavy medium enrichment, enrichment by electrostatic and magnetic separation, enrichment by hydration, enrichment by calcination, and enrichment by flotation and agglomeration.

The studies were performed using the facilities of Esan Eczacıbaşı Industrial Raw Materials Ind. and Trade Inc.

MATERIALS AND METHODS

Chemicals and Instruments

The following chemical substances of analytical reagent grade were purchased from the corresponding sources. Hydrochloric acid (HCl) and hydrofluoric acid (HF): Merck (Darmstadt, Germany); Lithium tetraborate ($Li_2B_4O_7$), hydroxylamine hydrochloride ($NH_2OH.HCl$), and ammonium fluoride (NH_4F): Sigma-Aldrich (Taufkirchen, Germany).

Chemical analysis of the sample was performed with X-Ray Fluorescence (XRF) Spectrometer (Panalytical Axios Model) and structural analysis was performed with X-Ray Diffraction (XRD) instrument (Panalytical X-Pert Pro Model). A differential Thermal Analyzer (DTA) (Orton ST 746 Model) was used for thermal analysis of the sample. Other laboratory equipment used in this study is jaw crusher with tungsten-carbide rim (Retsch BB 100 model), sample divider (20 compartments) (Retsch), tungsten-carbide ring grinder (Retsch-RS 200), precision balance (Mettler Toledo AB 204S model), fan oven (Electro-Mag), ash furnace (max temperature 1200 °C) (Protherm PLF 125 model), grain size device (Malvern Mastersizer 2000 model).

Sample Preparation and Characterization

In this study, a clay containing magnesite, which was obtained from the magnesite quarry of Esan Eczacıbaşı company located in the Alpu region of Eskişehir (Turkey), was used as a magnesium source. The entire clay sample was laid on the sample tray and dried in a 105 ⌖C fan oven for 15 hours. After the sample was dried, it was reduced to 4 mm size by passing it through a tungsten-carbide jaw crusher. All the comminuted material was passed through the sample crusher 3 times and then reassembled. Thus, homogeneous mixing of the crushed material was ensured. According to the information obtained from previous studies, the reaction rate increases as the particle size decreases. For this reason, the entire material was ground to a 75 µm size with a tungsten-carbide grinder at 1200 rpm for 1 min. The entire ground sample was passed through the sample grinder 3 more times and then recombined. Thus, homogeneous mixing of the ground material was ensured. After the final milling, a representative sample of 500 g was taken and used in the experiments.

Loss on ignition of sample

The sample in the glass weighing bottle was dried in an oven at 105 °C for 2 hours. The sample taken out of the oven was taken into a desiccator, cooled to room temperature, and 1 g was weighed with an accuracy of 0.1 mg and placed in a porcelain crucible, which reached a constant weight at 1000 °C. The sample in the porcelain crucible was heated at 1000 °C in an ash furnace for 1 hour. The crucible removed from the ash furnace was transferred to a desiccator, cooled to room temperature, and weighed.

Chemical Analysis with XRF

The sample in the glass weighing bottle was dried in an oven at 105 °C for 2 hours, and after being taken out of the oven, it was taken to the desiccator and cooled to room temperature. 1 g of weight was taken from this sample and after adding 5 g lithium tetraborate, which was kept at 400 ÉC for 5 hours, the mixture was ground in an agate mortar. The ground mixture was placed in a platinum crucible, and after the lid was closed, it was put into the ash furnace at 1150 °C. At the end of 20 min, the crucible was taken out of the furnace, ammonium iodate was added, and the lid was closed and put back into the furnace at the same temperature. Five minutes later, the crucible was taken off and the content of the crucible was transferred to the lid. The material in the lid was put back into the ashing furnace at 1150 °C and kept at this temperature for 5 min. After 5 min, the lid was taken out and left to cool at room temperature. After cooling, the glassy material on the cover was taken and loaded into the XRF device for analysis under calibration.

Thermal Analysis

The decomposition characteristics of the sample were determined by simultaneous DTA (Differential Thermal Analysis)/TGA (Thermogravimetric Analysis) test using Orton ST 746 instrument. The experimental conditions were intinuous heating from room temperature up to 1200ºC at a heating rate of 10ºC /min, N_2 – gas dynamic atmosphere, and using Alumina as a reference material. The data obtained by thermal analysis is reaction peak temperature and weight loss in the temperature ranges.

Calcination of Sample

Magnesite that is to be used in the production of metallic magnesium must be purified by calcining. Thus, the material will have an enriched magnesium content. It was studied at different temperatures (900-1200 °C) and times (3-5 h) to determine the optimum calcination conditions. Chemical, XRD, and DTA analyses of the products obtained as a result of calcination were performed.

Obtaining Magnesium Fluoride from Magnesite

It was aimed to obtain magnesium fluoride from raw and calcined magnesite material by using HF and NH_4F solutions. As a result of the XRD analysis results made on the samples obtained, it was determined that there was no high rate of MgF_2 (Sellaite) formation as a result of the experiments performed with NH_4F and even high levels of impurities were formed due to the NH_4F. For this reason, MgF_2 production experiments were carried out using concentrated HF in a polytetrafluoroethylene (PTFE) beaker and the most suitable conditions were determined. In this process, experiments were conducted using different concentrations of HF, and two different experimental methods, called "Drying" and "Filtration", were applied. For this purpose, 10 different experimental sets were prepared. XRD analysis and chemical analysis were applied to the products obtained as a result of the trials. The experimental sets applied using different reagent concentrations and different quantities of raw magnesite and calcined magnesite are summarized in Table 1.

In the drying process, the weighed main material was taken into a PTFE beaker, a certain amount of distilled water and concentrated HF was added to it and mixed for 30 minutes. The mixture was evaporated to dryness on the heating plate, and the residues in the beaker were analyzed.
In the filtration process, the weighed main material was taken into a PTFE beaker, and a certain amount of distilled water and concentrated HF was added to it. The contents of the beaker were filtered through a blue-band filter paper after stirring for 30 minutes. The residue on the filter paper was dried in an oven at 105 °C.

Table 1: The experiment sets prepared to obtain MgF_2.

Experiment No.	Main Material	Material Quantity (g)	Reagent Volume (mL)	Water Volume (mL)	Method Used
1	$MgCO_3$	10.415	20	20	Drying
2	$MgCO_3$	10.835	20	20	Filtration
3	$MgCO_3$	10.021	30	20	Drying
4	$MgCO_3$	10.090	30	20	Filtration
5	$MgCO_3$	10.053	30	-	Drying
6	MgO	10.060	20	20	Drying
7	MgO	10.036	20	20	Filtration
8	MgO	10.135	30	20	Drying
9	MgO	10.017	30	20	Filtration
10	MgO	10.089	30	-	Drying

RESULTS AND DISCUSSION

Determination of Loss on Ignition and Chemical Analysis

As a result of the analysis performed in the calibrated program by the XRF instrument, it was determined that there was 44.28% MgO in the material. The chemical structure of original sample and also loss on ignition value is given in the Table 2. When the same sample was analyzed in a semi-quantitative program with the XRF instrument, it was observed that it contained trace amounts of chromium (0.024% Cr_2O_3), nickel (0.0182% NiO), copper (0.0452% CuO), strontium (0.0277% SrO) and barium (0.0545% BaO).

Table 2: Chemical analysis results for the clay containing magnesite.

Sample	**Content (mass %)**								
	LOI*	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**TiO_2**	**CaO**	**MgO**	**Na_2O**	**K_2O**
Clay containing magnesite	44.90	6.90	0.96	0.72	0.10	2.02	44.28	0.01	0.09

*LOI : Loss on ignition

Structural Analysis

In the XRD spectra, peaks of clay minerals can be seen in areas where °2 Theta is less than 10. When the XRD spectrum of our sample (Fig. 1) was examined, it was thought that it contained chlorite or montmorillonite according to the distance between the layers. The sample was treated with ethylene glycol to examine whether the peak thought to be chlorite was actually a montmorillonite derivative. As it is known, if a montmorillonite-derived structure is found in the sample, it is expected that the peak, which was around 5 in the XRD analysis performed after the treatment with ethylene glycol, will shift to around 17. However, as a result of the analysis after this process, it was seen that there was no shift in the relevant peak (Fig. 2), and it was thought that this peak belonged to the chlorite derivative.

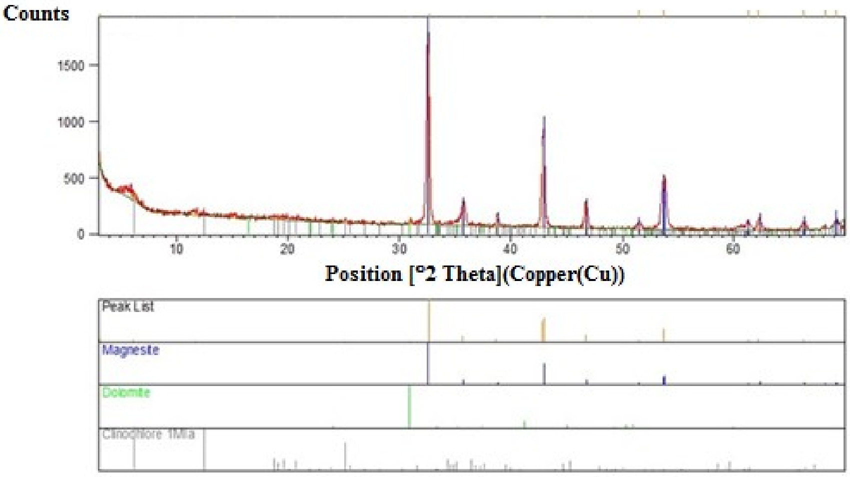

Figure 1: XRD spectra of original sample.

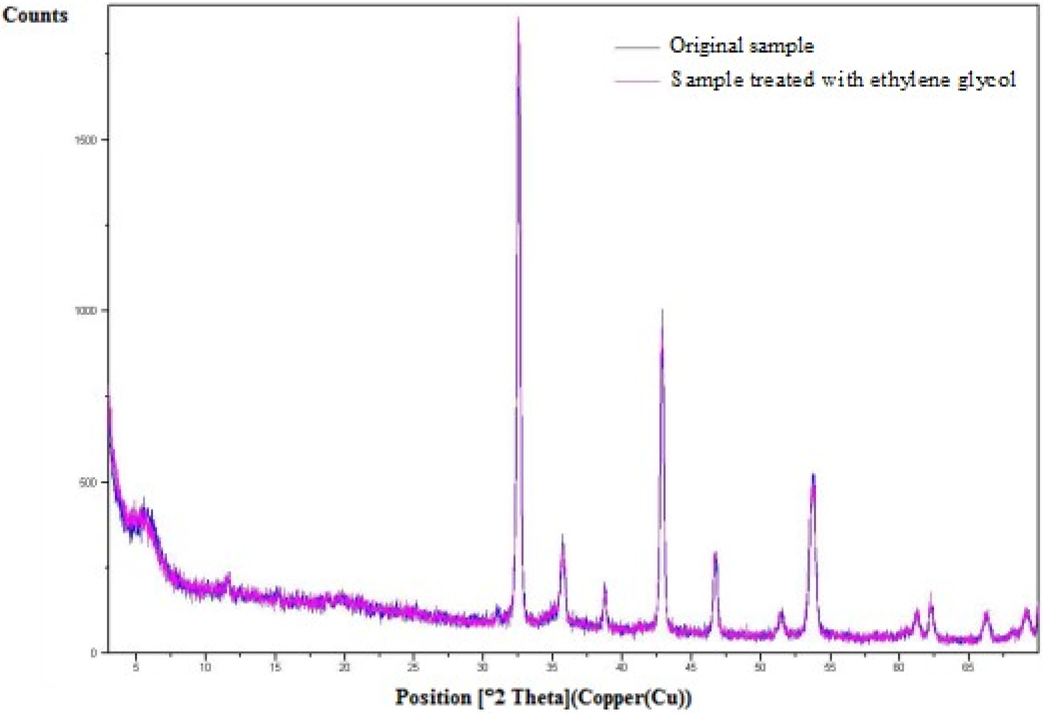

Figure 2: XRD spectra of the original and ethylene glycol treated samples.

Thermal Analysis

The typical DTA/TGA curve of the sample is presented in Fig. 3. It is seen that there is a weight loss in the range of 500-650 °C in the TGA curve, and endothermic peaks occur in the range of 500-700 °C and 800-1000 °C in the DTA curve. The weight loss in the TGA curve indicates the conversion of $MgCO_3$ to MgO as a result of CO_2 removal. This decomposition is also the cause of the endothermic peak in the DTA curve in the same temperature range. It can be said that the second endothermic peak is caused by the decomposition of $CaCO_3$ in the dolomite structure by releasing CO_2. The TG thermogram shows a loss of mass of approximately 45%, which is consistent with the determined loos on ignition value (Table 2).

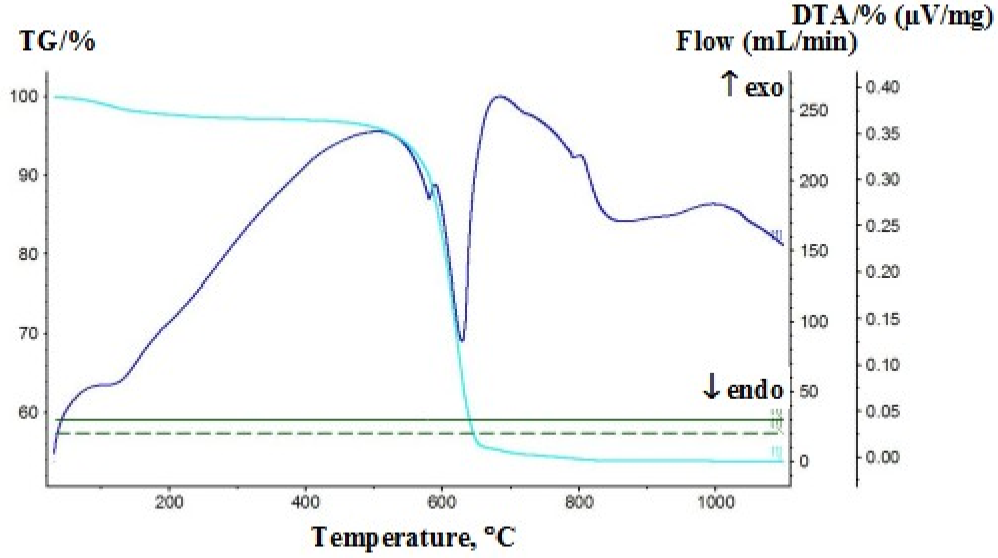

Figure 3: DTA/TGA analysis curves of sample.

Calcination of Sample

In the calcination method, hydrates and carbonates in magnesite are broken down by using high heat. The raw material was subjected to various calcination processes. The temperature and time parameters of the calcination studies are given in Table 3.

Table 3: Parameters for Calcination.

Sample	Temperature (°C)	Time (Hour)
1	900	3
2	1000	3
3	1000	4
4	1100	3
5	1200	3
6	1200	4
7	1200	5

Chemical analysis, XRD analysis, DTA, and particle size analyses of the products obtained as a result of calcination were performed. It was determined that as time and temperature increased in the calcination process, the sintering increased and the color of the sample darkened.

Table 4: Chemical analysis results for the calcinated samples.

No	Sample	LOI (%)	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	TiO_2 (%)	CaO (%)	MgO (%)	Na_2O (%)	K_2O (%)
4877-206646	Original	44,90	6,90	0,96	0,72	0,10	2,02	44,28	0,01	0,09
4878-206647	900 °C- 3 hours calcination	0,90	19,30	1,49	1,02	0,15	3,26	73,70	0,01	0,13
4879-206648	1000 °C- 3 hours calcination	0,37	18,15	1,48	1,02	0,15	3,30	75,37	0,01	0,13
4880-206649	1000 °C- 4 hours calcination	0,27	19,05	1,50	1,04	0,14	3,28	74,59	0,01	0,08
4881-206650	1100 °C- 3 hours calcination	0,17	18,35	1,49	1,03	0,15	3,32	75,39	0,01	0,05
4882-206651	1200 °C- 3 hours calcination	0,18	18,50	1,51	1,04	0,15	3,32	75,27	0,01	0,01
4883-206652	1200 °C- 4 hours calcination	0,10	17,75	1,58	1,05	0,15	3,37	75,95	0,01	0,01
4884-206652	1200 °C- 5 hours calcination	0,20	19,00	1,55	1,03	0,16	3,28	74,74	0,01	0,01

When the chemical analysis results of the calcined samples were evaluated, it was decided that 3 hours at 1000 °C was appropriate due to the MgO content of 75.37%. In the same application, the CaO content of the sample was determined as 3.30%.

The loss on ignition analysis gives us information about whether there is a volatile compound in the material. When the results of the chemical analysis were examined, it was determined that the calcination process performed at 900 °C for 3 hours (Ignition Loss of 0.90%) was not sufficient for the completion of the calcination. It has been determined that the presence of volatile compounds (CO_2 from $MgCO_3$) still continues in the material and the calcination process has not been completed. However, when the calcination study was performed at 1000 °C for 3 hours and the others were examined, it was seen that there was no significant difference between the chemical analyses.

No	Conditions	Sample No	LOI%
1	900 °C, 3h	4878-206647	0.9
2	1000 °C, 3h	4879-206648	0.37
3	1000 °C, 4h	4880-206649	0.27
4	1100 °C, 3h	4881-206650	0.17
5	1200 °C, 3h	4882-206651	0.18
6	1200 °C, 4h	4883-200652	0.1
7	1200 °C, 5h	4884-206653	0.2

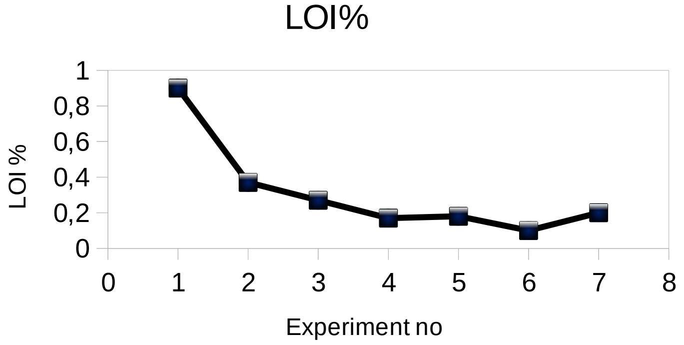

Figure 4: LOI% Values of Calcinated Samples.

It was also observed that different phase formations begin to occur in samples where calcination conditions exceed 1000°C and 3 hours. Phase formation is undesirable because it causes the structure to become more stable and the chemical processes to be applied become more difficult. In this case, 1000 °C temperature and 3 hours are considered suitable as the optimum calcination parameter.

In order to determine whether there are other trace elements in the calcined sample, the sample was analyzed in a semi-quantitative program with the XRF instrument. As a result of the analysis, it was determined that there were traces of chromium, nickel, copper, and strontium in the sample, among other elements.

Obtaining Magnesium Fluoride from Magnesite

In XRD analysis, how pure the material is determined by the height and sharpness of the peak density of the relevant substance. When the XRD spectra of MgF_2 products prepared with the experimental sets given above (Table 1) were examined, two results were obtained:

(i) The yields of the experiments using $MgCO_3$ as the input material are higher than the experiments using MgO.

(ii) When the main material is the same, the peak intensity of the products obtained by the drying method is higher than the products obtained by the filtration method.

Table 3 shows the peak intensity values derived from XRD examination of the products acquired as a result of the applications listed in Table 1.

Table 5: Peak intensity values of sellaite products obtained by using raw and calcined magnesite.

Experiment No.	Main Material	Method Used	Sellaite peak intensity
1	$MgCO_3$	Drying	384
2	$MgCO_3$	Filtration	379
3	$MgCO_3$	Drying	332
4	$MgCO_3$	Filtration	285
5	$MgCO_3$	Drying	319
6	MgO	Drying	225
7	MgO	Filtration	133
8	MgO	Drying	242
9	MgO	Filtration	106
10	MgO	Drying	210

All the peaks seen in the XRD spectrum (Fig. 5) of the product obtained as a result of experiment No. 1 in Table 1 are the main and side peaks of the sellaite mineral (MgF_2) expected to be obtained. There is no impurity. Figure 6 also shows the XRD spectrum of the product (experiment No. 2) with the second highest peak intensity, which was obtained as a result of the filtration process.

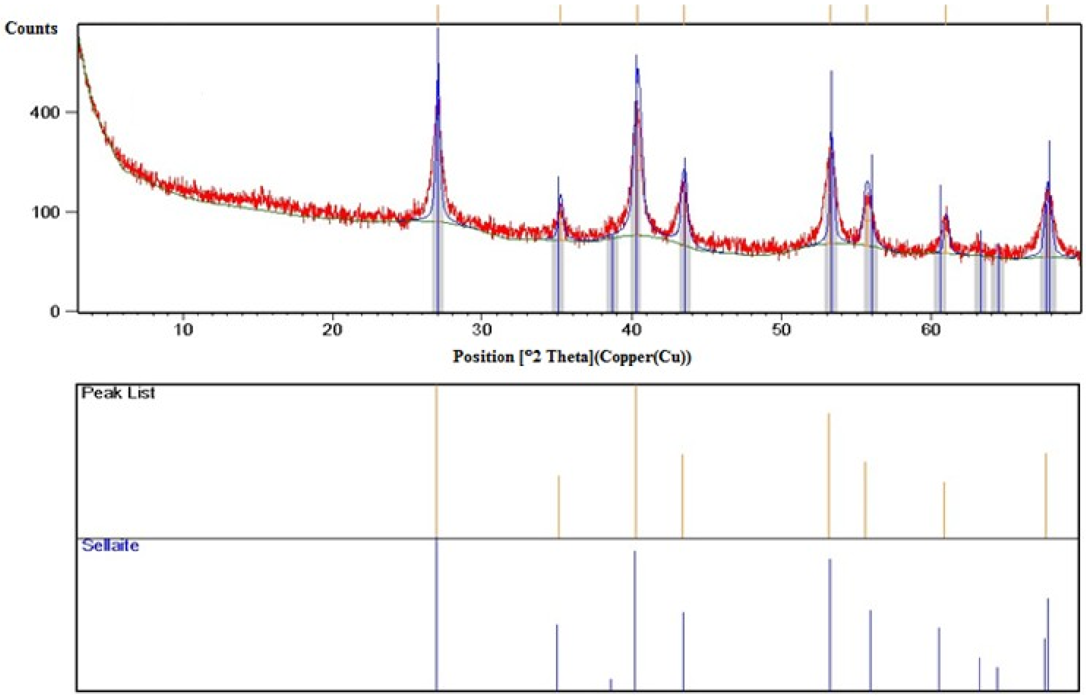

Figure 5: XRD spectrum of sellaite obtained experiment no 1.

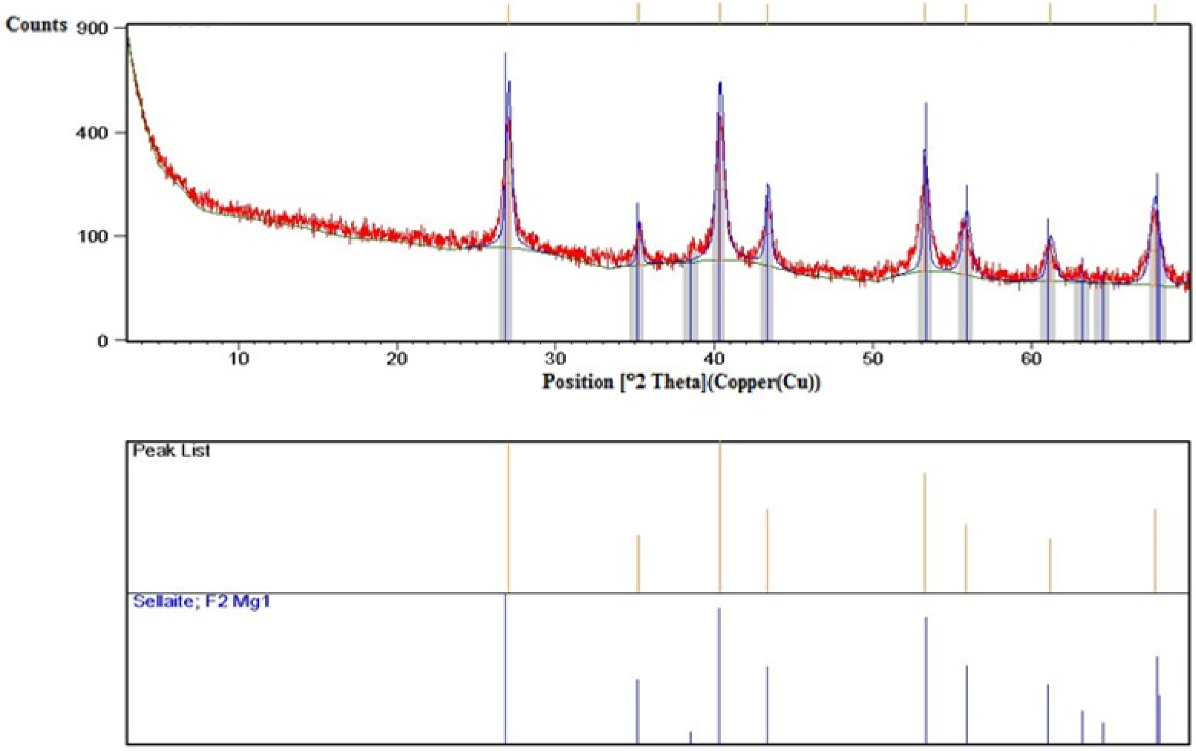

Figure 6: XRD spectrum of sellaite obtained experiment no 2.

The sellaite formed by employing raw magnesite as the main material and the drying technique has the maximum peak intensity value, as shown by the XRD spectra and data in Table 5.

CONCLUSION

The obtained results of experiments employing HF and raw magnesite or calcined magnesite to obtain MGF_2 revealed that raw magnesite had a better productivity than calcined magnesite. As a result, in production processes that do not need heat processing, it is not necessary to calcinate the material.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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