

Preparation of nano-ammoniated ammonium carnallite from using industrial effluents and saline

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ABSTRACT

Precipitation of magnesium hydroxide from magnesium chloride (Saline) followed by calcination, is important method for production of magnesium oxide and magnesium metal. The chemical purity of magnesium produced is dependent on composition of saline and industrial effluents. To precipitate and recover magnesium hydroxide from solution containing magnesium salts, a strong base is needed (like ammonia). Anhydrous magnesium chloride is used in magnesium metal production such as in production of metallic compounds and to enhance the productivity of olefin polymers such as cordierite, forsterite, enstatite spinel which are used in various industries. In this work the high pH (10.5 – 14) in chemical fertilizer company effluents rich with (ammonium nitrate and ammonium sulfate) and a mixed streams effluent were used to prepare magnesium chloride, anhydrous magnesium chloride and magnesium oxide. The (XRD) x-rays diffraction and (FT-IR) Infra- red and (EDS) scan electron microscope analysis (TEM) high resolution surface analysis shows the extent of purity, crystal size and magnesium carnallite yield. The products were aged at 50 °C for 30 min and calcined at 500 °C to produce magnesium oxide. The ammonium chloride products were reacted with ammonium carnallite which is then calcined at 700 °C to produce ammoniated ammonium carnallite. The carnallite was characterized by TEM, TGA and EDS. The product is used in magnesium metal preparation.

Keywords: saline, industrial effluents, magnesium oxide, magnesium carnallite.

INTRODUCTION

Magnesium is mainly present as Mg^{2+} in water solutions, but also as $Mg\ OH$ and MgO . In seawater it can also be found as $MgSO_4$. Water solubility of magnesium hydroxide is 12 mg/L. Other magnesium compounds are clearly soluble; for example magnesium carbonate (600mg/L). Magnesium sulphate adds a bitter flavor and has a water solubility of 309 g/L at 10 °C.

A Large number minerals contains magnesium, for example dolomite (calcium magnesium carbonate $Ca\ Mg\ (CO_3)_2$) and magnesite (magnesium carbonate; $MgCO_3$) Magnesium is washed from rocks and subsequently ends up in water. Magnesium has many different purposes and consequently may end up in water in many different chemical industries add magnesium to plastics and other materials as a fire protection measure or filler [1]. It also ends up in the environment from fertilizer application and from cattle feed. Magnesium sulphate is applied in beer breweries, and magnesium hydroxide is applied as a flocculent in water treatment plants. Magnesium is also mild laxative [2]. During World War II magnesium was applied in fire bombs to cause major fires in cities. The development of these bombs introduced a method to extract magnesium from sea water.

Magnesium is a dietary mineral for any organism but insects. It is a central atom of the chlorophyll molecule, and is therefore a requirement for plant photosynthesis. Not only magnesium cannot be found in sea water, but also in rivers and ram water causing also naturally spread throughout the environment. Three magnesium isotopes occur

naturally, which are all stable and consequently not radioactive also eight instable isotopes. The human body contains about 25 g of magnesium, of which 60% is present in bones and 40% present in muscles and other tissue. Magnesium is an ingredient of many enzymes. There are no known cases of magnesium poisoning. Magnesium is the lightest of all the commonly used metals. It is one of the most abundant element in the earth's surface, amounting to about 2.5% of its composition. Most pyre metals, including magnesium are too soft for structural use. However strength properties to those of many aluminum alloys are obtained by alloying magnesium with other metals, and, in some cases, by heat treating [3] and [4]. Magnesium is used as an alloy in other metals most obtain aluminum. Magnesium alloys are applied in cars and planes. Magnesium melts at about 650°C, its alloys, used in forum dry work, represent approximately one-third of total worldwide demand for the metal [5]. Magnesium is also used in desulfurization with other metals, specifically steel. Sulfur has a deleterious effect on the properties of steel, and the increasing demands of the market have forced the steel industry to provide products with lower sulfur content. Magnesium has a high affinity for sulfur, and when injected into molten iron or steel, it will reduce the sulfur content dramatically. One of the fastest growing structural markets for magnesium is die castings, automotive die casting (cylinder head covers, wheel,..etc.) and non-automotive die cast parts ranging from computer components, luggage frames, bicycle frames, fishing reels ,video and digital camera housings. The expectation of increased utilization of magnesium in automotive applications has stimulated renewed commercial interest in this metal [6]. Two principle production processes are in use today. Electrolysis of magnesium chloride and thermal reduction of magnesium oxide. This study magnesium chloride and magnesium oxide were prepared. Magnesium carnallite was prepared from magnesium chloride and products were characterized by XRD, Thermal analysis TGA, EDS, Transmission electron High Resolution TEM, and FT-IR spectroscopy.

MATERIALS AND METHODS

2.1 Raw materials

The composition of saline from Alexandria salt company as the Mg^{2+} concentration is listed in Table (1). The composition of waste effluents rich with ammonia from chemical and fertilizer company is listed in Table (2).

Ammonia water 25%, solid ammonium chloride, sodium sulphate and absolute ethanol used as analytical grade materials. 10% of (mass fraction) complete solution of gelation, lauryl sodium sulphate was used as dispersant agent.

Table (1) composition of main elements in liquid Bittern in g/L

Li	Ca	Mg	Na	K	Br	B	Cl	SO ₄	CO ₃ ²⁺	I
0.0031	1.6	73.8	21.7	9.8	12	0.07	218	3.2	0.5	0.005

Table (2) composition of waste effluents rich with ammonia from Chemical and Fertilizer Company

Sample No	pH value	PO ₄ mg/L	Cond. mS/cm	TDS mg/L	Ca mg/L	NH ₄ mg/L	SO ₄ mg/L	Mg mg/L	COD mg/L
1	9.9	24.23	18.69	9.35	413	0.234	128	127.58	40.5
2	10.08	19.99	16.31	8.19	314	0.339	260	100.12	34.2
3	10.04	16.92	19.75	9.86	21.98	0.226	40	18.56	8.5

*1= ammonium nitrate effluent

*2= ammonium sulfate effluent

*3= Mixed effluent of the nitrogen fertilizer company

2.2 Precipitation of Mg(OH)₂ white powder

2.2.1 Saline was pretreated by adding 1.5 times equivalent quantity of sodium sulfate as much as the quantity Ca⁺ in bittern, in order to eliminate the influence Ca²⁺ on the precipitation process.

After addition the bittern solution was stirred at 50°C. The addition and steering was repeated several times later, Ca⁺⁺ ion was precipitated into Ca(OH)₂ and removal from bitters solution.

2.2.2 Precipitation of MgOH: 100 ml of saline solution after calcium precipitation was introduced into three necked flask in water both 20°C⁰ –mixed with 200ml of the industrial (ammonium Nitrate) effluents. Only 5 ml ammonia 20% was added and 15 ml ethanol and 8 ml (gelation – and lauryl sodium sulfate) were added into the reactor.

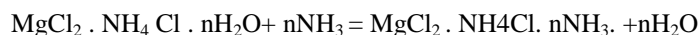
The suspension was stirred 30 min at 20 °C and aged 60 min at 50°C.

In a typical experiment was made using the industrial effluents ammonium sulfate and mixed industrial effluent after then all precipitation were dried under vacuum at 80-100 °C for 22 hrs.

2.2.3 The preparation of Ammonium carnallite:

Solid ammonium chloride and the precipitated Magnesium chloride were mixed in a ratio of 4:1 and anhydrous magnesium chloride was achieved through gas solid reaction with reaction temperature of 240 °C and reaction time of 150 min [7].

The dehydration mechanism of this precipitation method can be written as follows:



The anhydrous magnesium chloride of high purity was obtained when calcined the product from 240°C up to 750°C only hold 10 min.

2.3 Characterization of products:-

2.3.1 Phase and crystallographic structure of samples were characterized by XRD, which was recorded by using (XRD – IKIGAKU Rint 2500) using Cu K alpha-radiation.

Fig(1)_a XRD pattern shows bichofite 94% and magnesia 24%, prepared from Ammonium nitrate effluent. Fig(2)_a XRD pattern shows, bichofite 88% and magnesia 12% .Fig (3) XRD pattern shows ammonium carnallite, syn- NH₄ Mg Cl₃ 6H₂O 99% from mixed effluent stream.

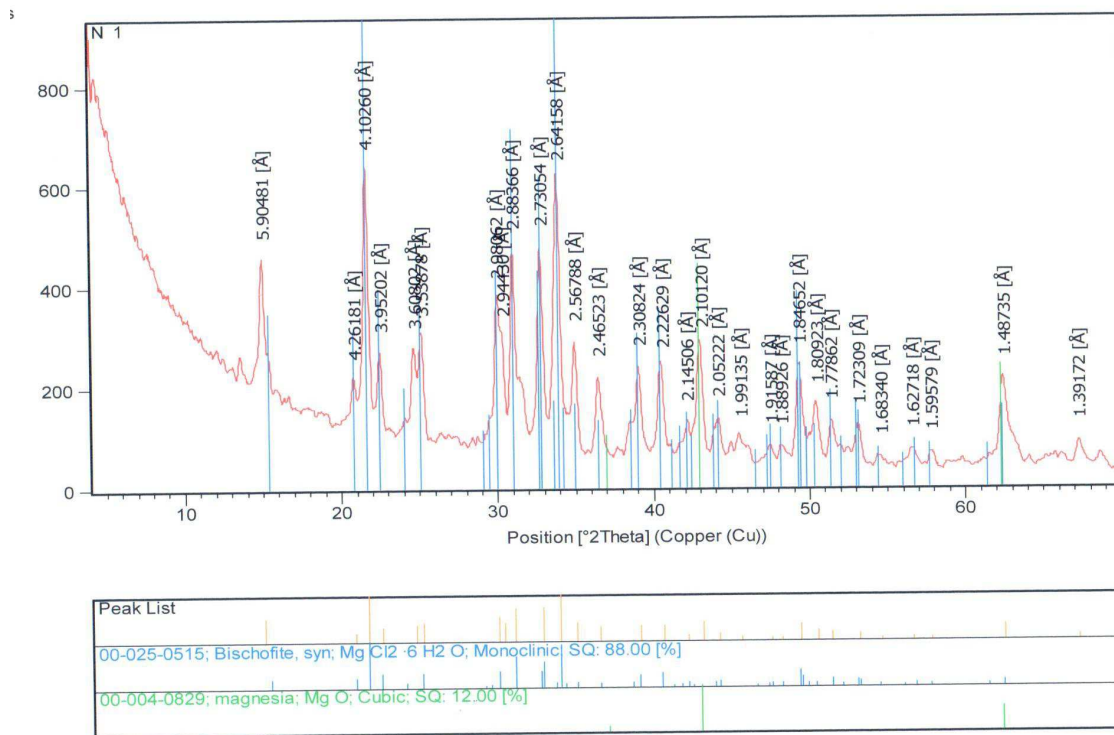
2.3.2 Scanning electron microscope (SEM; JEOL JSM-T 20) equipped with energy dispersive X-ray spectrometry (EDS; JED—2140) for the micro structural observed and qualitative add quantity were used to observe the morphology of ammonium carnallite elemental analysis Fig(4) morphology of NH₄ Mg Cl₃ 6H₂O and its content.

2.3.3 Analytic techniques surface layer characterization transmission (TEM) high resolution technique shows micrograph of nano-MgCl₂ precipitated in Fig (5)_a, Fig(5)_b and Fig(5)_c TEM pictures are shown respectively. Fig (6) shows micrograph of nano-AmmoniumMgCl₂ precipitated.

2.3.4 The Thermo-gravimetric analysis (TGA) was used as technique to measure the weight changes of substance (MgCl₂ and Ammonium carnallite) as a function of temperature or time. A plot of mass % are function of temperature is thermogram. A Shimadzu TGA-50H detector was used to perform the themrogravimetric analysis. A heating rate 10°C min⁻¹ was used in a nitrogen atmosphere using platinum pass, and sample mass was weight to approximately 5.714 mg.

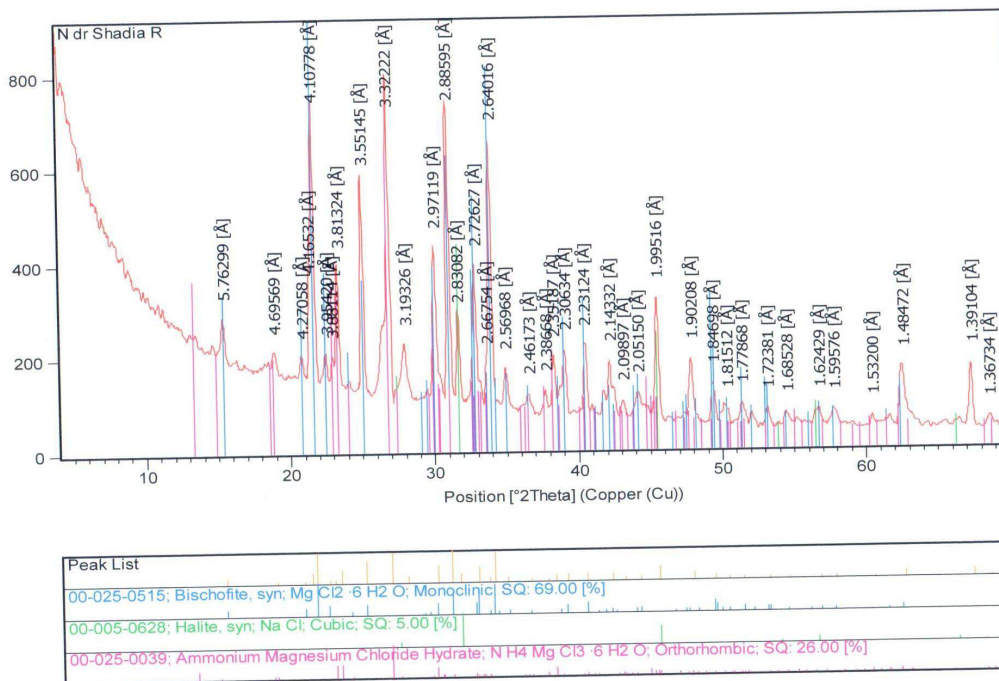
RESULTS AND DISCUSSION

3.1 XRD pattern for products precipitated from industrial effluents of Nitrogen fertilizer company, the effluents contains high pH value (10.5 -14) due to high ammonium content. Saline was mixed with twice it volume by industrial effluent magnesium chloride was precipitated and then aged at 50°C for 1 hr before drying process– Fig(1)_a shows the XRD pattern of Bischofite MgCl₂ .6 H₂O 88% and magnesia MgO 12% after the aging process and drying at 100°C 22 hr. The residual water content carried to the sublimation step causes the magnesium chloride product to react with the water to form detrimental amount of magnesium oxide.



Fig(1)_a XRD pattern of Bischofite MgCl₂ .6 H₂O precipitated from the ammonium Nitrate effluent and saline

Fig(1)_b shows the XRD pattern of Ammonium Magnesium chloride Hydrate NH₄ Cl₃ · 6H₂O orthorhombic 26% after the ammonization process. The product was prepared from the ammonium Nitrate effluent and saline.



Fig(1)_b XRD pattern of Ammonium Magnesium chloride Hydrate NH₄ Cl₃ precipitated from the ammonium Nitrate effluent

Fig (2)_a XRD pattern of magnesium chloride shows bichofite synthesis MgCl₂·6 (H₂O) with 74% and aged 1 hr at 50°C. Magnesia (MgO) 24% was also produced.

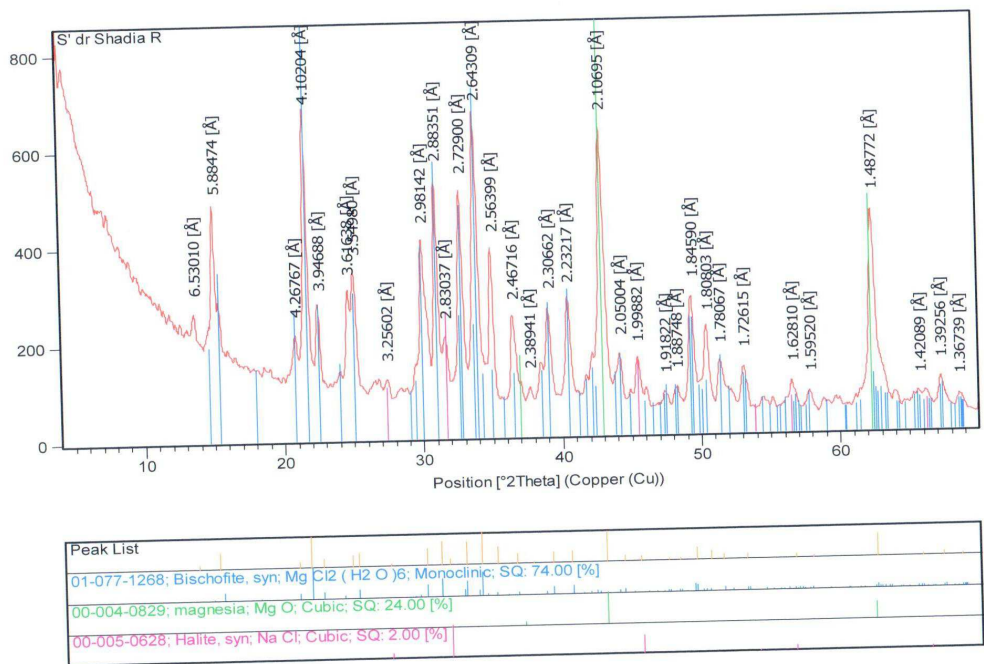


Fig (2)_a XRD pattern of magnesium chloride precipitated from ammonium sulphate effluent and saline

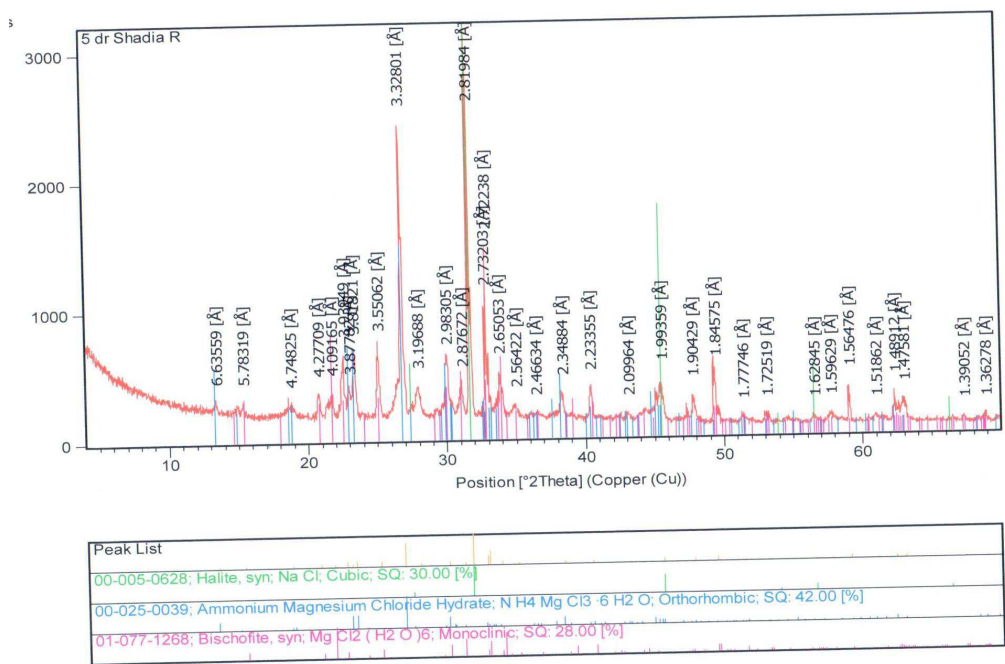


Fig (2)_b XRD pattern of Ammonium magnesium chloride Hydrate : NH₄MgCl₃.6H₂O precipitated from ammonium sulphate effluent and saline

Fig (2)_b XRD pattern of ammoniation process showing synthesis of Ammonium magnesium chloride Hydrate : NH₄MgCl₃.6H₂O, orthorhombic 42%. Our results agreed with [10].

Both synthesized Ammonium Magnesium Chloride hydrate shows a content of MgO magnesia in Fig(1)_a and Fig(2)_a with 12% and 24% formation respectively. This may be due to incomplete decomposition of ammonium chloride leading to the low ammonium concentration in the gas phase resulting un-complete substitution reaction. The reaction occurred at 240°C for 2.5 hr. This resulting emerging of ammonia quickly from the solid into the gas without reacting with dehydrated ammonia carnallite and the increased magnesia content in anhydrous magnesium chloride is present. Although ammonization ammonium carnallite was held 10 min at 750°C.

Another important reason is the high water content carried to the sublimation step causes the magnesium chloride product to react with the water to form detrimental amounts of magnesium oxide.

Fig (3) XRD pattern of Ammonium carnallite and magnesium chloride hydrate Nano-particles showing no magnesia in content. The XRD spectrum contains multiple peaks which are clearly distinguishable. Most of the diffraction peaks are readily indexed to various crystal planes of ammonium carnallite, syn-NH₄ Mg Cl₃·6H₂O (01-0660). Some other peaks were detected for ammonium magnesium chloride Hydrate- Mg(NH)Cl₃(H₂O)6 and magnesium chloride Hydrate-MgCl₂(H₂O)12 and Magnesium chloride Hydrate -MgCl₂(H₂O)6. At temperatures above 500°C, MgO and Mg Cl₂ were formed simultaneously as the products of the dehydration. When it is heated to high temperatures, ammonium chloride is released quickly from magnesium chloride hexahydrate without protecting the hydrolysis. Therefore, too high dehydration temperature led to increase the magnesium oxide content. The water formed by dehydration step and the ammonium chloride formed by the sublimation step ordinarily can be removed as vapours by blowing an inert gas which is resistant to chemical action with magnesium chloride at the reaction temperatures.

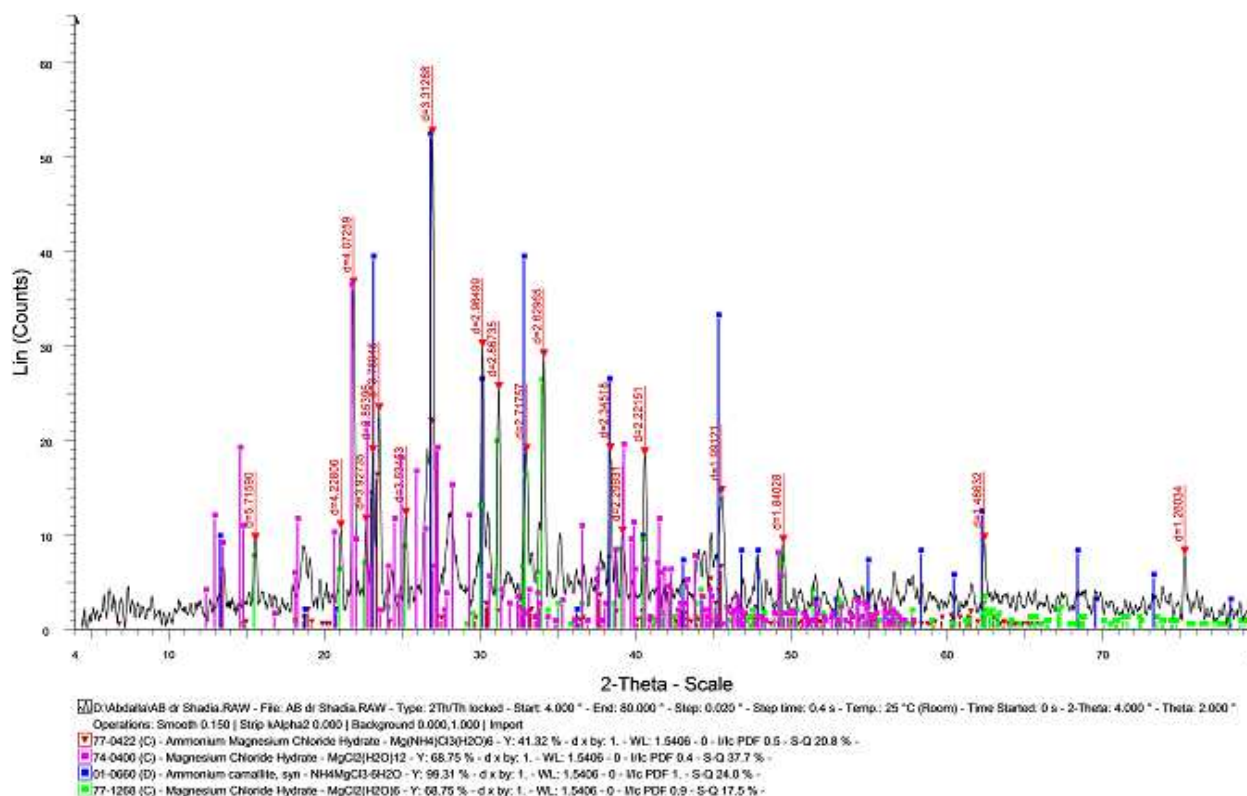
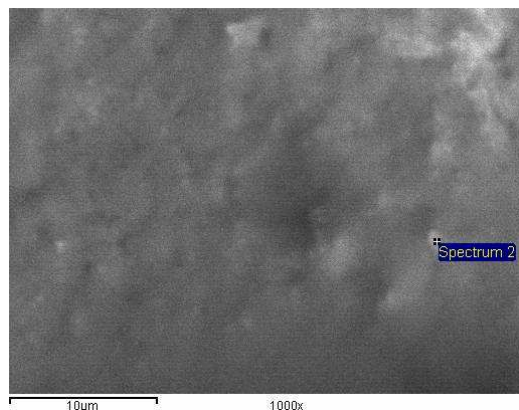


Fig (3) XRD pattern of Ammonium carnallite and magnesium chloride hydrate precipitated from mixed effluents and saline

3.2 SEM morphology of Nano- Magnesium carnallite:

The SEM micrograph of anhydrous magnesium chloride synthesized by ammoniation method is shown in Fig(4)_a. Ammoniation ammonium carnallite shows irregular polygon structures with obvious intergranular. The grain size ranges from 35,18 and 7 nm. On an average equal 17 nano size, are shown in Fig (5).

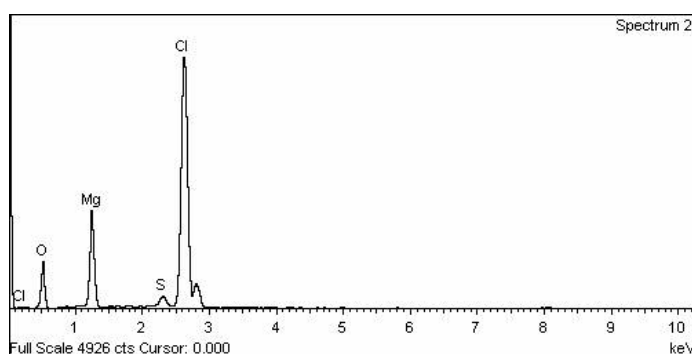
Fig(4) SEM image and Fig (4)_bEDS spectrum of carnallite Anhydrous Magnesium chloride Nano-particles. The atomic content of Mg, O, Si, Cl are 13.16 %, 27.89 %, 1.55 % and 57.89 % respectively.



Element	Weight%	Atomic%
O K	15.65	27.89
Mg K	11.22	13.16
S K	1.74	1.55
Cl K	71.39	57.40
Totals	100.00	

Fig(4)_a SEM image of Nano- Anhydrous Magnesium chloride

Table (3) EDS analysis of Anhydrous Magnesium chloride

Fig (4)_b EDS spectrum of Anhydrous Magnesium chloride

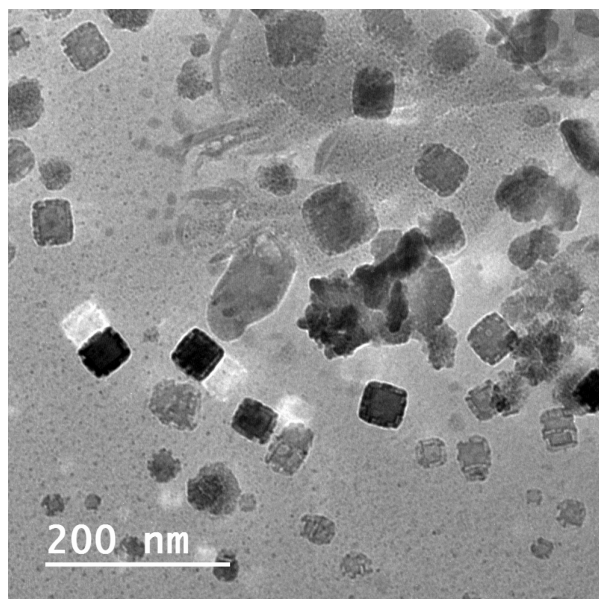
EDS indicating the content of mainly Magnesium, Chloride and Silicon in anhydrous magnesium chloride obtained, EDS analysis as shown Table (3). The MgO, KCl, SiO₂ and FeS₂ do not affect the preparation of metal magnesium by electrolysis with anhydrous magnesium chloride [9].

EDS spectrum shows that the product is mainly composed of Mg, O and amount of Cl. The O peak might come from magnesium oxides species and residue solvent and the surface of the particles, while Cl might be derived from the unreacted Mg Cl₂.

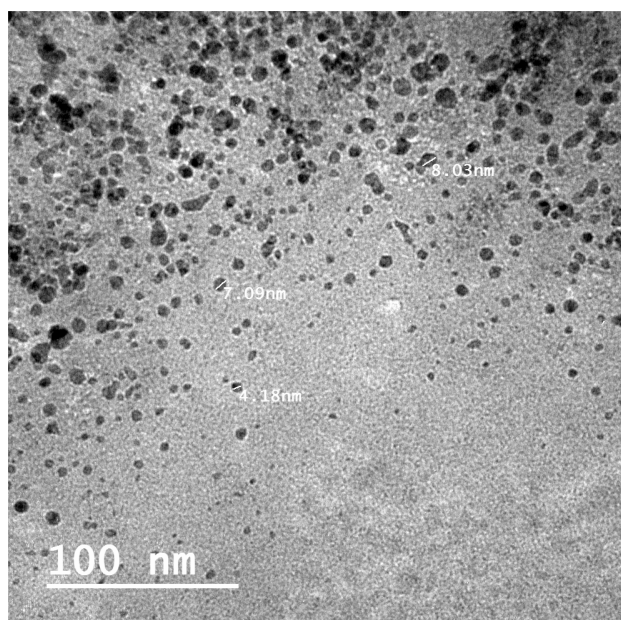
3.3 High resolution Transmission Electrone Microscope (TEM):

Fig(5)_a shows the spherical and rectangular morphology of aggregates for Anhydrous Magnesium chloride, Magnesium chloride and Magnesium oxide.

As shown in Fig (5)_b most of MgCl shows spherical morphology with particle diameters in the range 35 – 4nm. The electron diffraction patterns of the particles several diffraction rings. Diffraction intensity in the rings indicates evident discontinuity, as some arcs of ring are much brighter than the rest arcs of the same ring. This means that crystallites of coagulates are not randomly oriented in the particles.



Fig(5)_a High Resolution Transmission image and morphology of Magnesium chloride and Magnesium oxide and sodium chloride in spherical and rectangular aggregates

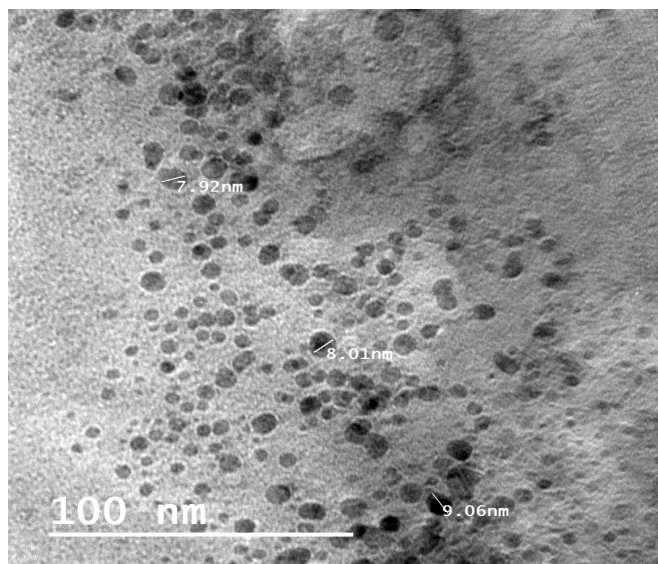


Fig(5)_b High Resolution Transmission image of Magnesium chloride and Magnesium oxide and sodium chloride in Nano size

The interplaner distance of value (A°) is one of the most important crystallography parameters that can be calculated from both the XRD patterns and electron diffraction pattern. In electron diffraction, distance from the spot to the center of circle or the radius of the bright circle is related to the d value according to the following equation:

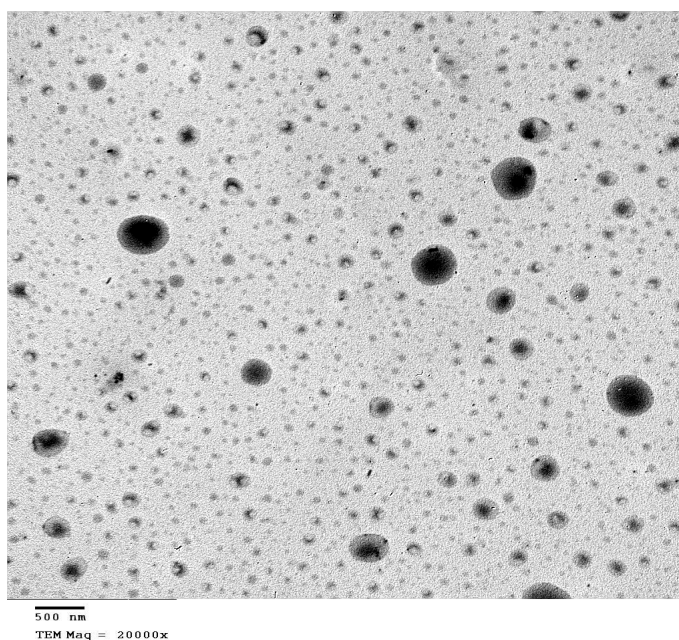
$$d = L \lambda / R$$

where d is the interplanar distance of crystal (A°), L the camera length (cm), λ the wavelength of the incident electron beam (A°) and (R) is the radius of the diffraction ring or the distance from diffraction spot to the diffraction center (cm). On the other hand the particles containing NaCl are much smaller, with sizes in the range of 4.18 nm, while the sizes of Mg Cl are in range of 8 nm.



Fig(5), High Resolution Transmission image of Magnesium chloride and Magnesium oxide in spherical Nano size. The electron diffraction of crystals

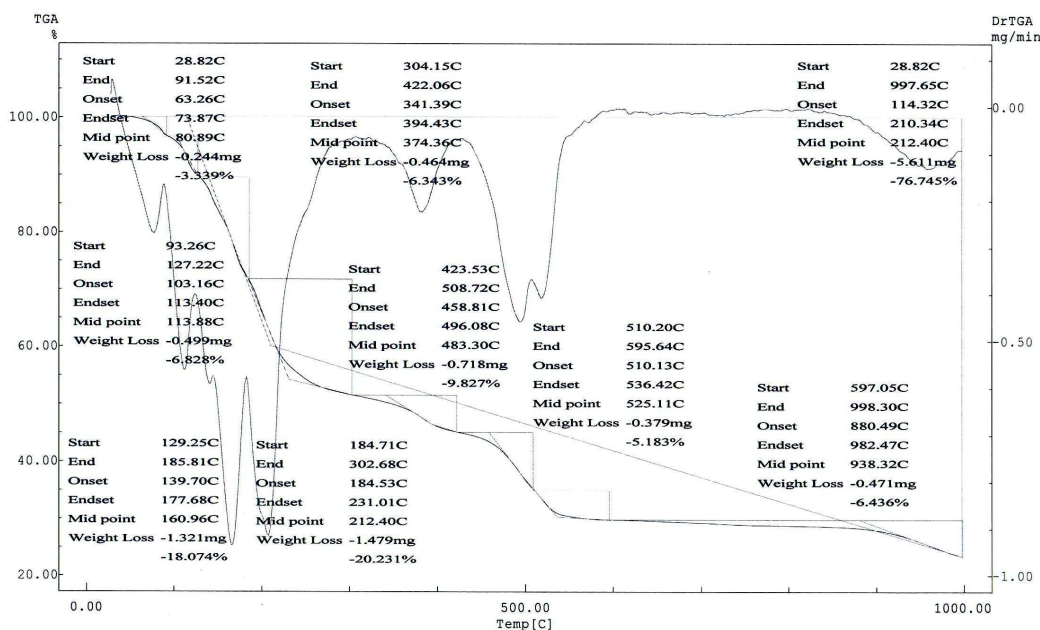
XUe Tiang et al., 2008 [10], showed similar results to our results.



Fig(6) High Resolution Transmission image of Carnallite Ammonium Magnesium chloride in spherical Nano size

The ammonium carnallite aggregates shown in Fig(6) are particles with spherical morphology and particles of different diameters in Nano range due to the difference in water % of molecules. Diffraction intensity in the rings are much brighter than the rest arcs of the same ring. This means that crystallite of the coagulates are not randomly oriented in particles.

3.4 The Thermogravimetric analysis (TGA):

Fig (7)_a thermograph of Anhydrous MgCl₂ .6H₂O

In all, six peaks obtained. The results are summarized in Table (4). On the basis of weight analysis, the first two peaks, corresponding to reaction temperature of 73 °C and 185^oC, are attributed to the formation of tetra and dehydrates. The observed reaction temperatures for these peaks may be compared with 76°C and 96°C observed by [11]. Peak 3 is due to the fusion of the dehydrated, Mellor [12] has reported 120° C as the melting point of the dehydrate

Table (4) Steps of Thermal analysis of Ammonium Carnallite

Peaks No	Reaction (i) Temperature	Phase changes
1	63-93 °C	MgCl ₂ .6H ₂ O → Mg Cl ₂ .4H ₂ O + 2H ₂ O _(g)
2	103 – 113 °C	Mg Cl ₂ .4H ₂ O →Mg Cl ₂ .2H ₂ O + 2H ₂ O _(g)
3	129 °C	Mg Cl ₂ .2H ₂ O _(s) → MgCl ₂ . 2H ₂ O _(L)
4	139 – 160 °C	Mg Cl ₂ . 2H ₂ O _(L) →MgCl ₂ . H ₂ O _(s) + H ₂ O _(L)
5	148 – 250 °C	H ₂ O _(L) → H ₂ O _(g)
6	302 °C	MgCl ₂ . H ₂ O →Mg Cl ₂ + H ₂ O _(g)

(i) Temperature corresponding to onset – endset of reaction peak; the peak temperature, which depend, upon the amount of the sample and rate of heating is not included[13].

The conversion of dihydrate to monohydrate commences at 139 -160 °C. The formation of liquid water in a phase change at temperatures above 103 °C has been established from the work of [14].

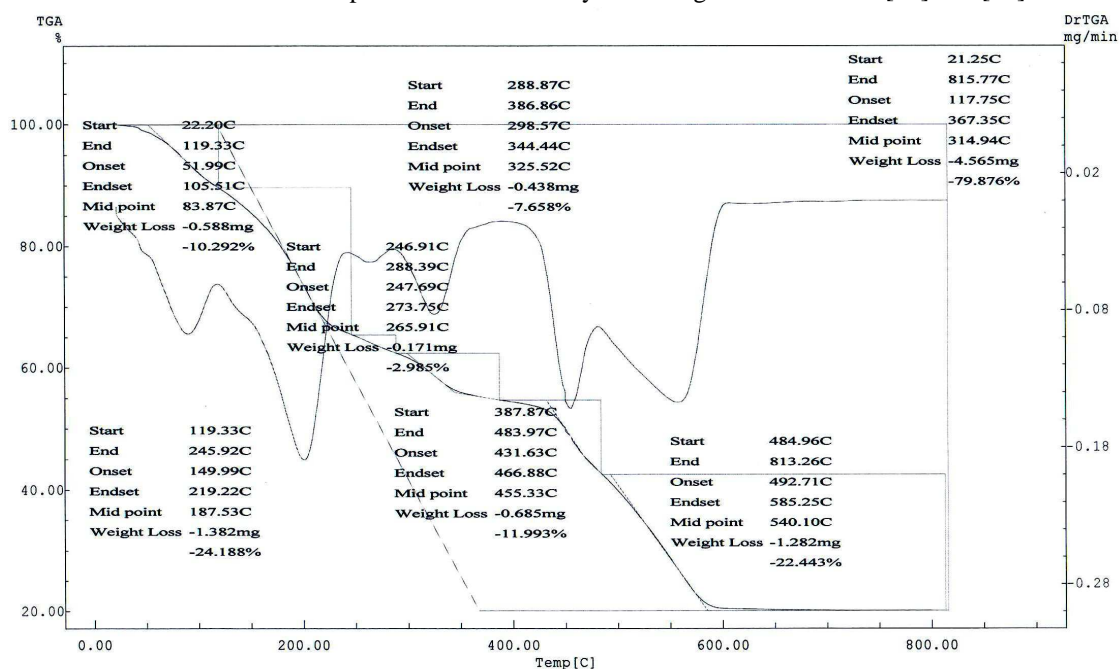
The formation of (liquid) water in the phase change corresponding to the fourth peak (160 °C). The last molecule of water of hydration is lost at 230 °C, also accompanied with considerable hydrolysis giving rise to peak 6.The thermograph obtained in the dehydration of NH₄ Cl. Mg Cl₂ . 6 H₂O appears in Fig (7)_b.

The presence of NH₄Cl in the molecule is known to weaken the water of hydration [15]bond due to which it can release the water of hydration more easily as compared to the chloride.

It showed stepwise dehydration which was not complicated by hydrolysis. At temperature blow 51.99°C, observed moisture in excess of the hex hydrate is lost. Peak 1 to 3 corresponding to reaction temperatures of 83 °C, 149 °C, 187°C are due to phase transformation: hex – to tetra hydrate, tetra- to dihydrate and dihydrate to anhydrous magnesium ammonium chloride.

Peak 4 corresponding to reaction temperature 246°C is due to the decomposition of the double salt itself , the ammonium chloride released sublimed off and could be seen to have deposited on the cooler parts of sample holder.

The data presented in Fig (7)_b enable determination of precise conditions for dehydration of hydrated magnesium ammonium chloride and for its decomposition to obtain anhydrous magnesium chloride [16] and [17].



Fig(7)_b Thermograph obtained in the dehydration of NH₄Cl.MgCl₂.6H₂O

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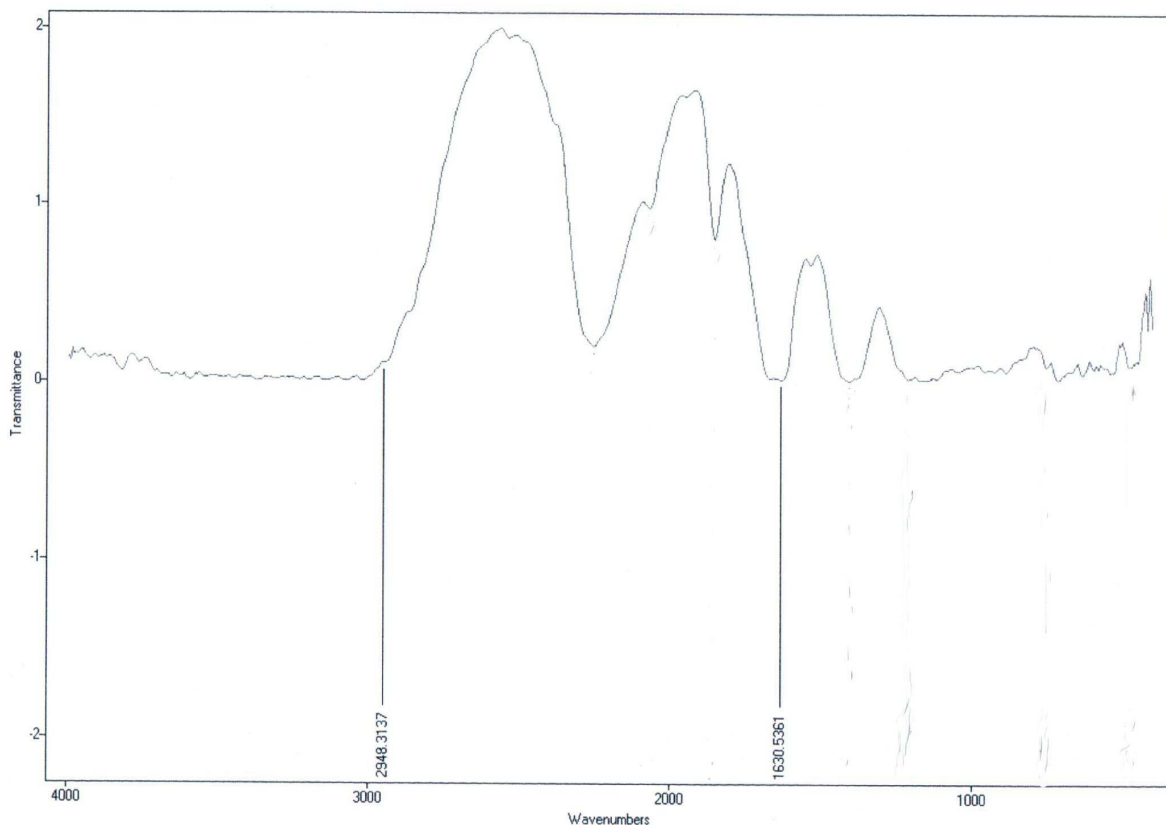


Fig (8) FT-IR spectrum of magnesium chloride prepared by precipitation process from mixed industrial effluents of Chemical Fertilizer Company

The formation of (liquid) water in the phase change corresponding to the fourth peak (160 °C). The last molecule of water of hydration is lost at 230 °C, also accompanied with considerable hydrolysis giving rise to peak 6. The thermograph obtained in the dehydration of $\text{NH}_4\text{Cl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ appears in Fig (7)_b.

The presence of NH_4Cl in the molecule is known to weaken the water of hydration [15] bond due to which it can release the water of hydration more easily as compared to the chloride.

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3.5 FT – IR Analysis of the prepared magnesium chloride and the ammoniated carnallite is shown in Fig (8) and Fig (9).

Fig (8) FT-IR spectrum of magnesium chloride prepared by precipitation process in 60 min stirring followed by 30 min aging process at 50°C. After then dried powder under vacuum at 100°C for 22 hours. The spectrum shows a small peak at 2948 cm^{-1} and another main peak at 1630 cm^{-1} indicating the presence of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$.

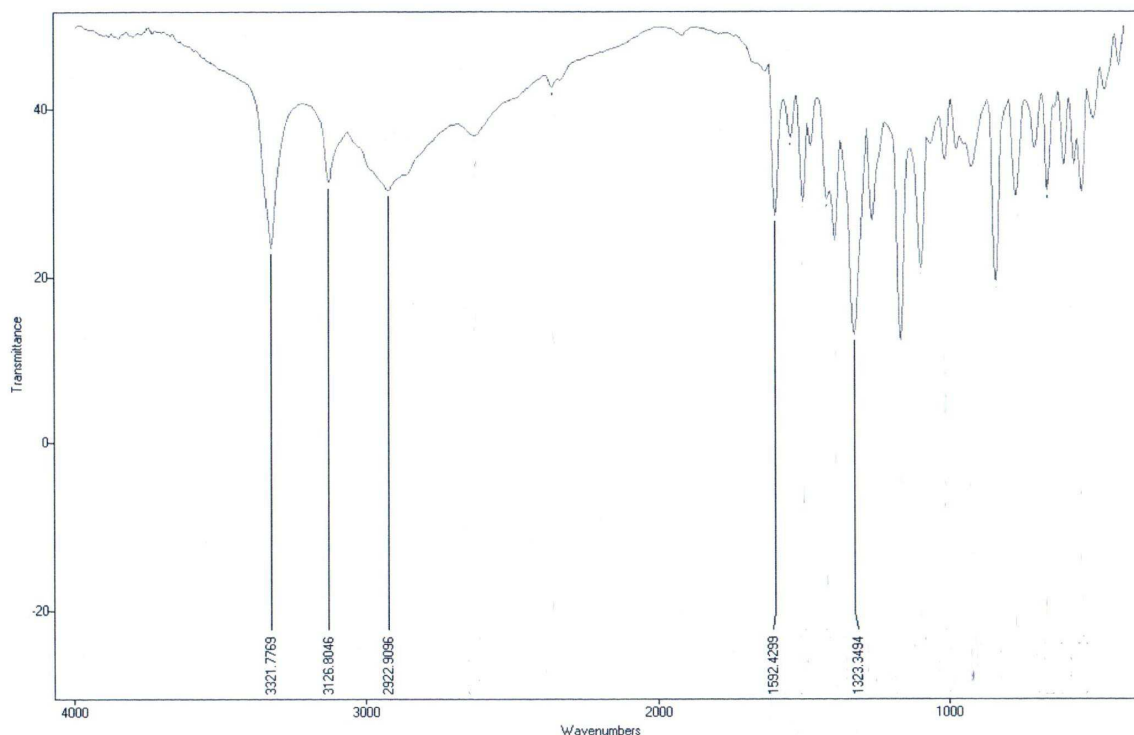


Fig (9) FT-IR spectrum of Magnesium carnallite prepared from $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and solid ammonium chloride by ammonization method

Fig (9) FT-IR spectrum of Magnesium carnallite prepared from $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and ammonium chloride when heated at 240°C for 2.5 hr. And calcined at 750 °C for 10 min. The FT-IR spectrum of Nano – ammoniated magnesium chloride shows main peaks at 3321 cm^{-1} and 1616 cm^{-1} respectively $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$. The three peaks at 3126 cm^{-1} , 2922 cm^{-1} and 1335 cm^{-1} indicates the presence of ammonium chloride.

The above five peaks confirms the existence of Ammonium Magnesium Chloride - Carnallite.

CONCLUSION

The method described in this paper affords a convenient method for the synthesis of ammonium carnallite without using complicated apparatus.

The results of XRD, EDS, FT-IR clearly show the formation of carnallite and TEM surface analysis was used to characterize the surface composition of the product.

The high residual water content carried to the sublimation step causes the magnesium chloride product to react with water to form detrimental amounts of magnesium oxide.

For highest product purity, the sweep gas should not contain more than 10 ppm, water. Larger amounts of water in the sweep gas may cause inferior products, i.e., one containing excessive amounts of magnesium oxide and water.

Anhydrous magnesium chloride particles can be obtained by ammonium method and are suitable for electrolytic preparation of metal magnesium.

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