The Phase Transition in Natural Gypsum

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In present study, the thermal behaviour of calcined gypsum specimens at temperature controlled laboratuar farin in the temperature range 120-1000ºC in atmospheric pressure by means of X-ray difractometer and scanning electron microscopy is examined. In this investigations, powder gypsum and calcined powder gypsum at different temperatures (120, 160, 180, 200, 250, 600 and 1000ºC) were used. Scanning electron microscopy observations and X-ray diffractometer results show that the transformation to bassanite (calcium sulfate hemihydrate) begins at *ca.* 120ºC, the transformation to anhydride complete at *ca.* 600ºC. Differential thermogram result was pulsed at these transformations.
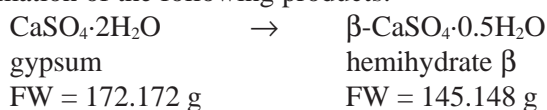
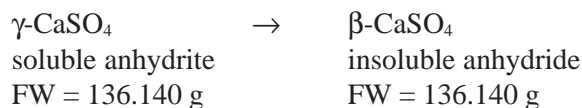**Key Words: Calcium sulphate phases, Gypsum, XRD, SEM, Hemihydrate.**

INTRODUCTION

Gypsum is the most common sulfate mineral and is usually found within evaporite sequences or associated with calcareous sedimentary deposits. Large deposits of alabaster gypsum are commonly observed at the sole of many large-scale tectonic dislocations and thrust faults[1] within evaporitic regions[2]. Gypsum is widely used in many fields of industrial technology, such as; building materials, plasterboards, soil reclemation and neutralization, fertilizer, gas desulphurization and producing sulphuric acid. Bassanite is an important compound in the cement industry and occurs commonly as a secondary mineral. However, bassanite is rarely found in nature and its rare occurrence has been difficult to understand.

Gypsum is a crystalline form of calcium sulphate combined with water known as calcium sulphate dihydrate, $CaSO_4 \cdot 2H_2O$. There are two crystal structures for the hemihydrate and anhydride, the γ and β forms. When dehydrated to the hemihydrate, $CaSO_4 \cdot 0.5H_2O$.

Generally, the thermal dehydration of gypsum is reported to lead to the formation of the following products:

$$CaSO_4 \cdot 2H_2O \quad \rightarrow \quad \beta\text{-}CaSO_4 \cdot 0.5H_2O$$

gypsum   hemihydrate β
FW = 172.172 g   FW = 145.148 g

γ-CaSO$_4$ →   β-CaSO$_4$
soluble anhydrite   insoluble anhydride
FW = 136.140 g   FW = 136.140 g

γ-CaSO$_4$ is called soluble anhydride because of its spontaneous hydration into hemihydrate under common atmospheric conditions and into gypsum upon immersion in water.

Gypsum shows a gypsum-bassanite-anhydrite transition sequence; and these phase transitions are controlled by the dehydration and rehydration processes[3]. The water molecules in gypsum are highly interactive with CaO and groups and are also essential constituents SO$_4^{2-}$ in the crystallographic arrangements[4] of gypsum. The dehydration process hence realigns the crystal structure or, in other words, the phase transitions are associated with a structural change. The different phases in this transition sequence, gypsum, bassanite and anhydride, have been characterized by a variety of experimental techniques such as X-ray difraction[4,5], inelastic neutron scattering[6], neutron diffraction[6,7] and infrared[8,9], Raman spectroscopy[10,11] and neutron and X-ray difraction[12]. A common feature in all these studies has been mainly to characterize the structure of individual phases and to understand the dehydradion process. Further, the existence of an intermediate bassanite phase with has been investigated in H$_2$O ≥ 0.5 some studies[4,12,13]. It has been established that the gypsum-bassanite transition is associated with a rearrangement of SO$_4^{2-}$ in its crystal structure because of the fact that they are strongly coupled with the water molecules.

The calcium sulfate dihydrate, which represents the stable phase in the CaSO$_4$·H$_2$O system under atmospheric conditions. Dihydrate occurs in natural gypsum deposits (natural or raw gypsum) and it is produced in large quantities in certain industrial processes, such as flue gas desulfurization (synthetic gypsum, in this case FGD gypsum). α or β calcium sulfate hemihydrate, as well as the essentially water-free CaSO$_4$ phases anhydride II and anhydride III, are formed during the dehydration process depending on the dewatering conditions (temperature, time, pressure). In addition to the hemihydrate other sub-hydrates with crystal water contents between 0.5 and 0.8 have recently been produced and investigated crystallographically[14-18].

Anhydride II occurs in various forms which are classified according to reactivity. Sparingly soluble anhydride is produced when gypsum is burnt at temperatures between 200 and 400°C and insoluble anhydride is formed in the temperature range from 400 to 700°C. The reactivity of sparingly soluble anhydride decreases with increasing production temperature.

The transformation of gypsum to bassanite (hemihydride) has been studied by many techniques such as differential thermal analysis,

thermogravimetry, heat capacity and dielectric constant measurements. These studies indicated that the transition temperature is between 100 and 200°C, depending on the rate of heating and pressure[19].

The thermal behaviour of gypsum has been shown to be somewhat unique. For example, the optical properties of gypsum as a function of temperature, monitored by Hutchinson and Tutton[14], change dramatically with the convergence of the refractive indices β and γ, on increasing temperature and their crossing over at *ca.* 90°C. At this point the optic axial plane becomes perpendicular to (010), which is parallel to the optic axial plane below 90°C, necessitating structural or symmetry modifications in response to the temperature variations. The thermal dehydration reactions and products of gypsum have been extensively studied at both negligible vapour pressures[4,15] and under various confining pressures[12,13], revealing a small stability field for gypsum, terminated by the onset of dehydration.

The thermal decomposition of gypsum has been studied by many prior investigations[20,21], yet many questions remain as to the exact nature of the structural changes that arise during the dehydration process. The outcome of all these studies is that the stepwise dehydration of gypsum, by 1.5 and 2.0 H_2O, is responsible for the formation of bassanite and anhydride phases, respectively.

In present study, the changes to bassanite and anhydride of gypsum has been studied by means of XRD analysis and SEM observations.

EXPERIMENTAL

The material used for present studies was S. Koçhisar gypsum from Ankara, Turkey. Natural gypsum is abundant in Turkey, total gypsum reserve is 1.6 billion tons and S.Koçhisar gypsum reserve is 150 million tons[22].

The powder gypsum specimens (-0.5 mm sized) were calcined at temperature controlled laboratuar farin (Electromag) under atmospheric pressure at different temperatures (120, 160, 180, 200, 250, 600 and 1000ºC) for 1 h. Powder gypsum and calcined powder gypsum specimens were carried out by XRD and scanning electron microscopy (SEM) for each specimens. The thermal behaviour of gypsum were carried out by DTG.

X-ray diffraction analysis of finely pulverized gypsum and calcined powder gypsum samples for the identification of the presented crystalline compounds and their mineralogical composition. The analyses were performed with a Shimadzu XRD-6000. The diffraction interval was between 2θ 20°-60° with step of 0.02°. SEM (Jeol/JSM-6335F) was carried out for gypsum and calcined gypsum specimens. Differential thermogravimetric analyses, Setaram 92 16 TG were carried out to determine

quantatively and qualitatively the various compounds presented in samples. Analyses were performed in sample in air atmosphere at a temperature range of 25-1000°C and the gradient of 5°C/min.

Chemical analyses (%) by ICP and anion chromatography showed that 60.63 SO_3, 24.93 CaO, 1 Al_2O_3, 0.8 Fe_2O_3 and 0.6 SiO_2. The trace elements of any significance were Sr and Ce (0.1 wt %). Each gypsum sample contains the impurities of < 4 %. Prior to the calculation of the weight loss resulting from water removal, this amount is accounted. Accordingly, the weight loss refers to pure gypsum. Furthermore, the sample of gypsum was weighed in the cell after the pressure had been lowered and before the temperature increased. At the end of the dehydration, the sample was also weighted in the closed cell in order to prevent spontaneous rehydration of the sample in contact with the humidity of the air. XRD studies and SEM observations were systematically carried out in order to characterize final products.

RESULTS AND DISCUSSION

Gypsum transforms into bassanite ($CaSO_4 \cdot 2H_2O$) by losing 1.5 molecules of crystalline water. In general, the existence and position of the perturbation not only depends on vapour pressure and reaction rate but also on the crystalline structure, thermal conductivity and impurity content.

Dry gypsum, with no free moisture, contains 21 % chemically bonded water by weight[23]. This water is released and evaporates during heating. Most of the studies[13,15,23-25] reported a sharp drop of gypsum mass from 80 to 200°C, followed by a gentle decrease in mass throughout the remaining heating.

Temperatures of the gypsum-bassanite and bassanide-anhydrite conversions for the material were determined by the TG measurement. The test result from the DTG analyses is shown in Fig. 1. The peak values are mainly due the dehydration or decomposition reactions of gypsum during heating. Chemically, gypsum will undergo two stages of dehydration. However, there is disagreement between researchers about the temperature at which the second dehydration will occur[16]. The overall trend is in some good agreement except that the peal values are greatly different.

During heating, gypsum undergoes two endothermic decomposition reactions in which the water of crystallization is removed. These are represented by eqns. 1 and 2.

In the first reaction, shown as the first peak in Fig. 1, gypsum is converted to calcium sulphate hemihydrate as follows:
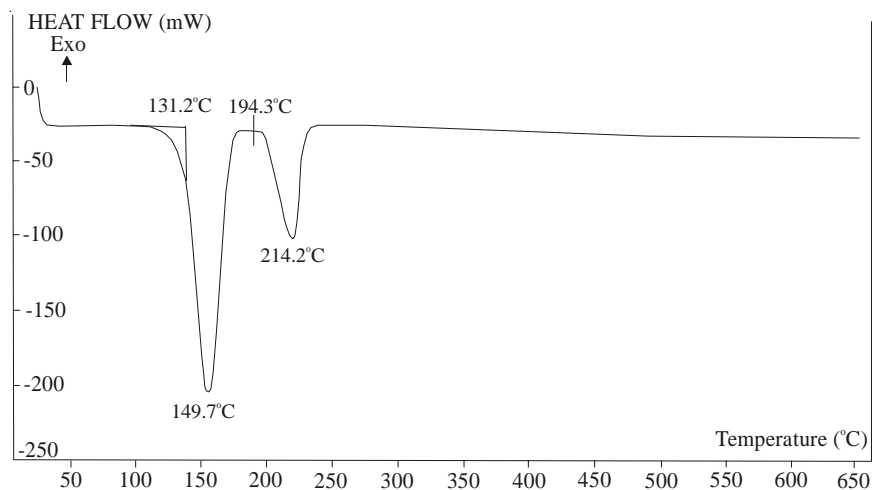
$$CaSO_4 \cdot 2H_2O \rightarrow CaSO_4 \cdot 0.5H_2O + 1.5H_2O \tag{1}$$

Fig. 1. Dehydration curve of gypsum

This reaction starts at about 100ºC and is completed by about 150ºC (Fig. 1). This range is affected by the rate of heating[24]. Both forms (α and β) are crystals, the α form has smaller crystals and is a higher energy form. As can be seen in the equation 1.75 % of the water of crystallization is vapourized. As the total water of crystallization is 20.9 % by mass, then $0.75 \times 20.9 = 15.675$ % of the total mass is water.

The mass loss remains almost unchanged up to 100ºC. Between 100 and 160ºC, the mass loss of the different boards decreases between 15 and 17 % as moisture is driven off. These results are reasonable as gypsum with no additives contains *ca.* 21 % by mass of water. Between *ca.* 160 and 650ºC, the mass loss remains fairly constant, This trend can be approximated by a linear. In addition, as stated earlier, with a lower heating rate employed, this mass loss would have occurred at lower temperatures.

In the second reaction in Fig. 1, calcium sulphate hemihydrate is converted to calcium sulphate anhydride as follows:

$$CaSO_4 \cdot 0.5H_2O \rightarrow CaSO_4 + 0.5H_2O \qquad (2)$$

This reaction occurs at *ca.* 210°C according to Andersson and Jansson[26] and at 300°C according to Groves[27] and at *ca.* 600°C according to Sultan[28].

The accurate composition of the initial calcium sulfate hemihydrate β is well known and its purity is equal to 96 %. The major impurity is calcium carbonate (2.5 %). Single crystals of gypsum were centimeter-sized and of natural origin.

Dry gypsum, with no free moisture, contains 21 % water by weight that is chemically bound in a crystal matrix. This water is released and evaporates during heating, but may re-condense elsewhere in the specimen. Some free moisture is also present in gypsum boards. The

equilibrium moisture content depends on ambient temperature and relative humidity. During heating this free moisture is also driven off as steam and may also re-condense elsewhere in the specimen.

Numerous samples were made to select the appropriate heating temperature in the 80-220°C range. Their components of crystallized form were determined by the X-ray diffraction measurements. Only gypsum (Fig. 2a) was found in the solidified and the raw material, gypsum and bassanite mixture in the samples made by heating them between 120 and 250°C (Figs. 2b-f). The probes heated at the temperature of 600 and 1000°C consisted of the anhydride (Figs. 2g-h).
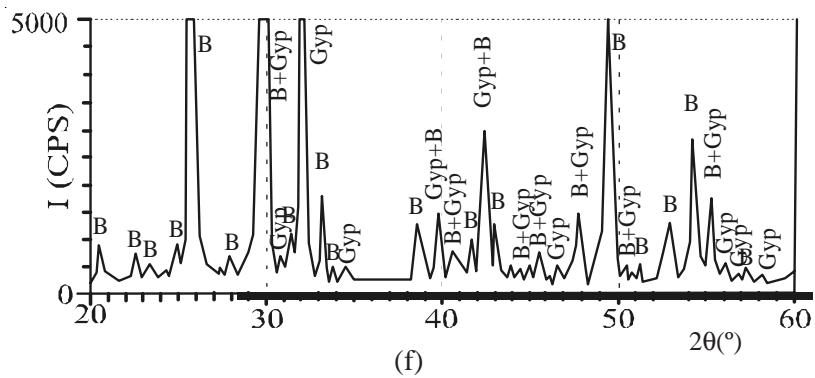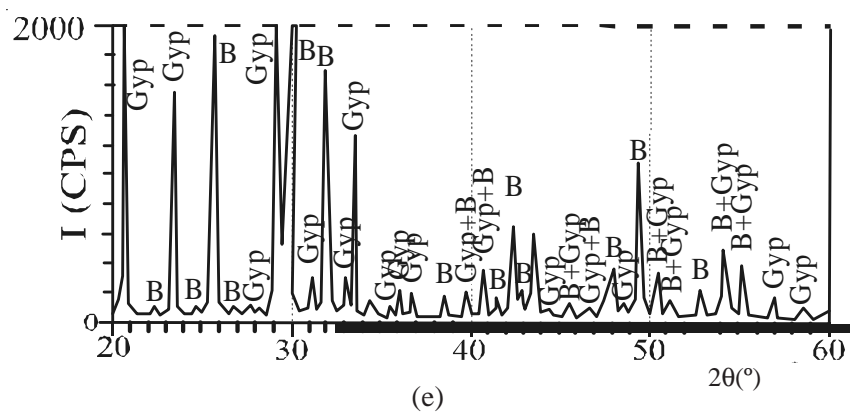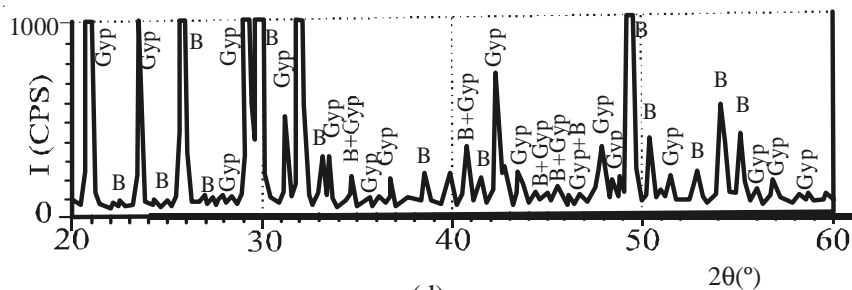

(a)

(b)

(c)

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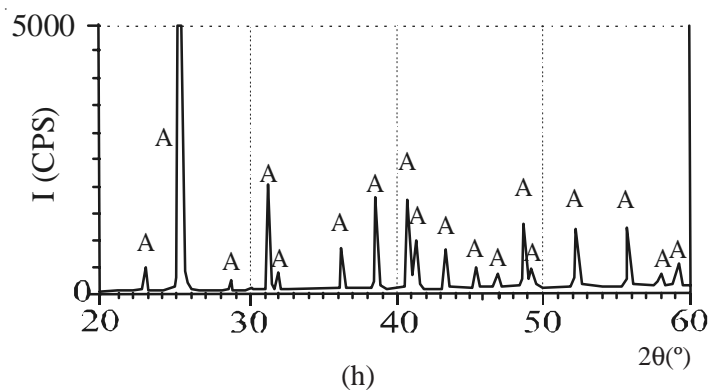

(e)

(f)

(g)
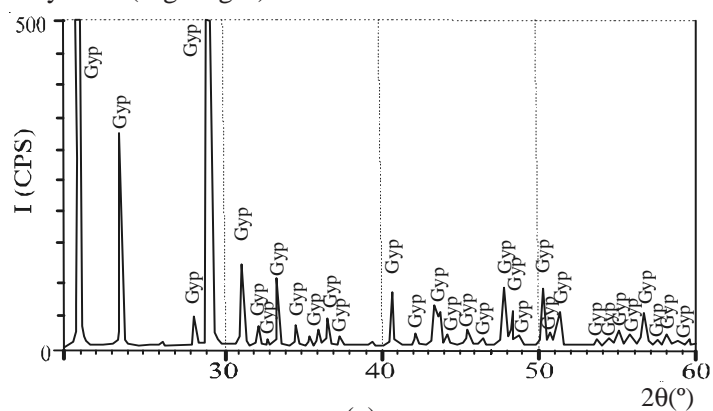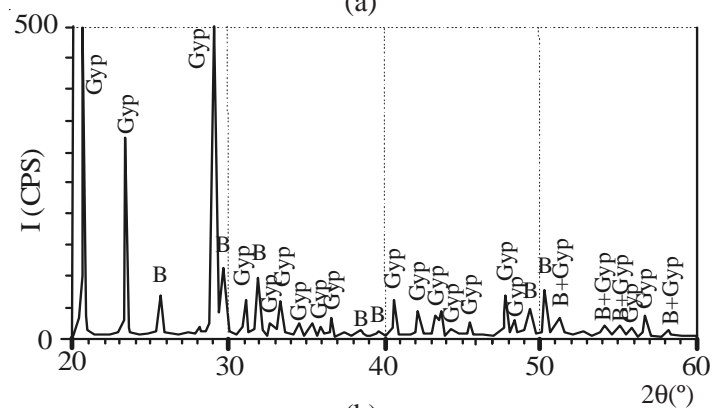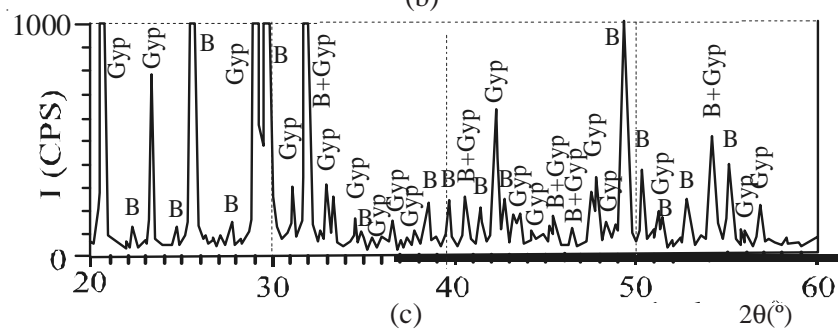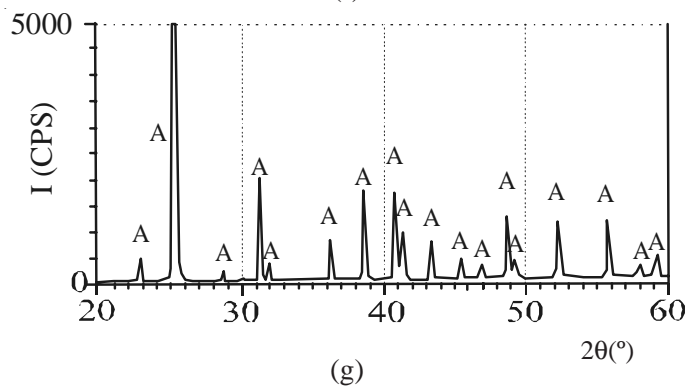
Fig. 2. XRD analysis results of of gypsum, hemihydrate mixtures and anhydride
       [(a) gypsum, (b) gypsum + bassanite at 120°C, (c) gypsum + bassanite at
       160°C, (d) gypsum + bassanite at 180°C, (e) gypsum + bassanite at 200°C,
       (f) gypsum + bassanite at 250°C, (g) anhydride (γ) at 600°C, (h) anhydride
       (β) at 1000°C] (G: Gypsum, B: Bassanite, A: Anhydride)

In Fig. 2f, the dehydration of gypsum into calcium sulfate hemihydrate
is complete, whereas the Fig. 2g shows a mixture of gypsum and hemi-
hydrate, a solid/solid transformation of gypsum into calcium sulfate hemi-
hydrate occurred without a lattice transformation. The gypsum as final
product cannot result from a rehydration of calcium sulfate hemihydrate
because we strongly controlled the mass of the product when the sample
was brought back to atmospheric conditions prior to XRD analysis. If the
gypsum lattice as the final product lattice does not result from the rehydra-
tion of calcium sulfate hemihydrate and if the dehydration of gypsum has
been complete. This study reveals that there is a transformation of gypsum
into calcium sulfate hemihydrate without lattice transformation in the case
of micron-sized needles of gypsum dehydration and with a partial lattice
transformation in the case of single-crystal dehydration. The lattice trans-
formation of gypsum into calcium sulfate hemihydrate involves important
changes even if they both crystallize in the monoclinic system (Table-1). A
topotactic transformation of gypsum into hemihydrate was often assumed
but not really demonstrated. Conversely, there is more information about
the topotactic transformation of hemihydrate into gypsum[21].

Bassanite-anhydride transition also established that a further increase
in temperature would remove the remaining water molecules and thus the
anhydride phase is formed from bassanite. These modes at elevated tem-
peratures became weaker and disappeared in the anhydride phase.

In fact, with the decrease of gypsum, the upper structural water
molecules disappear and the calcium sulfate sheet forms the new upper
plane. Later, the underlying structural water molecules migrate towards

TABLE-1
DATA ON THE CRYSTAL LATTICE OF THE DIFFERENT
CALCIUM SULPHATES

|	Matrix	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Cell volume (Å^3)	Cell content
$CaSO_4 \cdot 2H_2O$	Monoclinic	5.670	15.201	6.533	90	118.6	90	494.37	$4(CaSO_4 \cdot 2H_2O)$
$CaSO_4 \cdot 5H_2O$	Monoclinic	12.019	6.930	12.670	90	90.23	90	1055.30	$12(CaSO_4 \cdot 5H_2O)$
γ-$CaSO_4$	Orthorhombic	12.077	6.972	6.304	90	90.00	90	530.80	$6(CaSO_4)$
β-$CaSO_4$	Orthorhombic	7.006	6.998	6.245	90	90.00	90	306.18	$4(CaSO_4)$

the edges of the sample (or of its steps), then escape through them. The described phenomenon comes close to the observations (Fig. 3) made in transmission electronic microscopy. The appearance of vacancies caused by the leave of the water molecules was observed. Simultaneously, the gypsum loses its atomically flat surface with the emergence of some superficial cracks on the calcium sulphate upper plane to form micro-sized clusters. The same phenomenon is observed in all places of the sample and thus, is not provoked by the presence of the tip. Gypsum and hemihydrate's heat evolution goes through a number of stages and the setting generally correspondes to the location of the large peak in the heat evolution curves that is related to the formation of prismatic needle shaped calcium sulphate dihydrate crystals with a degree of interlocking.
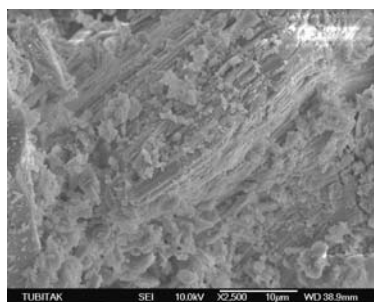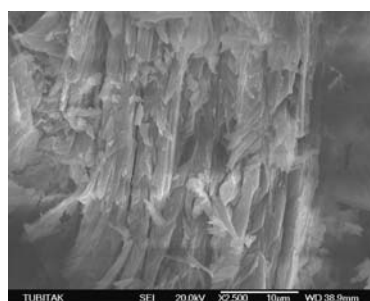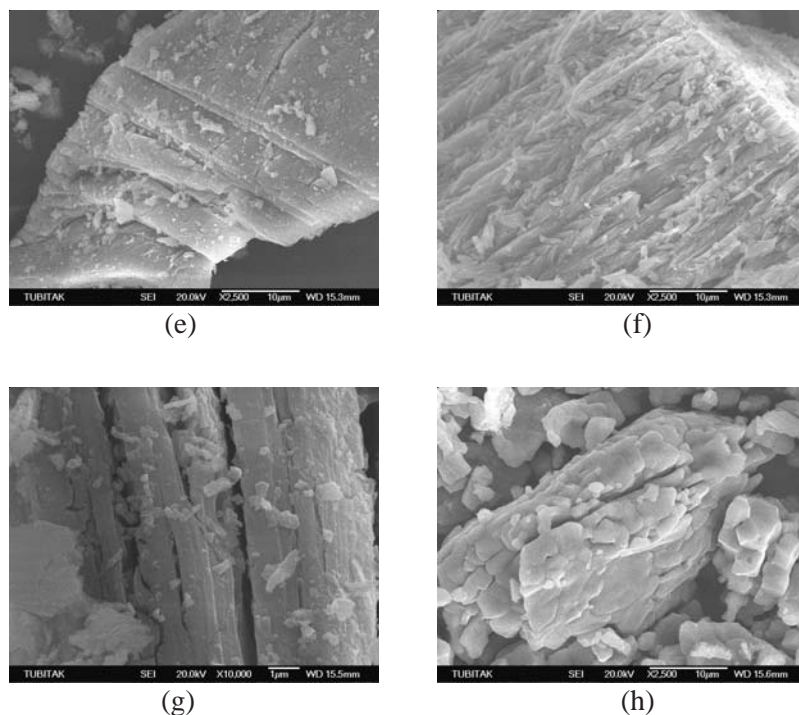

(a)
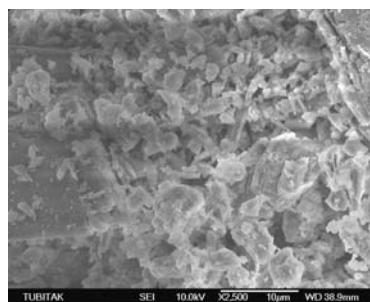
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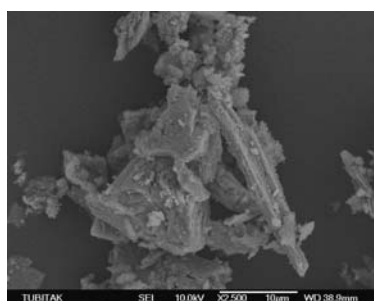
(c)

(d)

Fig. 3. Scanning electron microscope image of gypsum, hemihydrate mixtures and anhydride [(a) gypsum, (b) gypsum + bassanite at 120°C, (c) gypsum + bassanite at 160°C, (d) gypsum + bassanite at 180°C, (e) gypsum + bassanite at 200°C, (f) gypsum + bassanite at 250°C, (g) anhydride (γ) at 600°C, (h) anhydride (β) at 1000°C]

Two forms of anhydride, soluble (γ) and insoluble (β), are known to exist and there are no distinguishable spectral features for these two forms. However, γ-form undergoes rapid rehydration and transforms $CaSO_4$ into bassanite, even under ambient conditions.

The anhydride formed from the dehydration of gypsum is known to absorb water from the environment and to be converted into hydrates. In the absence of distinguishable spectral features for γ- and it is different β-$CaSO_4$, difficult to assign the dehydrated gypsum to a particular phase of anhydride.

Conclusion

XRD analysis results show that the specimen are gypsum at 25°C. It calcined at 120°C, starts to transformation to bassanite. At 160, 180 and 200°C, the transformation to bassanite is maximum. At 250°C, the transformation was completed to bassanite. At 600 and 1000°C, the specimens formed were anhydride.

Depending on water vapour pressure, the thermal path varies and consequently the dehydration products also vary. At 600°C or below, there is only one dehydration step from gypsum to γ-CaSO$_4$. In between 120-250°C, calcium sulfate hemihydrate is an intermediate product between gypsum and γ-CaSO$_4$. An original result of this study is that, depending on the microstructure of the initial sample of gypsum, the lattice of the intermediate calcium sulfate hemihydrate varied. This study indicates that SO$_4^{2-}$ undergone considerable changes in its crystallographic environment during the phase transition sequence in gypsum.

ACKNOWLEDGEMENT

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