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Microscopic and Physico-Mechanical Properties of Hydrated Anhydrite Using Sulphate Activators

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ABSTRACT. Anhydrite deposits either as weathering products or original sediments are found, over huge gypsum bodies in the Ras Malaab area near the Gulf of Suez, Egypt. Anhydrite can be converted to a useful building material by partially transforming the anhydrite into gypsum using chemical activators. The used activators are: $ZnSO_4$, K_2SO_4 and $MnSO_4$.

The Physico-mechanical properties of hardened natural anhydrite such as dry and wet compressive strength, bulk density, water absorption and apparent porosity are discussed. The results show that the addition of 3% $MnSO_4$ gives the highest values of dry (~ 175 kg/cm^2) and wet compressive strength values (~ 100 kg/cm^2). These increase of activators percentage leads to the decrease of both water absorption and apparent porosity values.

X-ray diffraction analysis (XRD) is used to detect the percentage of transformed gypsum. A polarizing microscope was used to describe the micro-structure, cleavage planes, crystal structure and the new phases which were confirmed by scanning electron microscope (SEM).

Many factors were found to control the gypsification process such as type and percentage of activators, time of curing, difference in potentiality and electronegativity, in addition to the position of the elements of activators in the periodic table.

Natural anhydrite which forms as a caprock or as a weathering layer over a huge gypsum deposit makes exploration for gypsum ores difficult. In the Ras Malaab quarry, Gulf of Suez, about one million tons of anhydrite would be quarried as waste material. The thickness of this anhydrite ranges from 2-4 m and extends in intermittent form for about 1 square kilometer in exploited area. These deposits overlie alabastrine gypsum deposits and kaolinitic shale deposits. This current paper would be considered the first work in Egypt to utilize natural anhydrite for building purposes using some chemical activators. The main effect of the activator is to accelerate the anhydrous form of gypsum which is one of the most widely distributed mineral deposits in Egypt. Geologically, anhydrite is deposited as a surface layer overlying gypsum deposits and as a weathering product of gypsum.

The objective of this research is to study the alteration of natural anhydrite for making it suitable for building purposes through the effect of chemical activators. The activators used in the present work are: $ZnSO_4$, K_2SO_4 and $MnSO_4$.

The stability relationship of gypsum ($CaSO_4.2H_2O$) and anhydrite ($CaSO_4$) are of considerable interest because most natural marine evaporite deposits consist essentially of gypsum and/or anhydrite. The hydration reaction of anhydrite agitated in pure water has been demonstrated by Posnjak. (1940) to take place via the solution phase. His results which are based on solubility data for calcium sulphate phases in water show gypsum to be the least soluble phase below 42°C.

Thermodynamic studies by MacDonald (1953) show that hydrostatic pressure assists hydration by driving the components of the following reaction to a state of lesser volume:

$$CaSO_4 \text{ (anyhydrite)} + 2H_2O \text{ --------------- } CaSO_4.2H_2O \text{ (gypsum).}$$

However, when lithostatic pressure exceeds the hydrostatic pressure and confined water is allowed to escape, the equilibrium temperature for the above reaction is lowered. Several investigators also postulated that certain salt solution decreases the solubility of anhydrite relative to gypsum to the point that anhydrite is the stable phase at temepratures well be below 42°C. This change in solubility is based on thermodynamic consideration of vapour pressure relationships by Posnjak (1940), MacDonald (1953) and Kelly *et al.* (1941).

Hennicke (1923) introduced in Germany a mortar-forming process which utilized solution of "alkali salts; acids and bases" with ground anhydrite. These solutions accelerated the hydration process. Further investigations of acceleration processes have been carried out by Ottemann (1950) and Gelmorth (1953).

Leiniger *et al.* (1957) determined the relative effectiveness of activators yielding the following qualitative series:

$$K^+ > Na^+ > NH_4^+ > Mg^{++} > Fe^{++} > H^+ > Al^{+++} > Ca^{++} \text{ and } SO_4^{--} > Cl^- > OH^-.$$

Conly and Bundy (1958) investigated potassium and sodium sulphate in detail because of their efficiency in activation and their presence in natural water. They came to the conclusion that the direct precipitation of anhydrite from sea water is unlikely. They also studied the phase rule and reaction velocity which indicated that accelerated hydration of anhydrite takes place through the medium of transient surface complexes in dilute solution and that concentrated solutions may precipitate double salts.

Hamori (1976) described the process of hydration of Hungarian natural anhydrite, which is activated by a mixture of portland cement and potassium acid sulfite for use in the building industry. In order to observe the hydration process, the natural anhydrite was activated by a mixture of lime and sodium sulphate or by portland cement and sodium sulphate.

The properties of expansive anhydrite mortar (P-900) are described by Janiczek *et al.* (1980). This mortar, when activated (*e.g.* with Na_2CO_3), has a relatively short setting time and high compressive strength. Expanding agents are $NaHCO_3$ or NaH_2PO_4 and the mortar is suitable for guniting in mines.

The development of an anhydrite plaster was discussed by Singh *et al.* (1981). A number of accelerators were tested through temperature and humidity conditions.

Kamel (1990) discussed the effect of $(NH_4)_2SO_4$; Na_2SO_4 and Na_2CO_3 as accelerators on Egyptian anhydrite and studied the mineralogy, rate of gypsification, physico-mechanical properties and the microstructure of anhydrite after the treatment by these activators.

Experimental Work

A representative channel sample was collected from the anhydrite deposits at Ras Malaab area. The chemical composition of this sample was determined. The percentage by weight of its oxides is as follows:

SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	SO_3	L.O.I
Nil	Nil	0.33	Nil	35.65	1.69	0.44	0.15	46.26	15.05

The mineralogical composition of the sample was determined using X-ray diffraction technique. The diffraction pattern is given in Fig. (1). The chemical and mineralogical composition of the sample indicate that it has a very low percentage of gypsum mixed with anhydrite.

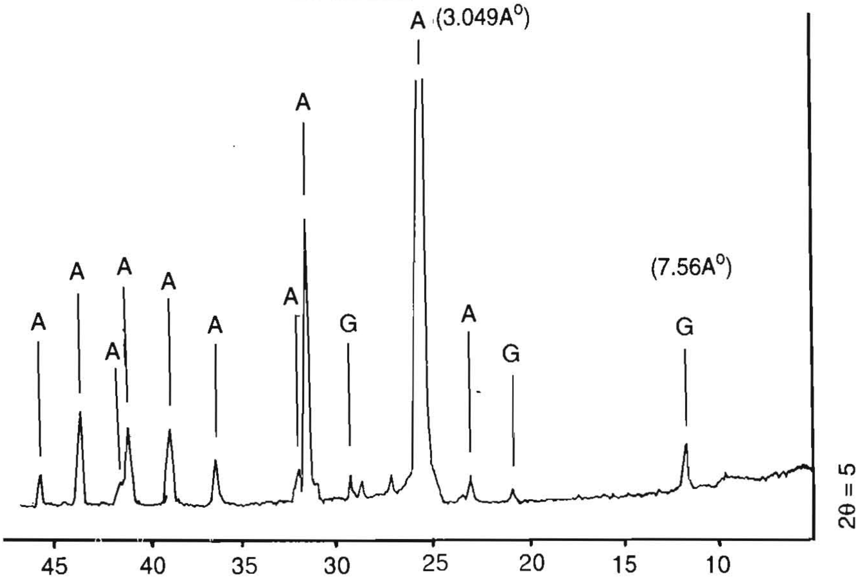

Fig. 1. X-ray diffraction pattern of natural anhydrite collected from Ras Malaab area, Gulf of Suez region, Egypt.
G = Gypsum A = Anhydrite

The representative sample was ground to pass a 90 micron sieve. Different percentages of chemical activators were added to the natural anhydrite at 1%, 2% and 3% by weight (with respect to natural anhydrite). The chemical activators used in this work were $ZnSO_4$, K_2SO_4 and $MnSO_4$. They were chosen to vary in oxidation states. These were mixed with water using a w/s ratio : 0.3. The slurry was mixed by stirring for 2 minutes then poured into two inches cubes. After one day, the cubes were demoulded and cured at room temperature. The mineralogical composition was determined, using X-ray diffraction, after 7, 14, 21 and 28 days.

Dry and wet compressive strength, bulk density, water absorption and apparent porosity were measured for the demoulded cubes at 7, 14, 21 and 28 days.

Results and Discussion

Attempts have been made to explain the acceleration of transformation on the basis of changes in the solubility of calcium sulphate, (Rohland 1908). Researchers who embraced the gel theory explained acceleration in terms of lyosorption and gelatin.

Acceleration of gypsification process may also occur by one of the following mechanisms:

1. In case of reduction of the induction period which could be brought about either by:
   i) Increasing the effective initial surface area.
   ii) Increasing the rate of supply to the growing lattice.
2. The main effect of accelerators is to modify the rate at which calcium sulphate is transformed to and built into the lattice of the growing phase (gypsum).
3. The most likely mechanism is that accelerating salts increase the rate of dissolution of anhydrite.

The rigidity of plaster in general is due to the development of a skeleton of interlocking crystals. It is evident that the strength of the formed mould will depend upon:

a) The shape and size of the component crystals.
b) The strength of the bond between the various crystals.
c) The strength of the individual crystals.
d) The amount of empty space in the set mass, which is determined by the water content of the mixture, (Ridge 1960).

X-Ray Diffraction Analysis

The X-ray diffraction pattern of natural powder anhydrite is illustrated in Fig. (1) which shows the main mineral is anhydrite (3.049 A°) with traces of gypsum (7.56A°). Crystal structures present in amounts less than 5% may not be detected by this method.

The addition of $ZnSO_4$ in different percentage (1, 2 and 3%) may lead to the conversion of anhydrite into gypsum, which increases systematically with both the time of curing and $ZnSO_4$ addition from 1% to 3% (Fig. 2). This result can be noted by the relationship between the heights and areas of the two peaks : 2.867 A° (gypsum) and 2.849 A° (anhydrite).

The efficiency of K_2SO_4 as chemical activator for the hydration process of anhydrite was also studied and shown in Fig. 3. Generally, the rate of hydration is slower than in mixtures using $ZnSO_4$. Curing time plays an important role in transformation, but the increase in additive percentage up to 3% of K_2SO_4 leads to decrease in the rate of conversion. In fact, the addition of more than 3% of K_2SO_4 will reverse the hydration reaction.

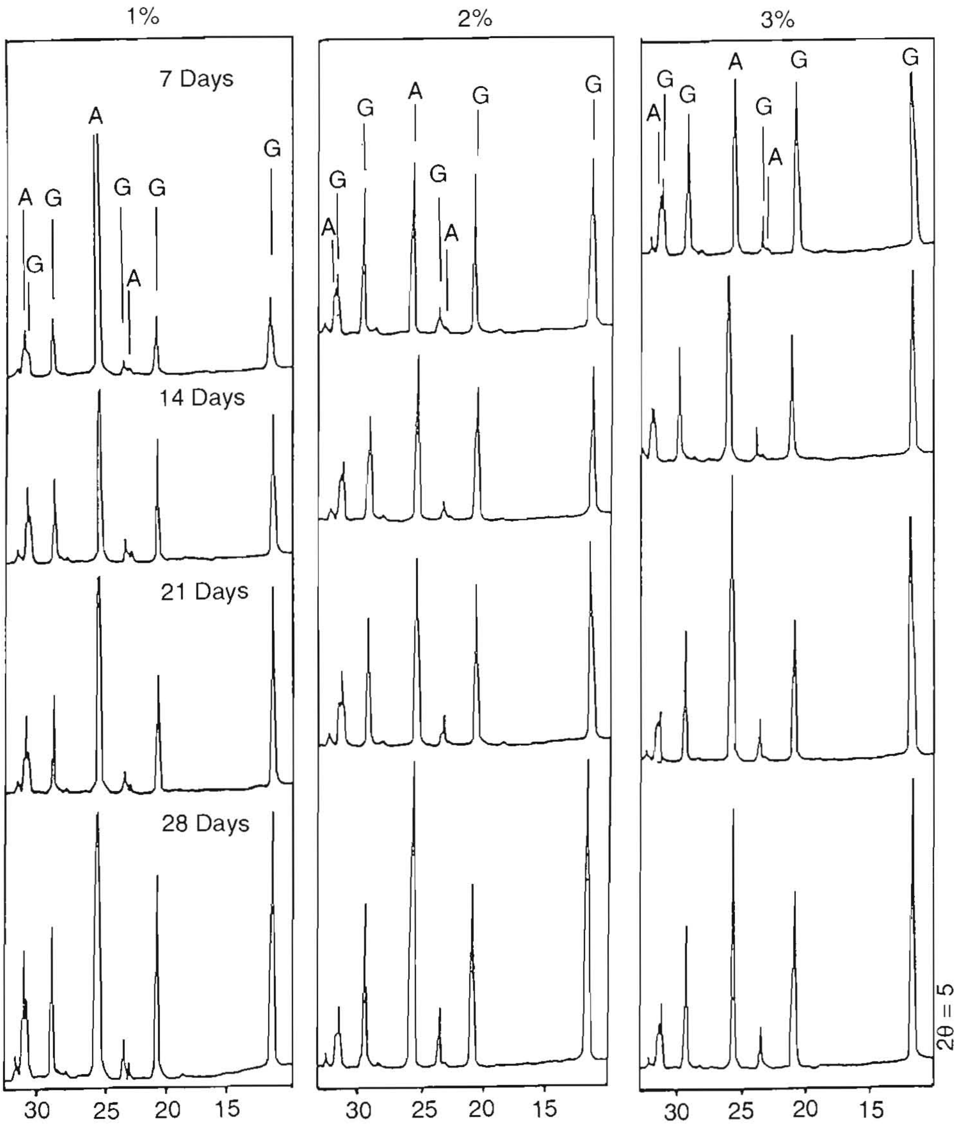

Fig. 2. X-ray diffraction patterns of natural anhydrite containing 1%, 2% and 3% of $ZnSO_4$ at different curing times. (Cu-kα radiation).
A: Anhydrite G: Gypsum

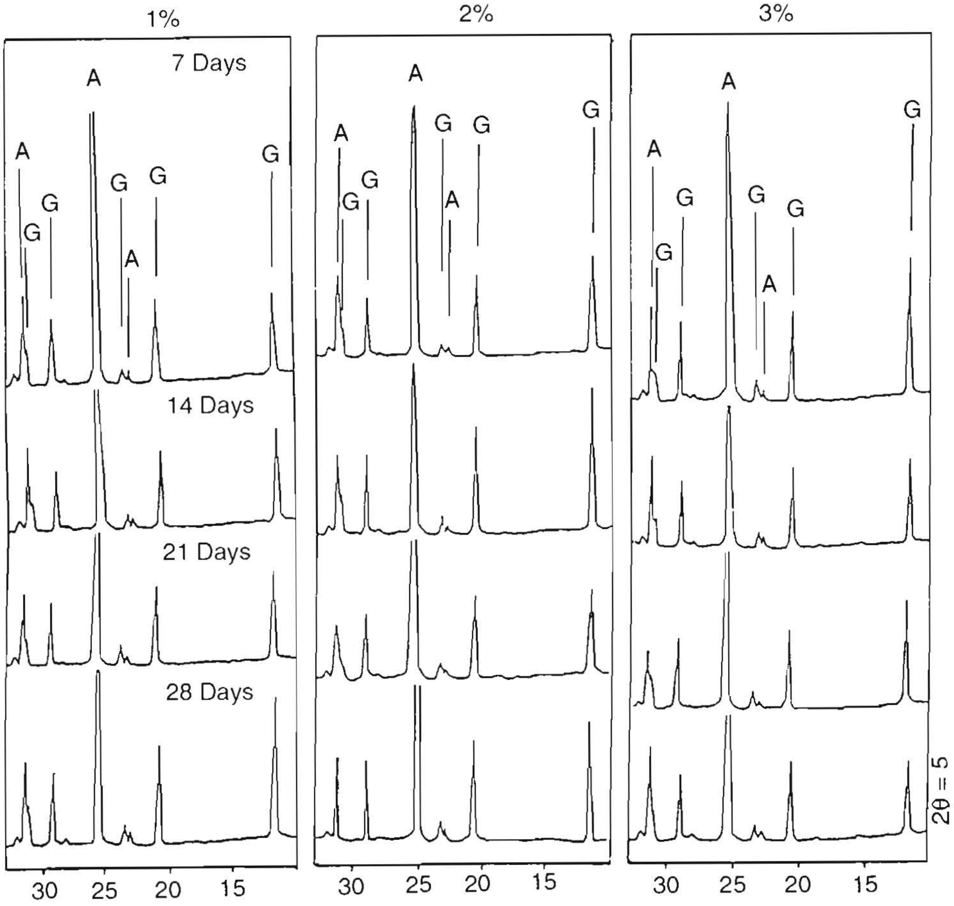

Fig. 3. X-ray diffraction patterns for natural anhydrite containing 1%, 2% and 3% of K_2SO_4 at different curing times. (Cu-kα radiation).
A: Anhydrite G: Gypsum

Acceleration of the transformation reaction by the addition of $MnSO_4$ is increased with an increase of the two main factors: 1- time of curing and 2- percentage of additives. The variation in the peak area of gypsum at 7.56 A° with the increase in curing and quantity of added $MnSO_4$ used is shown in Fig. (4).

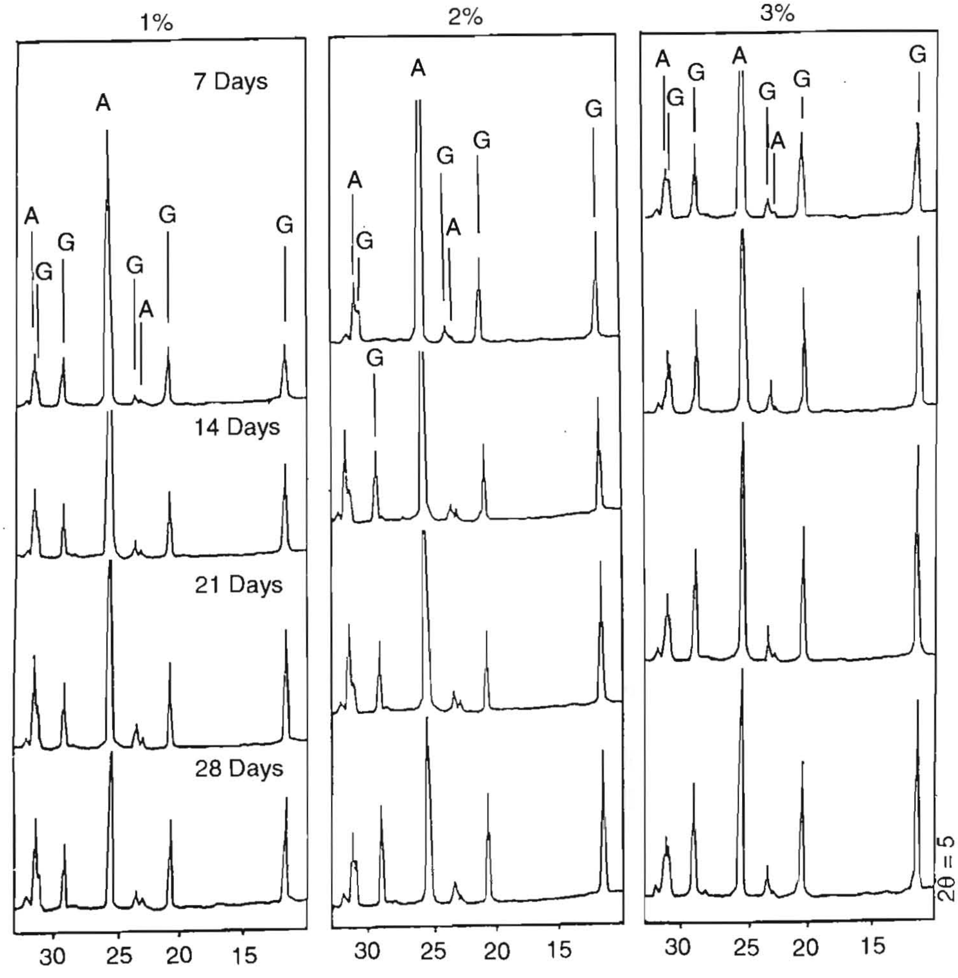

Fig. 4. X-ray diffraction patterns for natural anhydrite containing 1%, 2% and 3% of $MnSO_4$ at different curing times. (Cu-kα radiation).
A: Anhydrite G: Gypsum

Physico-Mechanical Properties

The interrelationship between dry compressive strength at different percentages of activator salts added and time of curing are illustrated in Fig. 5 (a, b & c). Generally, the increase in the percentage of activators added from 1% - 3%, lead to a decrease in the strength.

Salts that produce high dry strength values produce also high wet compressive strength values. Values of wet compressive strength are about 60% of the dry compressive strength, Figs. 6 (a, b & c).

Examination of Fig. 7 (a, b & c) shows that salts which have the maximum strength values, either wet or dry, would have the maximum bulk density values. The variation in compressive strength (dry and wet), as well as bulk density values is due to the effect of the gypsification process. Gypsum formed due to this process fills empty spaces in the cube sample. Variation in the ability of accelerator salts to transform anhydrite into gypsum depends upon the type of salt and quantity added.

The relationship between apparent porosity and curing time, Fig. 8 (a, b & c) confirms the above relations, in which the apparent porosity is a reflection of the water absorption, Figs. 9 (a, b & c). As the curing time increases the apparent porosity decreases.

The activators may work in many ways, and the results may differ depending on type of salt, the percentage added and their arrangement in the Hofmeister series. The addition of different quantities of these salts may affect the solubility of anhydrite, change the effective initial surface area of anhydrite and modify the rate at which anhydrite is transformed to and built into the structure. The gypsification process (number of gypsum crystal formed) has a great effect on the physico-mechanical properties. Theoretically, the transformation process needs about 21% water to transform all anhydrite into gypsum. It was found, however, that the addition of 30% water is necessary for the process for workability. The difference between these two figures may be computed as empty spaces and may be filled with new gypsum crystals.

Microscopic Work

Photographs of anhydrite treated with different chemical activators : $ZnSO_4$, K_2SO_4 and $MnSO_4$ at 7 and 28 days of curing are shown in Figs. 10 and 11.

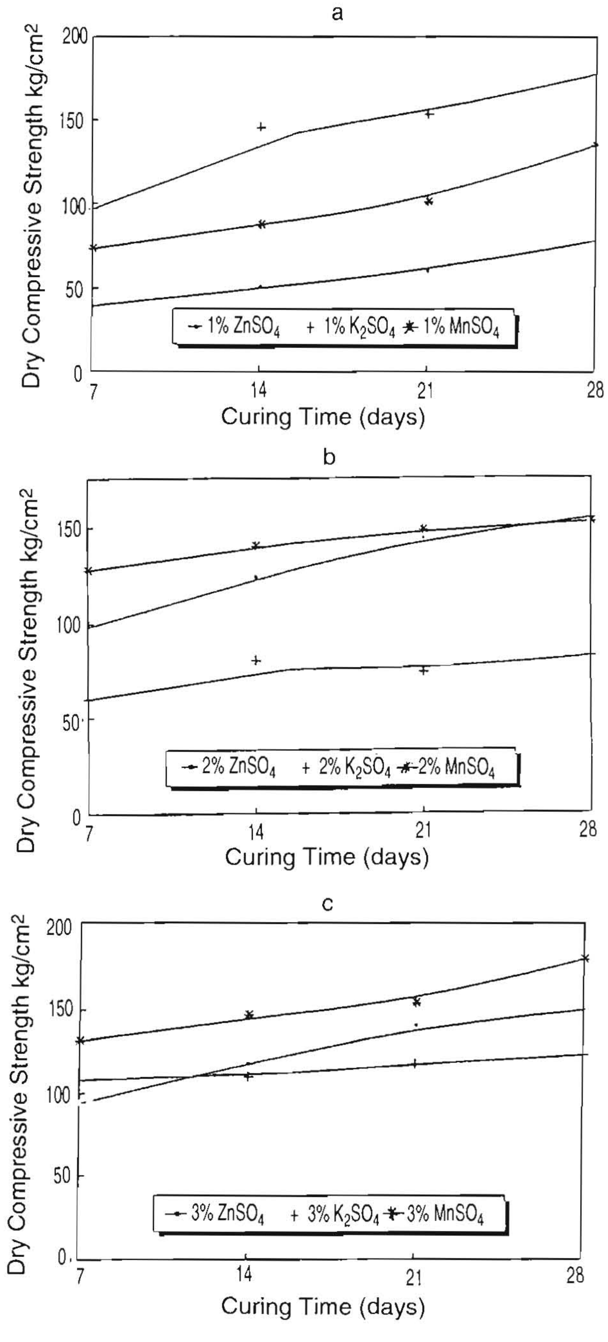

Fig. 5. Relationship between dry compressive strength and curing time using 1%, 2% and 3% of different chemical activators.

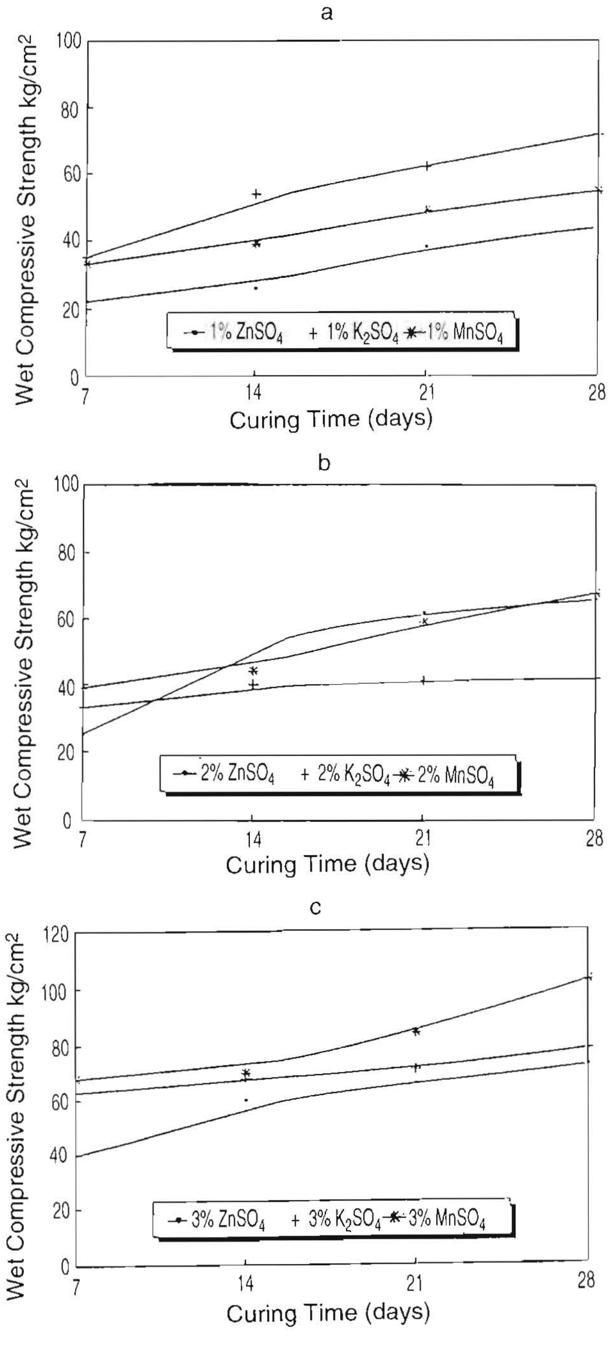

Fig. 6. Relationship between wet compressive strength and curing time using 1%, 2% and 3% of different chemical activators.

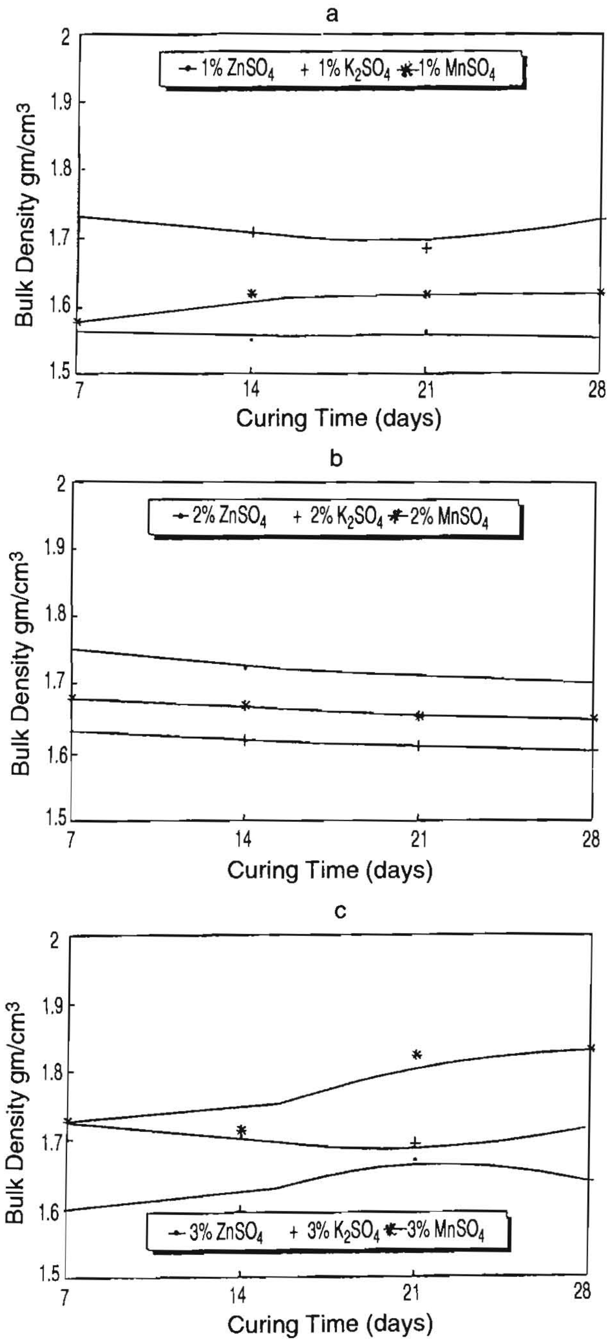

Fig. 7. Relationship between bulk density and curing time using 1%, 2% and 3% of different chemical activators.

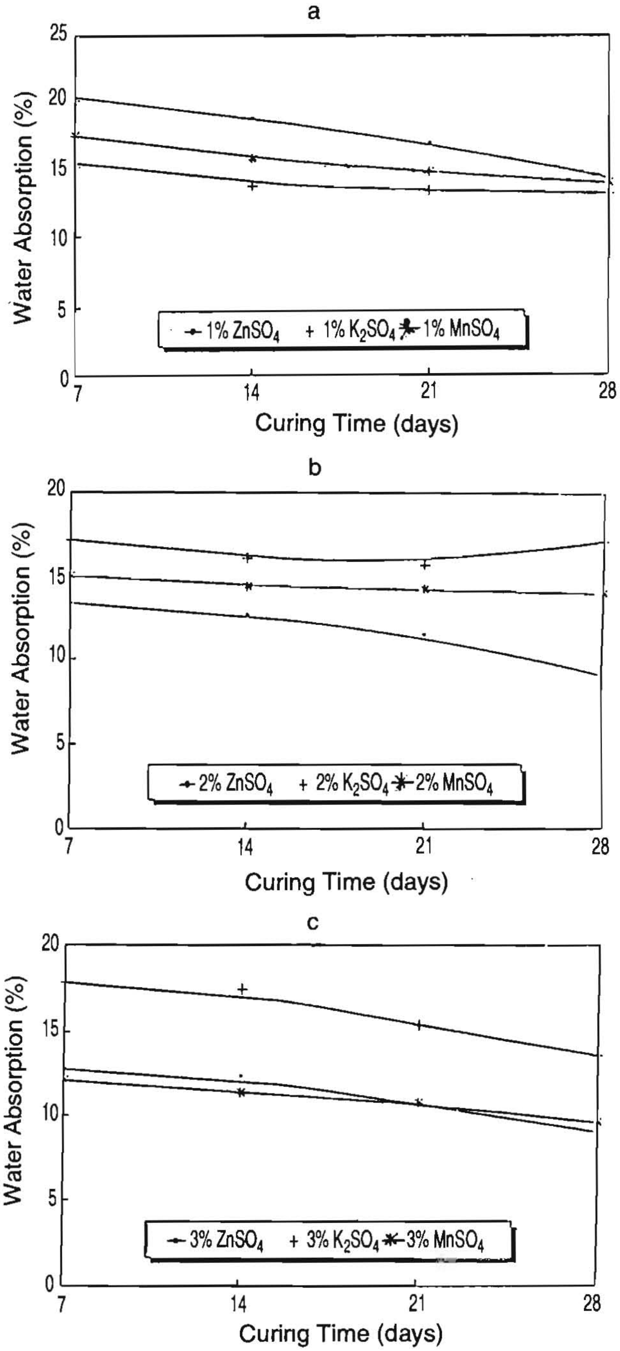

Fig. 8. Relationship between water absorption and curing time using 1%, 2% and 3% of different chemical activators.

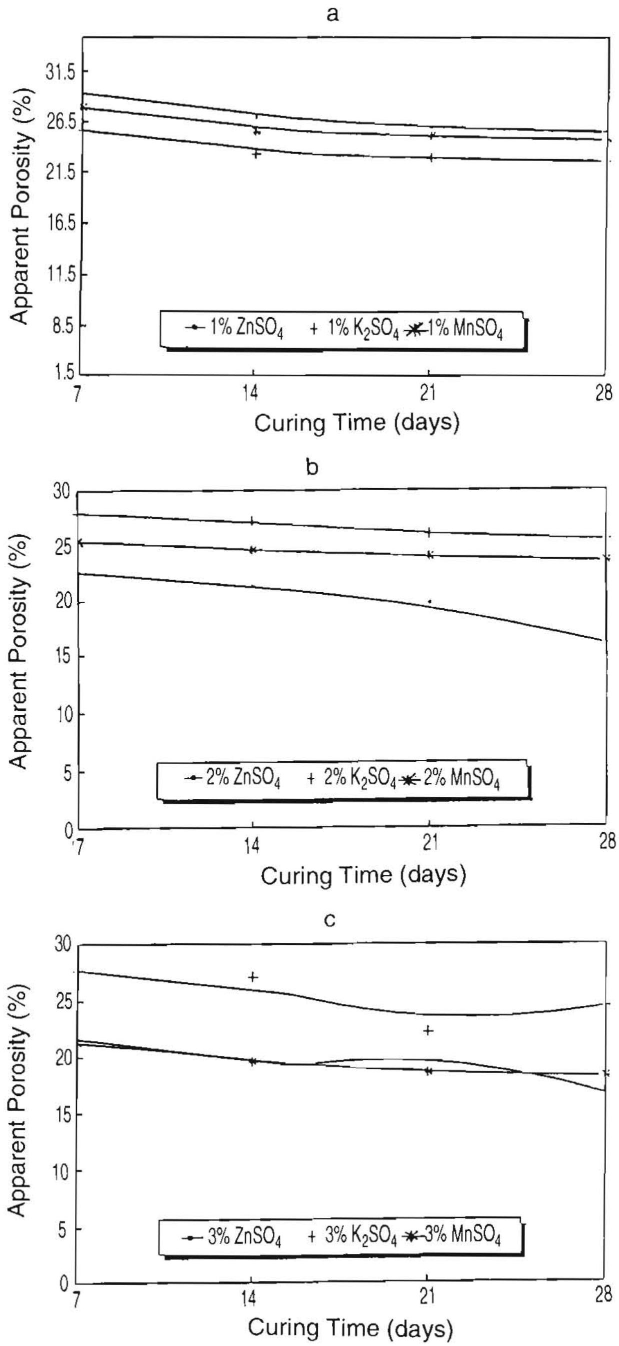

Fig. 9. Relationship between apparent porosity and curing time using 1%, 2% and 3% of different chemical activators.

The use of $ZnSO_4$ affects the microstructure of anhydrite crystals. The process of transformation into gypsum attack the (001) plane of anhydrite crystals, Fig. 10 (A&B) appearing as a white rind along the edges. The same feature is seen in samples treated with K_2SO_4 as shown in Fig. 10 (C&D). The anhydrite crystals show rod-like shape. Hardie (1967) believed that this rind is a form of bassanite or hemihydrate, but the current author does not believe so, because XRD does not show that.

When $MnSO_4$ is used in the transformation process, gypsum crystals attack the anhydrite crystal along the (001) direction as in Fig. 10 (E), and corroded the edges and boundaries to form new, small needle-shaped crystals of gypsum. These recrystallized during curing into elongate crystals of gypsum parallel to (010) and (110) as shown in Fig. 10 (F).

These results were examined and checked using SEM. Figures 11(A) to 11(F), show in detail the gypsification process of anhydrite crystals and where it does take place. In Fig. 11 (A), in which $ZnSO_4$ was used as the chemical activator, the anhydrite crystals are characterized by a dark center (anhydrite) surrounded by a small white-rind (gypsum). This sample taken after 7 days of curing. After 28 days of curing, Fig. 11 (B), the gypsification process is dominant and the attacked anhydrite crystals have begun to connect to each other (grain to grain boundaries) to form a white patch made up of gypsum.

The use of K_2SO_4 as an accelerator for the gypsification process is reflected in Fig. 11 (C&D), showing anhydrite crystals parallel to (001) and (100) with dark centers after curing for 28 days. Fig. 11 (D), shows gypsum growing on the cleavage planes parallel to (001) and (010). The same features were recorded when $MnSO_4$ was used as shown in Figs. 11 (E) and 11 (F), at 7 and 28 days of curing, respectively. The relationship between the newly formed gypsum and the altering anhydrite due to the use of the chemical activators explain the high strength and low values of water absorption of treated samples.

Conclusions

The gypsification process of natural anhydrite is affected by many factors. These factors can be summarized as follows:

1- The concentration of activator salts added to the natural anhydrite is important. Three concentrations are used in this work, (1%, 2% and 3%

$ZnSO_4$, K_2SO_4 and $MnSO_4$). The increase in the concentration of accelerator was accompanied by an increase in the gypsification rate for $MnSO_4$ and $ZnSO_4$ but not for K_2SO_4.

2- Time of curing, will affect the rate and quantity of gypsum crystals formed.

The present work shows that the transformation process could be affected by other factors in addition to the above. These factors are:

1- The difference in potentials in acid solution containing the following cations:

Zn > Mn > Ca > K
–0.76 –1.18 –2.87 –2.93

2- The difference in electronegativity:

Zn > Mn > Ca > K
1.70 1.50 1.0 0.80

These differences in potentials and electronegativity lead to an increase in the ability of Ca ion to be affected by other elements higher in the series. These two reasons could explain the conclusion of Ridge (1960), which showed a low efficiency of K_2SO_4 on the formation of gypsum nuclei.

3- The third factor is that the Zn and Mn elements are amphioteric elements which have the ability to gain or lose elements, and this phenomenon has a great effect on the transformation of anhydrite into gypsum.

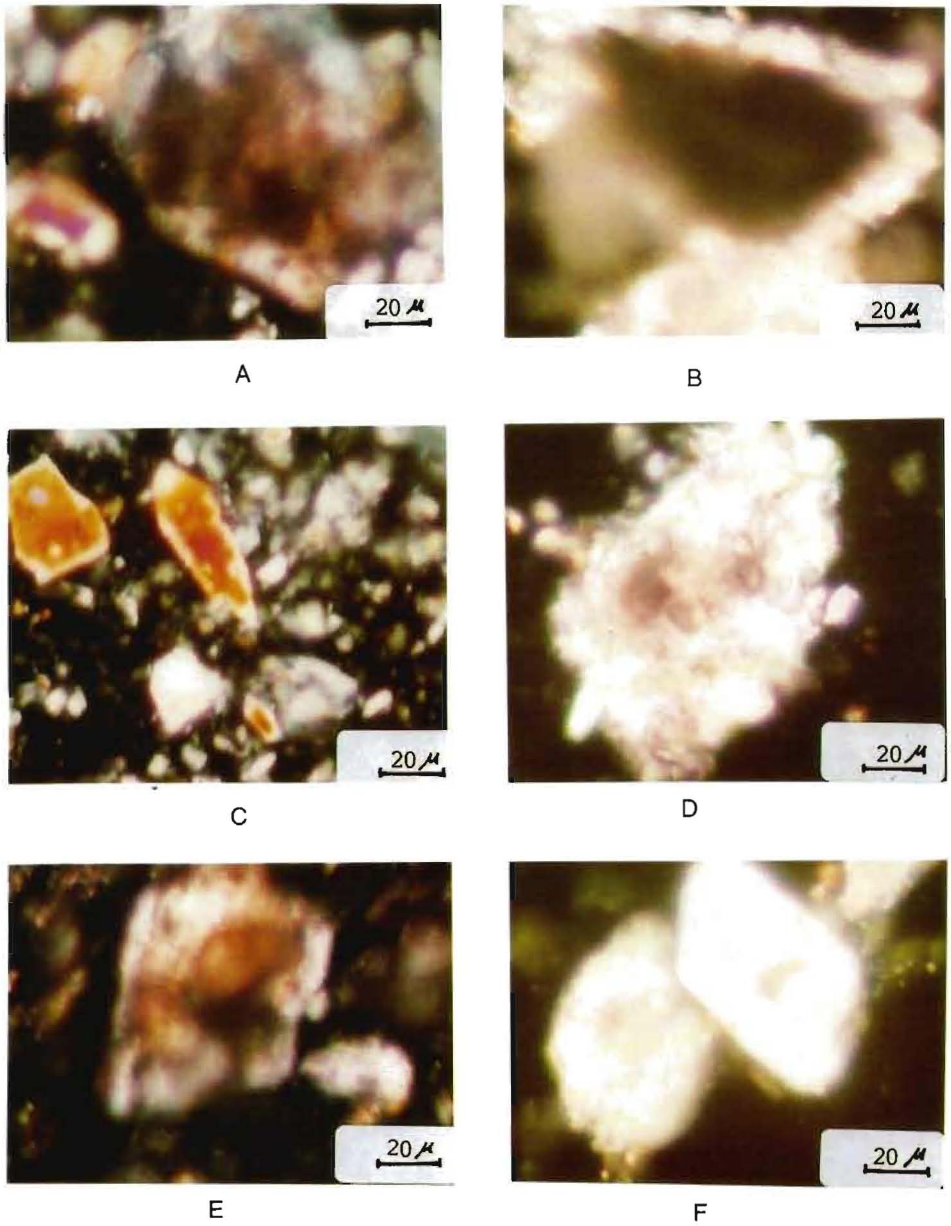

Fig. 10 (A and B). Anhydrite activated by $ZnSO_4$ and cured at 7 and 28 days, C.N.
(C and D). Anhydrite activated by K_2SO_4 and cured at 7 and 28 days, C.N.
(E and F). Anhydrite activated by $MnSO_4$ and cured at 7 and 28 days, C.N.

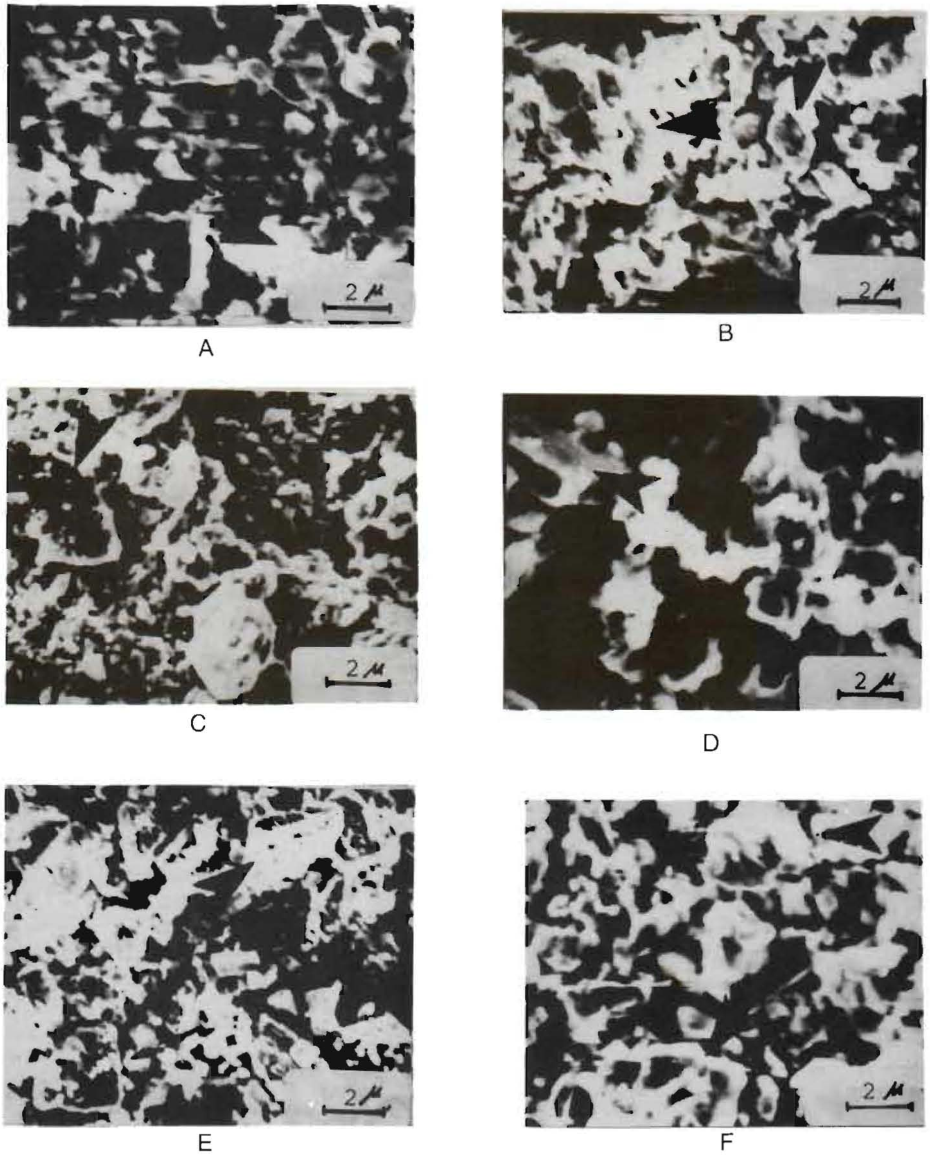

Fig. 11 (A and B). Gypsified anhydrite accelerated by $ZnSO_4$ and cured at 7 and 28 days, respectively, SEM.

(C and D). Gypsified anhydrite accelerated by K_2SO_4 and cured at 7 and 28 days, respectively, SEM.

(E and F). Gypsified anhydrite accelerated by $MnSO_4$ and cured at 7 and 28 days, respectively, SEM.

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الخصائص المجهرية والفيزيو – ميكانيكية لخام الانهيدريت المتحول باستخدام منشطات الكبريتات

علي أيمن عبد المنعم كامل

معهد بحوث البناء – ص .ب ١٧٧٠ – القاهره – مصر

توجد رواسب الانهيدريت الطبيعي بمنطقة رأس ملعب –خليج السويس – مصر – بكميات كبيرة إما على هيئة غطاء صخري متحول يغطي رواسب الجبس الضخمة بالمنطقة والتي تبلغ عدة ملايين من الاطنان أو على هيئة عدسات داخل خامة الجبس نفسها . ونظراً لوجود هذه الرواسب من خام الانهيدريت تعتبر منتج ثانوي لا يستخدم الاستخدام الأمثل . فقد كان هدف هذا العمل هو إمكانية استخدام هذه الكميات الكبيرة من الانهيدريت المجوى في صناعات مواد البناء . وذلك بإستخدام بعض أملاح الكبريتات المنشطة لعملية التحول من الانهيدريت (كمادة هشه ومجواه) إلى الجبس (مادة صلده يمكن تشكيلها واستغلالها) . وهذه الأملاح هي : كبريتات الزنك – كبريتات البوتاسيوم وكبريتات المنجنيز .

ويأتي الاهتمام بهذه الدراسة من انتشار مناطق استخراج وتصنيع الجبس في الوطن العربي ووجود خام الانهيدريت كمنتج ثانوي طبيعي لعملية التجوية لخام الجبس كعائق طبيعي في عملية التعدين .

وتمت دراسة ومناقشة الخصائص الفيزيو–ميكانيكية للانهيدريت المتحول باستخدام أملاح الكبريتات المنشطة مثل القابليه للانضغاط (جاف ومبتل) –الوزن

الحجمي - إمتصاص المياه وكذلك المساميه الظاهرية .

وقد تم استخدام الاشعة السينية المتفرقة لتحديد نسبة الجبس المتحول من الانهيدريت عند مدد زمنية مختلفة (٧ - ١٤ - ٢١ - ٢٨ يوم) . وكذلك تمت دراسة هذه العمليه التحولية للانهيدريت إلى جبس باستخدام المجهر المستقطب والمجهر الاليكتروني الماسح لدراسة التغير في التركيب الدقيق للبلورات وربط هذه التغير بالتغير في الخواص الفيزيوميكانيكية للمنتج الجديد .

وقد توصل الباحث إلى أن هناك عدة عوامل تؤثر على عملية تحويل الانهيدريت إلى جبس مثل النسبة المضافه من الملح المنشط ، الوسط الأيوني الهيدروجيني ، زمن التخمر ، والاختلاف في الخواص الكهروكيميائية السالبة لعناصر الاملاح المنشطه مثل المنجنيز والبوتاسيوم والزنك . بالاضافة إلى وضع هذه العناصر في الجدول الدوري .

وقد أثبتت التجارب ، أنه يمكن تصنيع مادة بناء ذات خصائص فيزيو-ميكانيكية جيده بقوة تحمل كبيرة من خامة الانهيدريت عند معالجتها بهذه الاملاح الكبريتية المنشطة .