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Economically the Sivas Basin Natural Anhydrite Potential, Reserve Estimation and Geochemical Characteristics, Central Anatolia, Türkiye

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Abstract

This study focuses on the economization of natural anhydrite, which has a wide range of uses and is environmentally friendly, in Türkiye. Anhydrite, which is one of the most common evaporitic minerals in the world, has almost no usage area in Türkiye. Evaporite deposits consisting of gypsum, anhydrite, halite, bassanite and selenite are prominent in the country, especially in Tertiary period sedimentary basins. The Sivas basin is one of these important Tertiary basins. Mining operates in the basin are carried out only on gypsum and anhydrite is not utilized. This study is carried out on the geological and geochemical characteristics of anhydrite, which is prominent with its usage areas in the world, its potential in the basin and its economic importance. The geochemical and mineralogical analyses are carried out on anhydrite samples taken from the basin. Anhydrite formations up to 300 meters in thickness are detected in the evaporite deposits that outcrop in most of the basin. In addition, a block model is extracted from the drilling data of a mining company operating in the basin and the reserve is calculated. As a result, it is concluded that the Sivas basin has a high potential in terms of anhydrite and should be brought to the national economy.

Keywords: Evaporite, Natural anhydrite, Calcium sulphate, Cement mortar, Nature friendly

Ekonomik Açıdan Sivas Havzası Doğal Anhidrit Potansiyeli, Rezerv Tahmini ve Jeokimyasal Özellikleri, Orta Anadolu, Türkiye

Öz

Bu çalışma, geniş bir kullanım alanına sahip olan ve çevre dostu olan doğal anhidritin Türkiye'de ekonomik hale getirilmesine odaklanmaktadır. Dünyadaki en yaygın evaporitik minerallerden biri olan anhidritin Türkiye'de kullanım alanı yok denecek kadar azdır. Türkiye'de özellikle jips, anhidrit, halit, bassanit ve selenitten oluşan evaporit yatakları Tersiyer çökel havzalarında belirgindir. Sivas havzası da bu önemli

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Tersiyer havzalarından biridir. Havzada madencilik faaliyetleri sadece jips (alçıtaşı) üzerinde yapılmakta olup, anhidrit işletilmemektedir. Bu çalışma, dünyada kullanım alanları ve ekonomik önemi ile ön plana çıkan anhidritin havzadaki potansiyeli, jeolojik ve jeokimyasal özellikleri üzerine gerçekleştirilmiştir. Havzadan alınan anhidrit numunelerinde jeokimyasal ve mineralojik analizler yapılmıştır. Havzanın büyük bir bölümünde yüzeyleyen evaporit yataklarında kalınlığı 300 metreyi bulan anhidrit oluşumları tespit edilmiştir. Ayrıca havzada faaliyet gösteren bir maden şirketinin sondaj verileri kullanılarak blok model çıkarılmış ve rezerv hesabı yapılmıştır. Sonuç olarak Sivas havzasının anhidrit açısından yüksek bir potansiyele sahip olduğu ve ülke ekonomisine kazandırılması gerektiği sonucuna varılmıştır.

Anahtar Kelimeler: Evaporit, Doğal anhidrit, Kalsiyum sülfat, Çimento harcı, Doğa dostu

1. INTRODUCTION

Gypsum, halite, and anhydrite are the most common sulfide minerals in the earth's crust. Gypsum ($CaSO_4.2H_2O$) occurs mostly as a chemically deposited sedimentary rock in a basin or sabkha environments. However, it can also occur as a result of the hydrothermal fluids, karstification and volcanogenic processes [1]. Anhydrite occurs as a primary mineral in a sabkha depositional or in deep basin environments. Anhydrite is also defined as anhydrous gypsum or anhydrous calcium sulfate in terms of rock formation. Gypsum and anhydrite can deposit simultaneously in a sedimentary environment. They have the ability to change into each other depending on the temperature, pressure properties of the environment and the conditions of being aqueous and/or anhydrous. These changes can sometimes be reversible [1-2].

When anhydrite is mixed with water, it can turn back into a solid and stable material such as gypsum dihydrate ($CaSO_4.2H_2O$) without the need for another linker [3]. Anhydrite and gypsum can be deposited in a very complex structure in an evaporite sedimentary environment. In order to reveal the characteristics of these deposits, many geological features such as field observations, petrographic examinations and geochemical analyses, depositional type, and structural/tectonic features should be examined.

Sivas basin is one of the important Tertiary basins where evaporitic sediments are intensively outcropped in Türkiye. In recent years, mining operations have been carried out in gypsum suitable for production at the upper levels of these evaporitic deposits to be used in gypsum production. As of 2022, gypsum production is carried out by open pit mining in five different areas in the region. In the production sites, anhydrite formations at the base levels in many areas of evaporitic sediments are left unoperated in the fields. This research is carried out because anhydrite, which has great potential in Turkey, especially in the Sivas basin, has almost no usage areas in the country. In this study, the usage areas of anhydrite in our country and in the world, laboratory studies on the geochemical properties of anhydrite in the Sivas basin, and reserve calculations for its potential are presented.

2. ANHYDRITE USAGE AREAS

Anhydrite and uncalcined gypsum are utilized in practically identical industries. Anhydrite is primarily used in the production of cement, alum plaster, ceramics, fillers, building materials, construction plasters, soil improvement, fertilizer, and sulfuric acid, as well as desiccant in pharmaceutical tablet products and bakery goods [4-8]. On the other hand, [9] suggested that calcium sulfate (dihydrate or gypsum) is suitable for use in construction and mold making, while anhydride or anhydrous calcium sulfates are suitable for use as fillers in various applications such as paints, plastics, rubber, coatings and cement.

Gypsum and anhydrite are used as SO_3 sources in the cement industry. After the crushing and grinding processes, gypsum, anhydrite, or a gypsum/anhydrite mixture is used as a setting retarder in the production process of Portland cement. According to [1], the addition of calcium sulphate also regulates the cement's early strength characteristics and product shrinkage throughout drying and curing. Portland cement's setting time is slowed down when small quantities of gypsum or anhydrite are added, although the cement's tensile strength is unaffected [10]. A study was carried out to evaluate the physicomechanical properties of samples obtained by adding different proportions of natural anhydrite to concrete mixtures. As a result of the study, it was stated that natural anhydrite added to concrete mixtures at certain ratios increased the strength and showed linking properties by acting like cement [2].

In the cement industry, calcium sulphate (gypsum or anhydrite) is one of the components of Portland cement that increases the time required for setting [11]. In another study, anhydrite ($CaSO_4$) and gypsum ($CaSO_4.2H_2O$) were mixed into two clinker samples at different ratios and compared in terms of strength. Accordingly, it was calculated that anhydrite samples had lower water demand, longer setting times, longer flow diameters, lower compressive strengths at 2 days, and higher compressive strengths at 7 and 28 days compared to gypsum samples. As a result, it was stated that it is possible to produce concrete with higher compressive strength and easier workability of anhydrite samples compared to gypsum samples [12]. In another study, the effectiveness of anhydrite in activating fly ash cement systems was investigated. In the study, it was concluded that the 3-day compressive strength of mortar containing up to 55% fly ash with the addition of 10% anhydride increased by approximately 70% and the strength increased in the following days. Mortar samples were achieved with a short initial curing period at high temperature (65 °C) before normal water curing. The activating effect of anhydride was significant for mortars prepared with early wet strength and high fly ash content, but less significant for advanced wet strength and low fly ash content.

The addition of anhydride also is caused smaller pore sizes and lower porosity for cement mortars with fly ash. Compared to gypsum in terms of equivalent SO_3 content, anhydrite is more effective in increasing the early wet strength but less effective than gypsum in increasing the later wet strength under the same curing conditions. However, when the comparison was made in terms of the same admixture amount, it was stated that the use of anhydrite is more advantageous since anhydrite is more effective in increasing the strength at both early and advanced wets. It is also stated that further research is needed as other properties of concrete containing anhydrite such as durability are not clear [13].

Anhydrite cement is widely utilized in the construction industry in many countries. It is gypsum calcined at high temperatures (600-700 °C) [14]. Alum plaster is a product obtained by mixing natural anhydrite or waste gypsum with a certain proportion of high viscosity α gypsum and increasing its adhesion and fluidity with additives. This plaster can also be applied with a high viscosity, pressure-resistant machine, and thanks to its fluidity, it can give a smooth surface with a hardness that can be walked on within eight hours. The high-strength hard wall plaster is also called gypsum cement. This plaster can also be used alone or as a mortar and is considered insoluble anhydride or semi-compound because it requires low-mixed water. It is also stated that the composition of this plaster may include various additives such as solidification retarder and/or accelerator and air entrainer [15].

Another important use area is in the agricultural industry, where gypsum and anhydrite have a beneficial effect on many crops. They can reduce the salinity of saline soils, increase the permeability of clay soils and provide sulfur, calcium and catalytic support to reduce fertilizer use and maximize crop production [11].

Anhydrite has also been used as a filler material in the coal mining industry in West Germany since the mid-1960s. Natural anhydrite can be grinded to less than 7 mm (30% is powder) and then mixed with water and an accelerator (Fe_2SO_4 and K_2SO_4) to produce a fast-hardening, high-strength product. This product can also be used to fill production-induced voids in underground mines [11]. Calcined anhydride has a high value added and has taken part in various industry sectors. It is used as an inert filler in plastics, as a linker or carrier for herbicides and pesticides in agricultural products and in pharmaceutical products such as aspirin tablets. It is also used as a desiccant and source of calcium in pizza dough and other bakery products. In addition, it absorbs moisture in products and can then be manufactured and stored without soaking for some time before use. Polyvinyl chloride (PVC) is used as a filler in thermoplastics such as vinyl siding, window frames, moldings, ducts and pipes, where the filler also provides acid resistance and low electrical conductivity and is also used in food packaging [1].

3. GEOLOGY OF THE SİVAS BASIN

After the closure of the Neo-Tethys ocean's northern branch during the Late Cretaceous–Early Paleocene period, The basin developed on a basement of Paleozoic–Mesozoic metamorphic, Jurassic–Cretaceous carbonate platform, and Mesozoic ophiolitic rocks overlying these units [16-19]. Tectonically, it is located between the Pontide, Kırşehir and Tauride tectonic units (Figure 1).

Upper Cretaceous (Maastrichtian) shallow marine limestones crop out at the bottom of the basin. Upper Maastrichtian-Paleocene volcano-sedimentary rocks and Paleocene-Eocene period volcanic and sedimentary rocks emplaced by cutting the basement rocks are located on this unit. Oligo-Miocene evaporitic deposits unconformably overlie these units. Upper Miocene-Pliocene units, which contain volcanic levels such as basalt in places, follow these units unconformably [19]. Young sediments of Pliocene-Quaternary unconformably overlie older units in different parts of the basin. Due to the fact that the Sivas basin has complex geology due to intense tectonic effects, it has been studied by researchers by dividing it into subgroups. Depending on the faults, it is divided into 4 different sub-basins: Pazarcık-Yıldızeli, Akçakışla-Düzyayla, Şarkışla-Celalli and Akkışla-Altınyayla [19]. According to the sedimentary sequences, they are divided into 5 groups as Maastrichtian-Paleocene (I), Eocene (II), Early Oligocene (III), Middle Eocene -Middle Oligocene (IV) and Late Miocene-Pliocene (V) [23].

The evaporitic deposits of the Sivas basin, which are the subject of this study, contain gypsum, anhydrite, halite, bassanite, selenite and occasional celestine formations and are outcrop in many areas of the basin (Figure 2). In recent years, many studies have been carried out on salt tectonics and hydrocarbon potential in the basin [16,23,24-36].

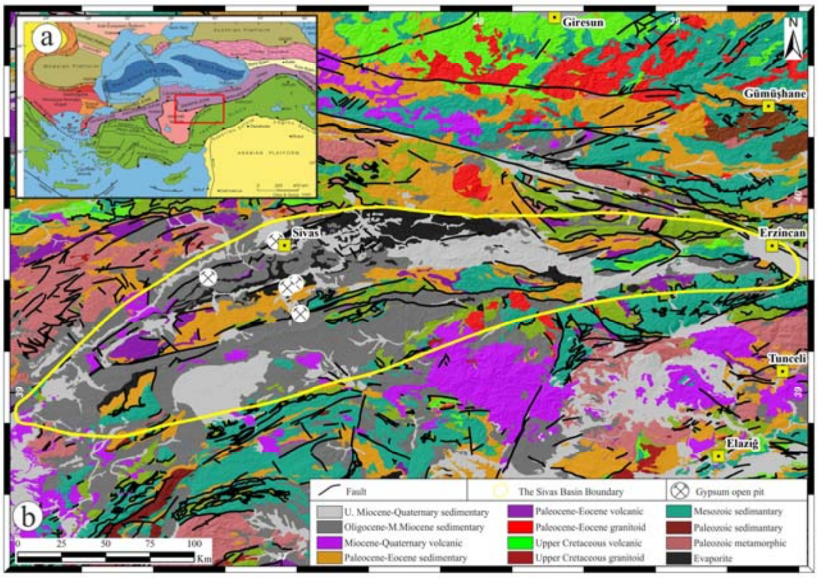

Figure 1. a) Turkey tectonic map [20], b) Geology of Sivas basin and its surroundings (simplified from [21])

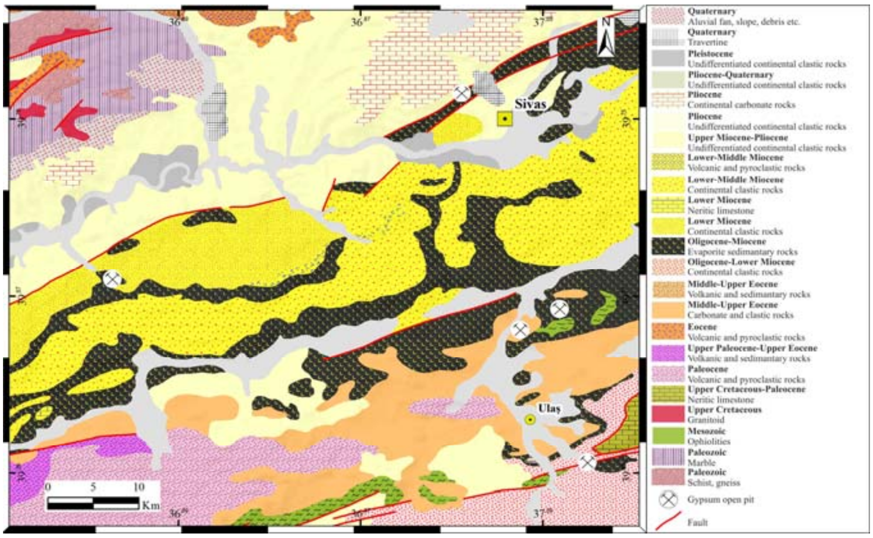

Figure 2. Geology map of the gypsum open pits and its surroundings (Simplified from [22])

The gypsum, which is outcrop in the northern part of the basin (Şarkışla-Celalli subbasin), is generally included in the Hafik Formation, which also includes sandstone, siltstone and conglomerate levels and consists of lagoonal deposits [26,27]. The thickness of the unit is reported to reach up to 750 meters. In the southern parts of the basin, it is named Tuzhisar, Küçüktuzhisar and Ortaköy Formations [25,37-41]. The thickness of the unit is reported to be 200-250 meters according to [40] and 500 m according to [42] The thicknesses of these units may vary from place to place. The main reasons for these differences are the uplifts due to intense tectonic activities in the basin [43] and diapiric uplifts due to salt tectonics [16,23].

4. ANHYDRITE POTANTIAL OF THE SİVAS BASIN

As of 2022, approximately 600,000 tons of gypsum was produced from five operating licensed sites within the Sivas basin borders. Approximately 45% of the production is used in cement factories and the remaining part is used in powder gypsum production in gypsum factories. These fields are within the borders of the Sivas province center and Ulaş and Yıldızeli districts. On the other hand, gypsum sites are planned to be operated in Gemerek district in the near future. Therefore, gypsum production will increase in the near future thanks to the powder gypsum and plate production facilities under construction in the region. In addition, the rich gypsum deposits in the Sivas basin constitute an alternative for cement factories in Southeastern Anatolia.

During the field studies where the gypsum mining sites near the southern parts of the basin, anhydrite layers are observed that the anhydrite is in the lower levels of the gypsum and not outcrop. The gypsum thicknesses are between 5 to 60 meters (Figure 3).

Since gypsum outcrops on the surface in the Sivas basin, it is relatively easy to reserve calculates. However, since anhydrite is under these gypsum units, drilling data are required to calculate its reserves. For this reason, the anhydrite potential of the site is modeled with the Micromine program, taking into account the drilling program carried out by a mining company operating in the region. Information on the location of the mining license area and exploration drilling logs cannot be given due to the agreement made during the acquisition of the drilling data. For block modeling, 64 exploration drillings with a total length of 5327 m are utilized. The drillings are distributed over an area of 310 m (N-S direction) x 930 m (E-W direction) with depths ranging from 12 m to 436 m.

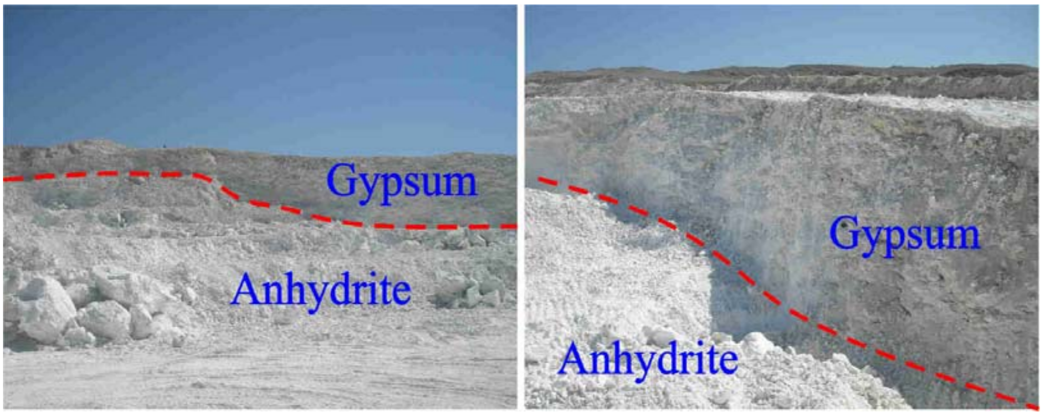

Figure 3. View from the evaporite deposits in the south of the Sivas basin.

The drilling elevations also vary between 1368.50 m and 1429.10m. The drilling data in the Excel file is imported into the package program and collar.dat, survey.dat, litho.dat, and assay.dat files are created. Subsequently, the drilling database was created and verified and the validity of the data was confirmed by determining that there were no missing or overlapping drillings, as well as no missing intervals in any drilling. Gypsum and anhydrite units were cut in the drillings. The dimensions of the sub-blocks forming the block model for the solid body were taken as 5 m in X, Y and Z directions. Thus, the volume of each sub-block is 125 m³. In addition, the block dimensions were allowed to be reduced by a factor of 5 for more precise modeling, especially at the points where the block intersects the land surface. Thus, a block of 1 m³ with dimensions of 1 m × 1 m × 1 m × 1 m can be formed in areas where the empty block model is in contact with another surface. To prepare the geologic block model, wireframe sets representing gypsum and anhydrite units were first created and then the spatial data of these wireframes were assigned to sub-blocks within the block model. A total of 722,435 blocks were calculated to create the solid body. Gypsum constituted 76.97% and anhydrite 23.03% of the blocks. The algorithm used for modeling was run based on the inverse square of the distance (IDP). The aim is to assign the composited gypsum and anhydrite data to all sub-blocks in the previously prepared block model on a distance-weighted basis using the anisotropic IDP algorithm embedded in the package program. The gypsum and anhydrite source block model and cross sections created with IDP is shown in Figure 4-6.

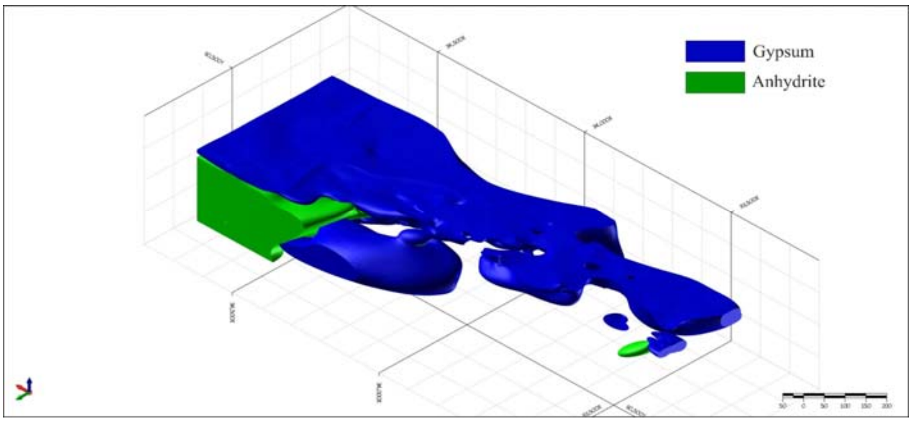

Figure 4. Gypsum and anhydrite resource block model with IDP (isometric view to the northwest)

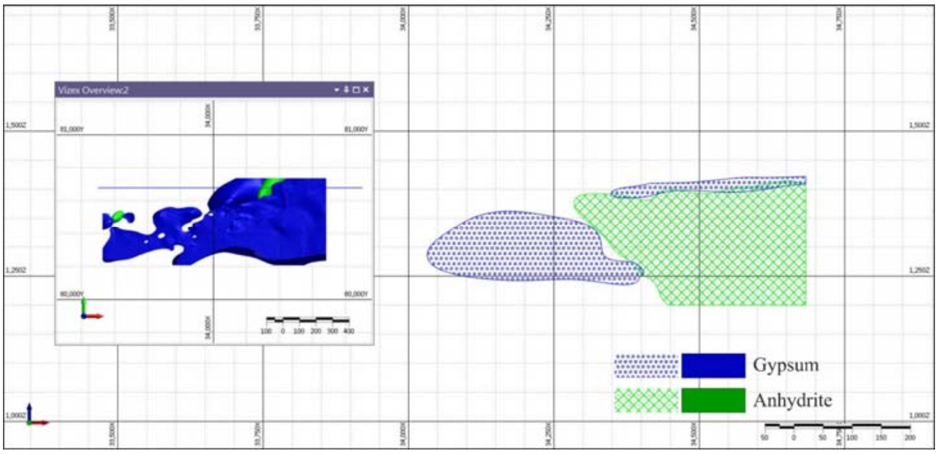

Figure 5. Cross section from the geological block model (view from the west)

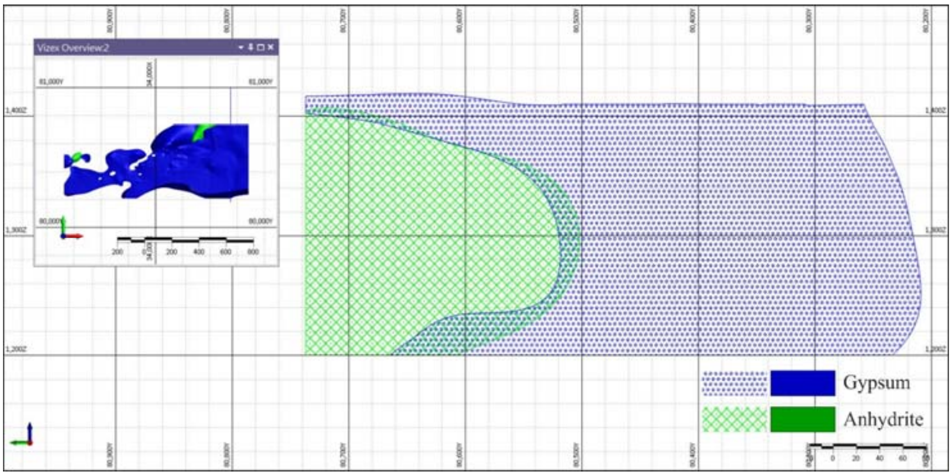

Figure 6. Cross section from the geological block model (view from the north)

5. LABORATORY RESULTS

Representative anhydrite samples collected during field studies were crushed and ground into powder samples for geochemical analyses and X-Ray Diffractometer (XRD) investigations. XRD, portable X-Ray Fluorescence (pXRF), and mineralogical analyses were performed in the study. XRD analysis was carried out at Istanbul Technical University, pXRF analysis at Sivas Cumhuriyet University and mineralogical analysis at Turkish Cement Industrialists' Association laboratories.

Bruker brand X-ray diffractometer was used for the extraction of X-ray diffractometer mineral patterns. The curves in the diagrams were extracted at 40 kV and 40 mA using Cu (copper) anode. K-Alpha1 [Å] value: 1,54060.

X-Ray Fluorescence analysis was performed by chemical analysis with a portable Thermo Scientific Gold+ brand XRF device. Mining Cu/Zn mode was kept for 120 seconds and analyzed.

Anhydrite is macroscopically white, gray, bluish, sometimes transparent, and semi-transparent in color and is generally observed in a massive structure (Figure 7a). According to the literature, the specific gravity of white anhydrite is 2.98 g/cm^3 and its hardness is accepted as 3.5 according to the Mohs hardness scale [44].

XRD, pXRF, and mineralogical analyses were performed on representative anhydrite samples taken from the mining sites in the basin. As an evaporitic mineral, anhydrite occurs together with other evaporitic minerals gypsum and halite. Therefore, gypsum and halite mineral patterns can also be observed on a minor scale, although gypsum is the main mineral detected in XRD analysis of powdered anhydrite samples (Figure 7b). The pXRF analysis shows the elemental distribution as S (39.04%), Ca (29.78%), Sr (1.20%) and trace amounts of other elements (Figure 7c). The reason for the observation of Sr element can be supported by the presence of celestine formations in the Sivas basin and the presence of celestine quarries operated from the past to the present. CaO (39.8%), SO_3 (56.9%), Crystal Water (3%), SiO_2 (<1%) and (Cl< 0.01%) values are also mineralogical analysis results of the anhydrite sample.

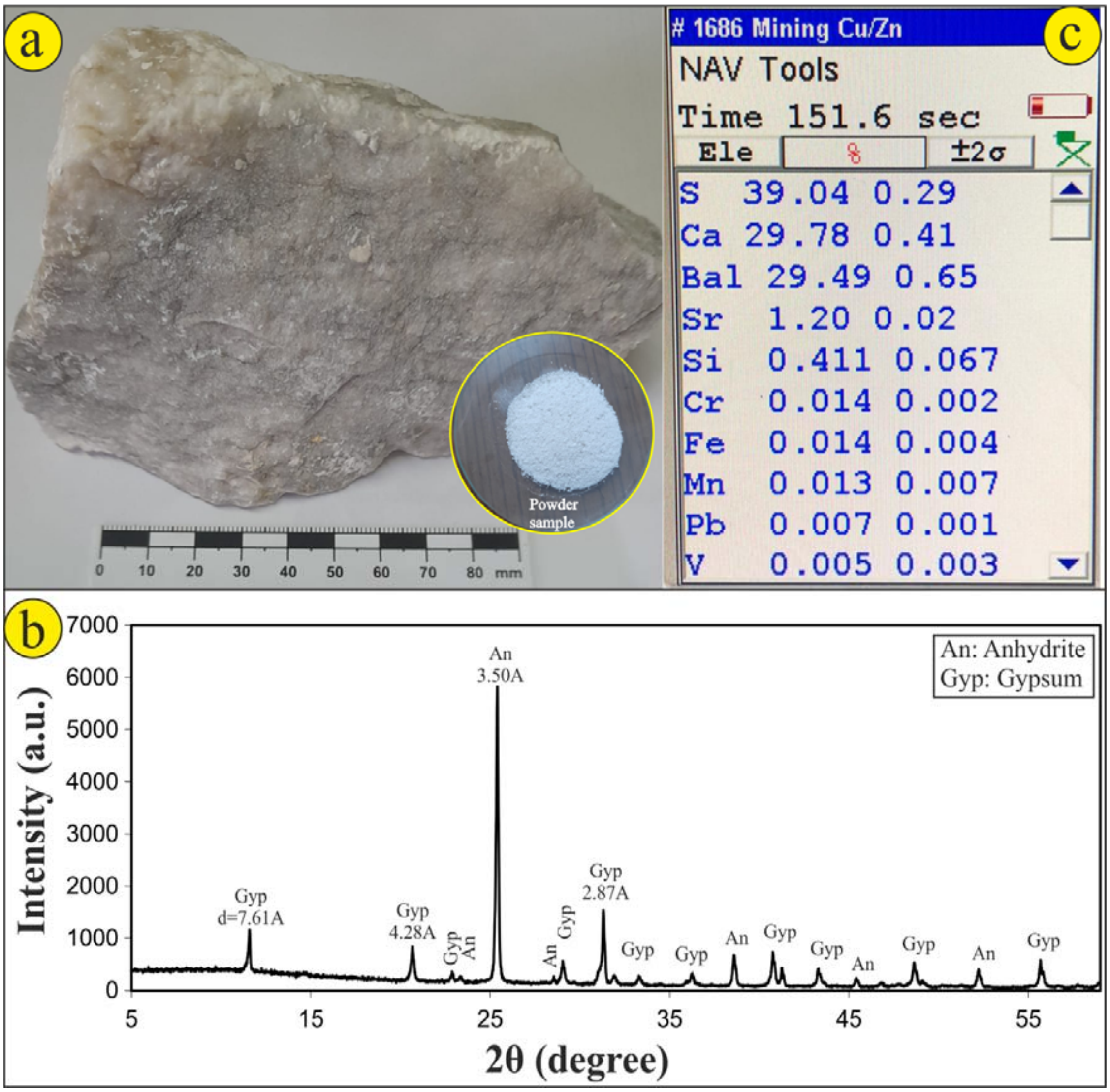

Figure 7. a) Anhydrite hand sample and its powdered form, b) XRD analysis result, c) pXRF analysis result

6. DISCUSSION AND CONCLUSION

This study is carried out on anhydrite, which is widely used in the world but has extremely limited use in Türkiye. Within the borders of the country, especially in the Tertiary basins, evaporitic deposits are widespread. Evaporitic deposits of the Sivas basin constitute one of them. The first thing that comes to mind when it comes to evaporites is gypsum. However, halite and anhydrite are also the most common evaporite minerals. So far only gypsum is being operated in the Sivas basin evaporites. In the lower levels of some license areas where gypsum is operated, anhydrite is left in place because it is not operated for any purpose. However, when the uses of anhydrite in the world are considered, it is seen that anhydrite is almost as important as gypsum and its usage areas are also wide. According to the literature, anhydrite, which is limited in some countries, is produced by the calcination of gypsum. In Türkiye, even though the operating cost is lower than that of gypsum because there is no stripping cost, these deposits are left in place without being operated. Therefore, it is extremely important to utilize the anhydrite potential in the country and especially in the Sivas basin.

In this study, the anhydrite reserve in a mining license area with a surface area of 28.83 hectares where gypsum is operated in evaporitic deposits in the region is calculated as 13,397,019.869 m^3. According to the block model, although there are drillings where the anhydrite thickness reaches 300 m, there are also drillings that do not cut anhydrite. This leads to the possibility that not every evaporitic mass that comes to the surface in the region will have anhydride at the bottom levels. Nevertheless, it should be taken into account that the anhydrite potential of the Sivas basin, which has a surface area of 212.034 hectares may be very high. For this reason, the specialist should conduct research and development studies in anhydrite uses areas in the country. Considering that gypsum and anhydrite are turned into products in today's world where environmental awareness is becoming more important day by day, it should not be forgotten consideration that gypsum-based products are an environmentally friendly sector.

7. ACKNOWLEDGMENT

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