The Effect of Ettringite Formation on Expansion Properties of Compacted Spray Dryer Ash

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ABSTRACT

The results of a series of laboratory tests performed to correlate swelling with ettringite formation are presented in this paper. A spray dryer ash was compacted according to ASTM Standard procedures (ASTM D698) and allowed free access to water over an extended period of time. Volume change was recorded while X-ray diffraction and scanning electron microscopy were used to measure changes in the mineralogical composition of the ash. After several days, the formation of ettringite like minerals was apparent. Swelling, however was minimal.

INTRODUCTION

Efforts by electric utilities to reduce the environmental impacts of sulfur emissions from coal burning power plants have led to a number of changes in the way exhaust gasses are processed. In the most widely used methods for treating oxides of sulfur, calcium is reacted with the sulfur to produce a solid that can be collected before exhaust gasses are discharged into the atmosphere. The solid is typically disposed of in a controlled landfill. In recent years, a substantial body of data on the physical properties of these flue gas desulfurization (FGD) products has been generated.[1-6] Samples of compacted FGD tested at various time intervals clearly show that the behavior of the material in an engineered structure changes with time. Much of this behavior change has been attributed to the formation of minerals comprised of varying proportions of the FGD constituents. Both strength and stiffness are typically equal to or greater than those found in most naturally occurring soils so identifying beneficial uses in lieu of landfilling has been a goal of both generators and regulators. One popular use in recent years has been in structural fills, particularly when sources of select fill are not abundant nearby. One concern in compacted FGD fills that might be used to support structures is that the formation of ettringite and other ettringite-like minerals will result in volume expansion (swell) leading to structural damage.

The mechanical properties of a particular combustion by-product depend on the coal, the combustion process and the desulfurization system used. Because these inputs all affect the engineering characteristics of the by-product, the performance of any

particular desulfurization material can only be determined by conducting the appropriate tests on properly constructed samples of the specific FGD material. A test program such as is outlined in the ASTM Standard Guide for Use of Coal Combustion By-Products in Structural Fills (E1861)[7] would provide the data necessary to satisfactorily characterize the geotechnical properties of FGD and other CCBs.

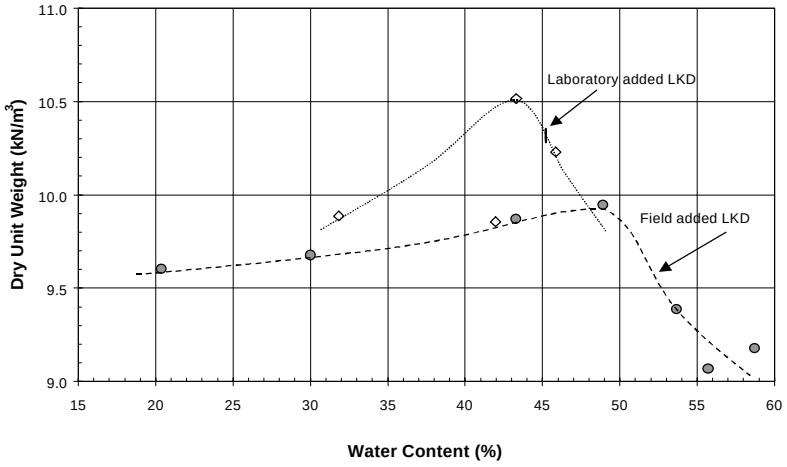

Figure 1. Compaction Tests on Spray Dryer Ash Samples

TEST PROGRAM

Samples of spray dryer ash were collected from three locations at the Coxendale, Virginia landfill operated by ReUse Technology Inc. Two samples were retrieved from locations where approximately 3% by weight lime kiln dust (LKD) had been added as a stabilizing agent. The third sample consisted of FGD as it arrived at the site before LKD was added. To this specimen, the 3% LKD was added in the laboratory. None of the ash collected had been compacted previously. The macroscopic characteristics of three FGD samples were determined by standard geotechnical tests. Each sample was also examined using X-ray diffraction and scanning electron microscopy. Standard Proctor compaction tests as shown in Figure 1 were performed. Once the compaction curves were established, an experimental program consisting of one-dimensional swell tests employing the modifications to ASTM Standard D3877[8] described by Adams[9] and suggested in ASTM E1861[7] was started. Nine samples, three from each material, were prepared. The tendency of soil to swell has been shown to increase with increasing density and decreasing water content at compaction.[10] Therefore, to maximize the tendency of the FGD to swell, the samples were compacted at a high density (95 -100% of Standard Proctor) and a water content well below the optimum value. Each specimen was confined laterally, subjected to only a nominal vertical load and allowed free access

to water. Swell was monitored for six months by recording change in sample height. Throughout the test samples of the FGD were analyzed for mineral content.

X-ray Diffraction

Samples were dried at 60°C for 18 hours, ground to a fine powder and mixed with15% by weight CaF_2 as an internal standard. The samples were run from 4.0 to 64.0° 2θ on a Philips 3100 X-ray generator using 45KV and 35mA monochromatic copper radiation at 1.0° 2θ/min with a step size of 0.05° 2θ. A quantitative analysis was performed on each sample using the internal standard method. Standard reference materials mixed with fluorite were used to derive calibration coefficients for each mineral detected.

Scanning Electron Microscopy

Samples of each ash were impregnated with epoxy, allowed to harden and then polished. The samples were carbon coated and analyzed using a PSEM by Aspex Instruments. The SEM was operated in the backscattered electron mode (BSE) with an accelerating voltage of 20 KeV.

RESULTS

The total increase in volume measured over the duration of the test program varied from less than 0.2 % to a maximum of only 0.7%. Figures 2 and 3 show the change in volume with respect to time for the samples compacted from the ash to which the lime kiln dust had been added at the Coxendale site. In Sample S-1, the majority of the volume increase occurred in the first few days whereas essentially all the volume change measured in Sample S-2 took place within hours of compaction. Figure 4 shows the response of the ash to which the lime kiln dust was added in the laboratory just prior to compaction. It is clear that the majority of the volume increase measured in this sample occurred within the first day of the test.

The FGD samples all consisted of three distinct mineral suites. The first was quartz (SiO_2), mullite ($Al_6Si_2O_{13}$), and a Ca-silicate/Al-silicate glass. These materials are consistent with ash derived from high temperature combustion of bituminous coal in a stoker boiler. The second group contained hannebachite ($CaSO_3 \cdot 0.5H_2O$) and calcite ($CaCO_3$), minerals typical of ash from a spray dryer in which lime is injected into the scrubber in a low temperature, low oxygen environment. The hannebachite formed because sulfur released during coal burning was unable to oxidize to sulfate (SO_4) but rather formed sulfite (SO_3), which then reacted with the lime. The third suite consisted of gypsum ($CaSO_4 \cdot 2H_2O$), and SAS (calcium sulfo-aluminate silicate hydrates). SAS, secondary minerals formed from the reaction of scrubber residue with water, are sulfate compounds morphologically and compositionally different from ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$) or thaumasite ($Ca_3Si(OH)_6(CO_3)(SO_4) \cdot 12H_2O$) identified by shifts in the diffraction pattern of either pure ettringite or pure thaumasite.

Changes in the textural characteristics and chemical composition of the samples over time were observed by SEM. Figure 5 shows the primary occurrence of pure ettringite in the samples. The majority of the ettringite formed in pore spaces from the reaction of

the calcium-aluminum-silicate with soluble sulfate in the pores in the first days of hydration. It tends to form characteristic needle shaped crystals radiating out into the pore space. For expansion to occur, the ettringite must first fill all the pore spaces in the FGD. The other primary reaction in the first few days of hydration was the formation of SAS. SAS formed in the pore space and within the FGD matrix. As shown in Figure 6, it occurs in poorly defined masses suggesting that it is poorly crystalline. To a lesser degree, thaumasite is also found within the matrix of the material. These reactions continue throughout the first weeks and months (Figures 7-9). Pure ettringite continued to form within the pore space but even after six months, there were still partially unfilled void spaces remaining. Figure 10 shows the occurrence of pure thaumasite in the matrix. Thaumasite, which is generally regarded as nonexpansive starts to become more prevalent after six months. Slower reactions also take place such as the formation of ettringite from gypsum (Figure 11).

SUMMARY AND CONCLUSIONS

Power plants using some type of desulfurization process produce over 25 millions tons of coal combustion by-products each year. Most of these CCBs are being disposed of in landfills or impoundments. High volume alternatives to landfilling (e.g. structural fills, embankments, road subbases) are desired, but before CCBs can receive widespread acceptance in construction, the suitability of the specific material in the design application must be verified. The focus of this research addressed the issue of swelling of a spray dryer ash. Of particular interest were the mineralogical composition of the material at select times and the effect of changes in the mineralogy on swelling. The research demonstrated that when the results of extended duration one-dimensional laboratory swell tests on properly compacted samples are examined, not all FGD materials swell. In the presence of water, all the spray dryer ash samples studied in this program formed ettringite and other silica alumina sulfates as well as gypsum, but the presence of these minerals was not accompanied by swelling. XRD and SEM data when combined can give an overall picture of the both the crystalline and noncrystalline components of the FGD. While the apparent amounts of ettringite, thaumasite, and SAS seen in the SEM increase over time, the crystalline composition of the material did not show significant changes and the glass component decreased. Taken together these imply that the SAS materials were formed in a weakly crystalline state.

The majority of the ettringite in the samples occurs as needlelike crystals filling the pore spaces. There was no visible evidence of expansion or microcracking. Expansion can only occur when all the pore space has been filled and there is still a reservoir of calcium hydroxide to supply both a source of calcium and to maintain a pH sufficient to drive the reaction. These conditions were not seen to exist in the system.

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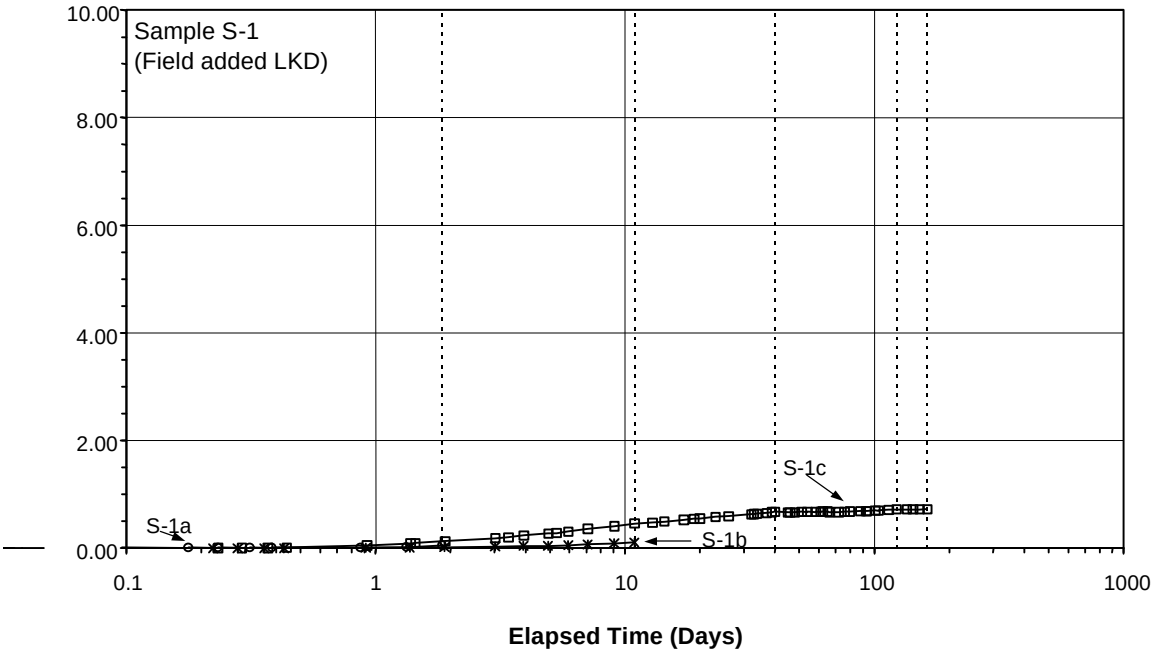

Figure 2. One Dimensional Swell Test for Sample S-1

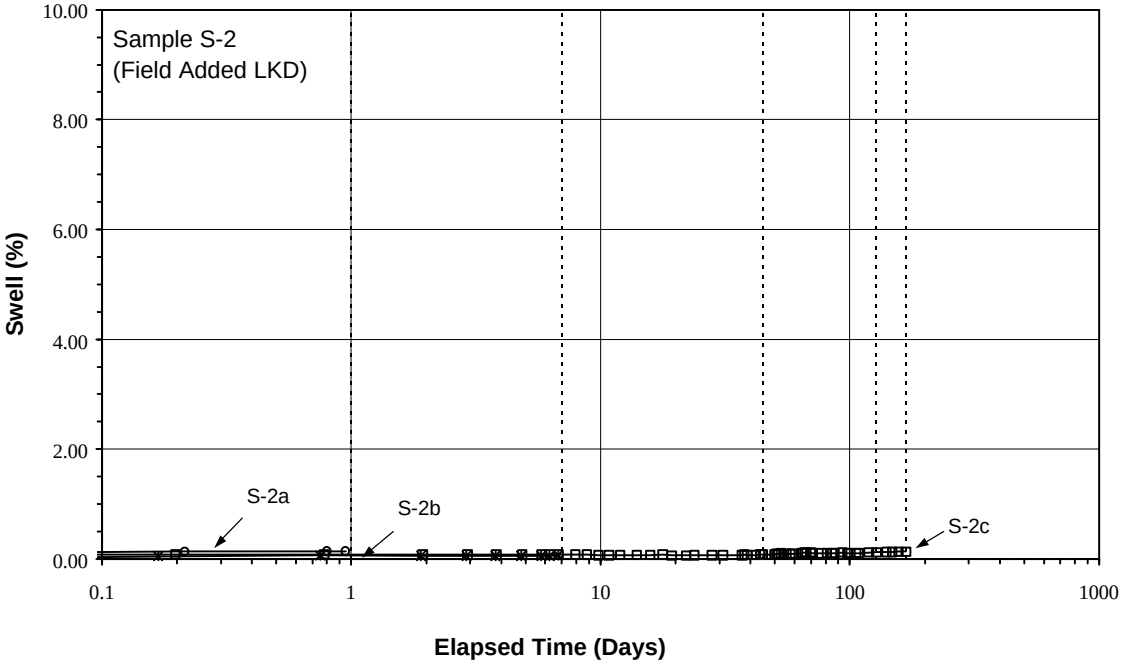

Figure 3. One Dimensional Swell Test for Sample S-2

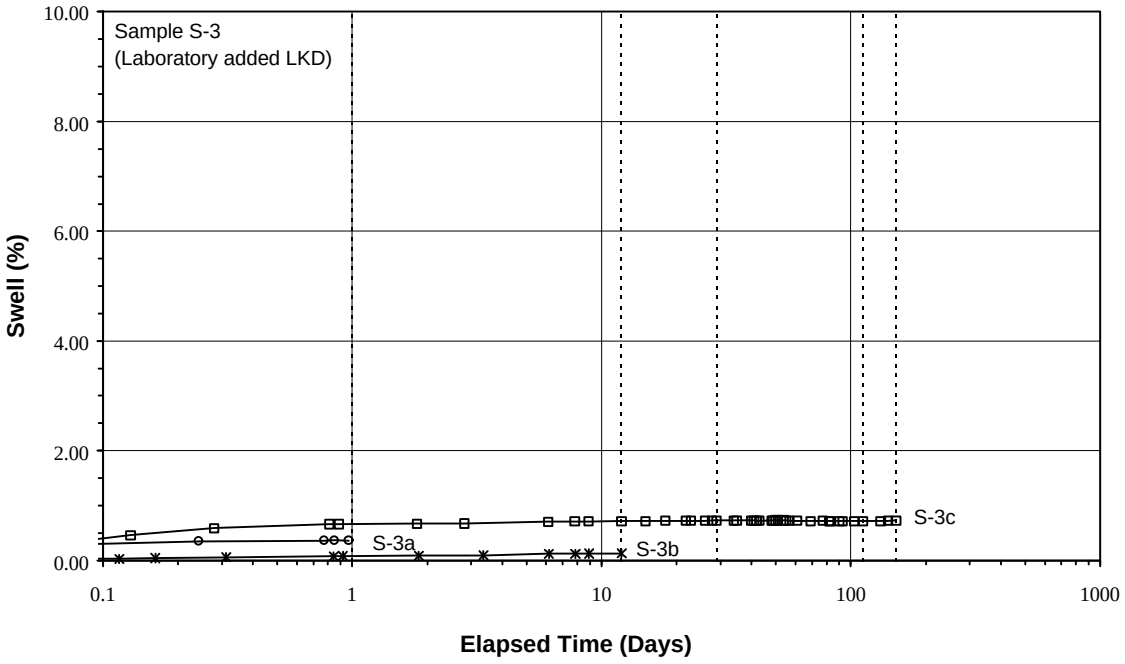

Figure 4. One Dimensional Swell Test for Sample S-3

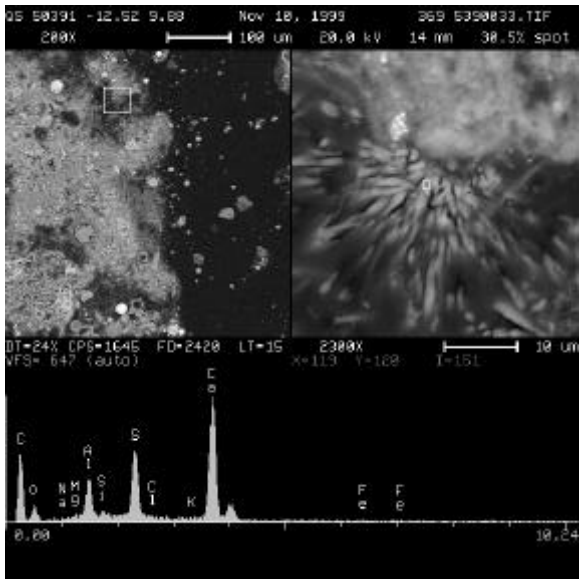

Figure 5. SEM micrograph of sample S-1 from 4/6/99 showing ettringite forming in the pore space of the FGD

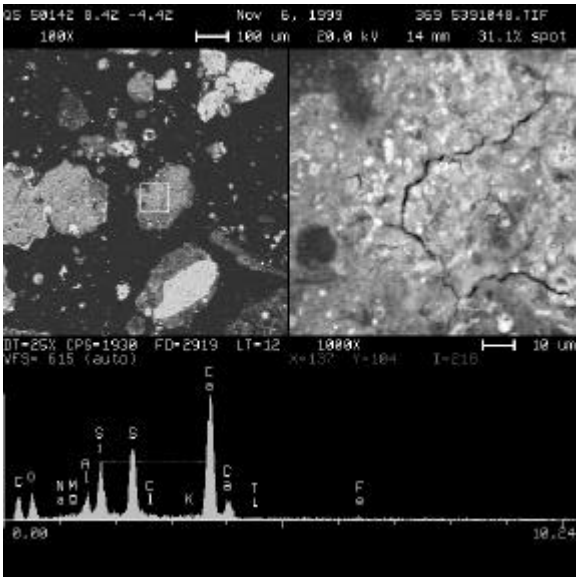

Figure 6. SEM micrograph of sample S-2 from 4/6/01 showing the formation of SAS in the matrix of the FGD

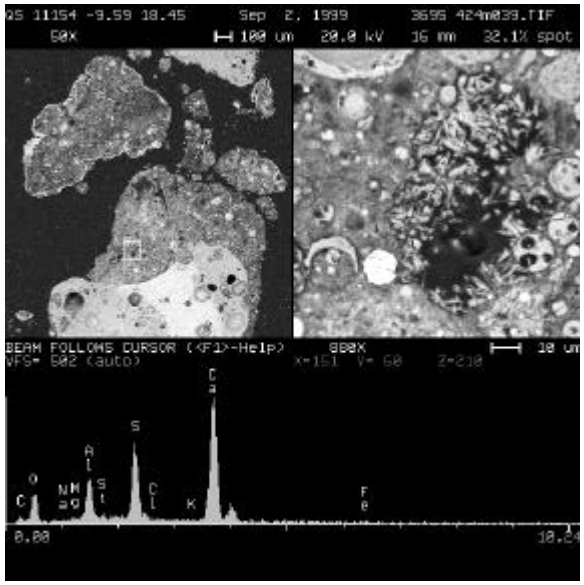

Figure 7. SEM micrograph from sample S-2 from 4/23/99, showing the formation of ettringite in the pore space of the FGD

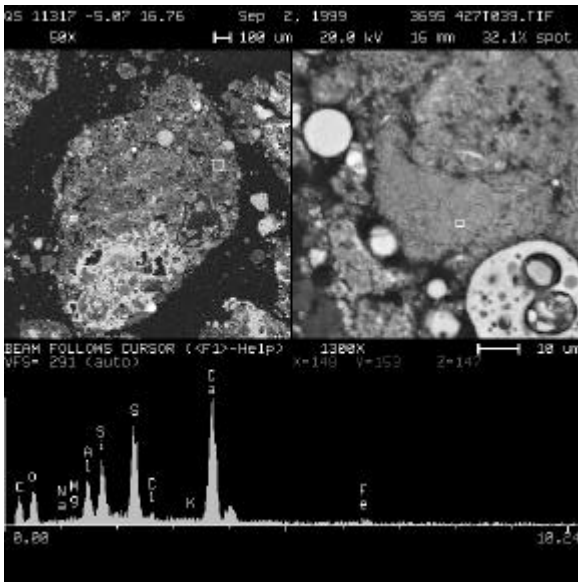

Figure 8. SEM micrograph of sample S-3 from 5/23/99 showing the formation of massive SAS

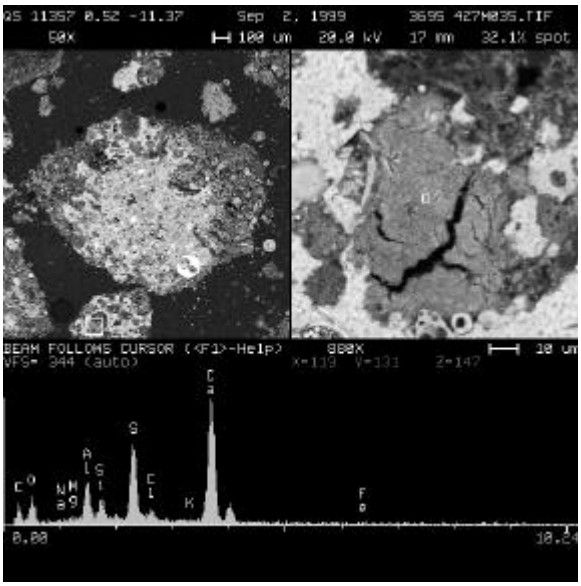

Figure 9. SEM micrograph of sample S-3 from 5/23/99 showing the formation of massive SAS in pore space of FGD

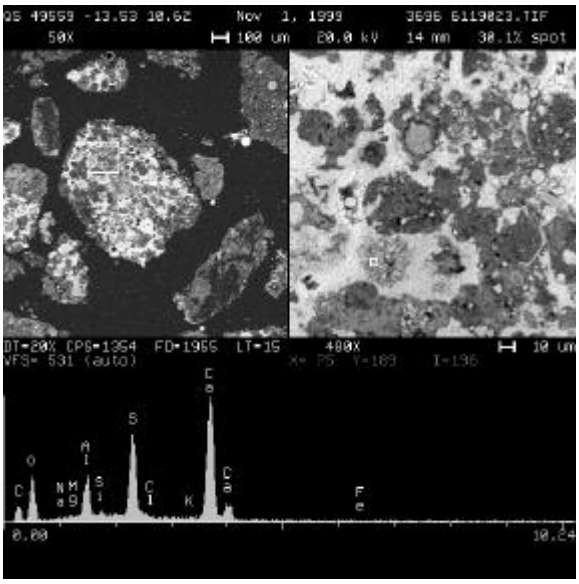

Figure 10. SEM micrograph of sample S-1 from 10/4/99 showing the formation of massive thaumasite in matrix of FGD

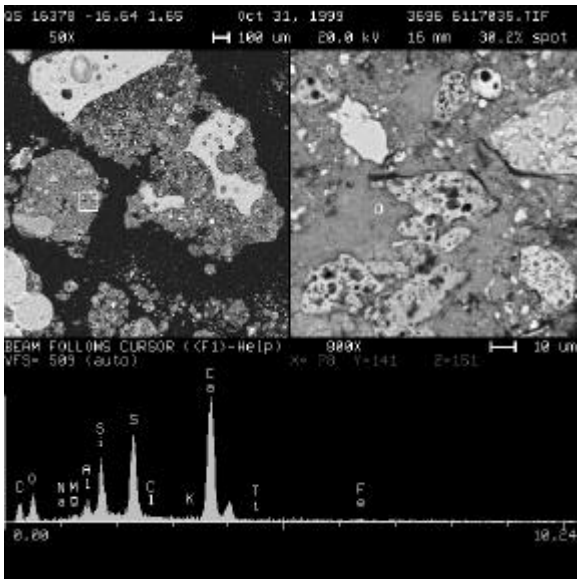

Figure 11. SEM micrograph of Sample S-3 from 10/4/99 showing an ettringite filled pore space in a matrix of gypsum (light material) and Ca/Al silicate (dark material)