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A Case History of Chemical Attack of a Clay Shale

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SYNOPSIS This paper describes the results of an extensive investigation made to determine the cause of excessive settlements of two 800 MW steam turbine units located at the Four Corners Steam Electric Station near Farmington, New Mexico. The units are located on a clay-shale formation with numerous gypsum seams. The settlement was originally attributed to the solutioning of these gypsum seams. It was found that the construction of a large unlined cooling pond raised the ground water table in the vicinity of the power plant. In this saturated environment, a chemical attack of the existing clay shales began. It is believed that the chemical reaction causing the degradation of the clay-shale has been identified and that a chemical solution to the problem has been found. The reaction involves the removal of the exchangeable cation from the clay lattice, which goes into solution. As the cations are leached out, the clays tend to weather toward the montmorillonite end of the transformation series.

INTRODUCTION

This case history presents the results of nearly 10 years of Geotechnical investigations conducted at the Four Corners Generating Station located in San Juan County approximately 15 miles west of Farmington, New Mexico. The project consists of five coal-fired electric generating units and a 39,000 acre-foot cooling pond. The cooling pond and Units 1, 2, and 3 were constructed in the early sixties. The foundation types utilized were bell bottom caissons drilled into the Lewis shale formation at a depth of approximately 30 feet. No significant problems were encountered with this portion of the project.

In the late sixties, Units 4 & 5 were added to the project. Both were 800 MW coal fired generating units. Prior to their completion, it was discovered that both units were undergoing excessive foundation settlements. These settlements were sufficient to cause visual deformation of some of the structural members. The foundation types employed were both shallow and deep foundations placed on weathered and unweathered materials, respectively.

The first grouting program was initiated in 1969 and it reduced the rate of settlement from approximately 1 inch per year to approximately 0.1-0.2 inches per year. However, an additional grouting program was required in 1976 with similar results to the first (see Figure 1).

In approximately 1977, it was noticed that the turbine pedestals were warping. Each turbine pedestal is supported by a mat foundation and is relatively lightly loaded, i.e., to approximately 2000 psf. It should be noted that the boiler foundations are loaded to approximately 15,000 psf. From this observation it was posulated that the settlement phenomenon may be independent of the applied load.

GEOLOGY

The Four Corners Power Plant is located in the southwest portion of the San Juan Basin. Surficial deposits in the basin generally consist of cretaceous age marine sedimentary rocks of the Fruitland formation and/or Kirtland shale. The deposits consist of interbedded sandstone, shale, and coal. The beds dip slightly to the southeast in the Plant area. The generating station rests on the so-called brown interval, consisting of the weathered portions of these units. The sandstone was moderately hard and moderately to severely weathered. The shale has completely weathered to a clay. This clay-shale was soft to very soft yet still retains the shale bedding characteristics. Characteristic of this unit was substantial amounts of gypsum and selenite which occur as individual grains throughout the unit and as lenses. Gypsum lenses up to 3/8 of an inch were commonly encountered and crystals up to a 1/2 inch were recovered. The gypsum tends to occur along and parallel to the bedding planes and joints.

This was underlain at a depth of approximately 30 feet by the so-called gray interval (Lewis Shale), also an interbedded shale which was occasionally carbonaceous or silty. Locally, the entire sequence grades to a mudstone. The sandstone was very hard, medium to fine grained, unweathered and probably silica cemented. The shale was slightly weathered to unweathered and was generally silty although it locally becomes clayey. There was virtually no gypsum found in this unit. Core recoveries were generally 100%. Where less than that, it was generally attributed to core breakage during extraction.

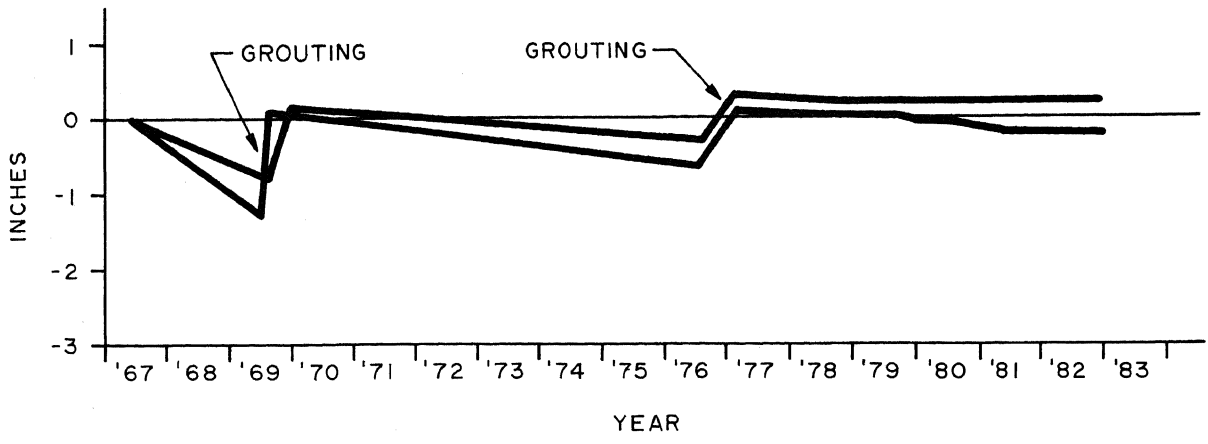


FIGURE 1
SETTLEMENT OF BOILER FRAME FOUNDATIONS

MINEROLOGY

The geologic depositional environment of this area was associated with evaporite formation. Alternate transgressing and digressing seas supplied the source minerals. The clay minerals found in the area consist of Kaolinite, Illite, Mixed-layer Illite, and Montmorillonite. The hyper-saline depositional environment also supplied considerable amounts of salts which can be found in the bedding planes in crystalline form. The principal salts found were calcium and magnesium sulfates with smaller amounts of chlorides and ocean type salts.

The clays formed during this depositional sequence contain large amounts of bound cations. Researchers such as Carrol and Starkey (1960) have found the most easily absorbed cation from sea water is magnesium. Other common cations are Calcium, Potassium, and Sodium. These cations were bound into the clay structure and locked in as the overburden pressure increases. The process of forming clay minerals in this way is called transformation. As defined by George Millot, "Transformation of clay minerals applies to those changes that modify a clay mineral without altering its two or three layered structural types" (Millot, George 1970). These minerals were relatively stable in the shale deposits because the lack of water in the desert environment allows these minerals to remain stable indefinitely.

Effect of Strong Bases of Degradation

It has been well documented that if the inter-layer ions of calcium-montmorillonite are exchanged under the influence of potassium hydroxide solution, the periodicity of the lattice will be reduced from 14-15 to 10 angstroms. In contrast, the potassium vermiculite treated with magnesium salts swells from 10 to 14 angstroms. This phenomenon is known as a base exchange.

Several areas of these clays were badly contaminated with Caustic Soda (Sodium Hydroxide). The pH of the groundwater was measured as high as 12. The areas of worst contamination exhibited large voids up to 1.5 feet deep beneath concrete

slabs at the ground surface.

This was physical evidence that the clays reacted or degraded much faster there than in other areas. The large settlements of the soil attest to the affect of sodium hydroxide on the clays.

The increase in montmorillonite minerals tends to decrease the amount of volume occupied by the solids of the soil column.

TEST RESULTS

Numerous geotechnical explorations have been conducted at the Plant site for various reasons. Several of these explorations have been conducted between Units 4 & 5 and the cooling pond. Four of these explorations have been isolated for analysis of the core recovery.

The borings were broken down to intervals of 5 feet in length and the average core recovery for each interval calculated. Only areas where a significant number of reliable data points were available were utilized (see Table I).

FOUR CORNERS
AVERAGE CORE RECOVERY SUMMARY
(Percent)

| Depth | 1969 | 1972 | 1974 | 1976 |
|-------|---------------|------------------|------|----------------------|
| 0-5 | 67.3 | 77.0 | | |
| 5-10 | 87.5 | 99.1 | 85.0 | 54.0 |
| 10-15 | 95.6 | 99.1 | 74.0 | |
| 15-20 | 88.8 | 99.8 | 82.0 | 69.5 |
| 20-25 | 100 | 100 | 83.6 | 68.0 |
| 25-30 | 100 | 98.4 | 91.4 | 92.5 |
| 30-35 | 100 | 100 | 93.0 | |
| 35-40 | 100 | 100 | 98.0 | 100 |
| | (4-7/8" & NC) | (4" Dbl. Barrel) | (NX) | (NX & 4" Dbl.Barrel) |

TABLE I

It should be recognized that core recovery was extremely variable, not only by types and conditions of equipment used, but such subjective factors as how long the driller has been away from home, or how late he stayed up the night before.

It was concluded that even accounting for different drillers and equipment, there appears to be a definite decrease in core recovery with time.

It was further reported by the grouting superintendent that the drilling of grout holes was considerably easier in 1976 than in 1969 or 1972. It was also found that the grout take was considerably higher in 1976 than 1969. Approximately 1,060 tons of grout was placed beneath the boilers and preheaters on Units 4 & 5. An additional 1,570 tons of grout was placed in the same area in 1976.

The rate of settlement of the equipment was reduced from approximately 1 inch per year to 0.1 inch per year, after the first stage of grouting. Nevertheless, the settlement continued (refer to Figure 1 on Page 1 of this text).

It should also be noted that 6-8 of the grout holes in the 1976 grouting program collected no free water even when drilled up to 20 feet below the static water table. This was taken as an indication that the localized permeabilities could be very low.

Several groundwater samples were taken from the area between Units 4 & 5 and the reservoir. All the analyzed samples proved to be 100% saturated in gypsum. If it is assumed that the gradient was away from the lake, then the groundwater beneath the units was incapable of dissolving any more gypsum. This was significant in that the settlement was originally thought to have been caused by the solutioning of the existing gypsum crystals.

A chemical analysis of the groundwater system revealed it to be high in sulfates but not saturated. It was also found that the concentration of dissolved salts in the lake water has almost doubled while the concentrations in the groundwater has remained nearly constant over the last 10 years. It was concluded from this that the soil controls the groundwater chemistry and not the lake.

An attempt to prove the solutioning theory was made by taking numerous thin sections of rock samples in an attempt to identify any changes in gypsum crystals with time. It was found that the crystals in areas that were loaded were more broken and distorted than those which were not. Hairline cracks (of approximately 0.1 mm) exist in the clays adjacent to gypsum crystals in loaded samples. In samples which have never been loaded or saturated, the cracks are up to 10 times wider (i.e., 1.0 mm). In samples where the soil was saturated but not loaded, the cracks were 2-3 times larger (i.e., 0.2-0.3 mm).

No voids exist between the gypsum crystals and the surrounding clays in loaded areas, large voids exist in dry unloaded areas. The clay appears to have flowed around the crystals

when loaded or the crystals have grown to completely fill the voids.

In no case was there any sign of solutioning of the crystals; all crystals showed similar geometry, sharp edges and points and unpitted faces. Cracks in the slides were empty, not filled with any salt or compound indicating substantial voids associated with crystal growth. Voids decreased with depth, practically disappearing by 30 feet. Clay density appeared locally higher with depth and appears to be locally higher adjacent to gypsum crystals.

Several series of scanning electron microscope analyses of the gypsum crystals were also performed to determine if solutioning was taking place. The results of the analysis indicated that there was no interface or direction of travel of the gypsum or silica ions. If solutioning of the crystals was taking place, some transition zone between the crystal and the clay should show a concentration of the dissolving salt. This zone was not found in any sample tested.

Foundations located in the brown interval have undergone considerable settlement, as can be seen in Figure 2. Further, the settlement appears to be a linear function. This linearity of the settlement rate suggests that some mechanism other than consolidation was taking place. Some sort of slow chemical reaction was the most likely suspect for this type behavior.

The pressure grouting operations conducted reduced the rate of settlement, but the linear trend continued. It should be noted that the site should be heavily over-consolidated. It has been estimated that up to 2,000 feet of over-burden may have been eroded from this site over geologic time.

Long term consolidation tests were performed on samples from the site. It was found that the mudstones consolidated much more than the sandstones, which was expected. Both sets of samples displayed primary and secondary consolidation rates. The primary consolidation generally ended after 3 or 4 days. However, the secondary consolidation continued throughout the duration of the tests (65 days). It was found that the secondary consolidation rate was very low and could only be measured over long time periods. This rate amounted to 0.01% per day and generally appeared independent of the applied load. Further, both undisturbed and remolded samples displayed this behavior.

GEOCHEMISTRY

Hydrometer tests were performed in order to identify the grain size distribution of the clays. These tests were very difficult to run because flocculation always occurred. Standard deflocculating agents like sodium silicate and ammonium hydroxide, made flocculation even worse. It was then hypothesized that there was an ionic imbalance in the clay water system with the strong electrical attractions of the clay particles causing the flocculation.

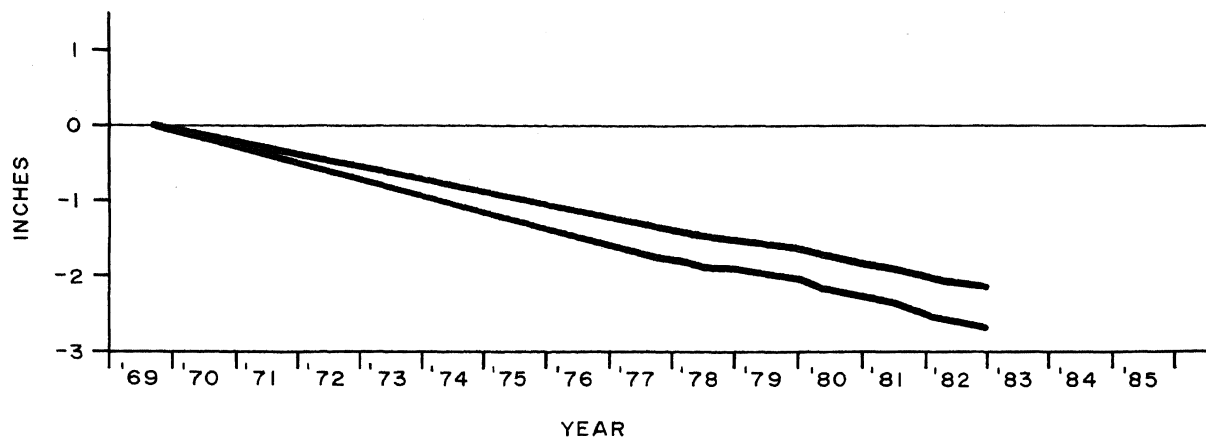


FIGURE 2
SETTLEMENT OF PRIMARY AIR FAN FOUNDATIONS UNIT 5

The calcium and sulfate ions appear to contribute to the action and were somehow locked into the clay structure. They appeared to be released or mobilized by the introduction of water, resulting in volume changes in the clay. Probably there were unfilled positions inside or on the periphery of the clay lattice structure.

HYPOTHESIS

One hypothesis is that the clay was in a transitional stage, weathering from shale to clay. X-ray diffraction techniques identified several montmorillonite and mixed layer portions which could chemically attach calcium ions to the inter-layer positions.

The mobile excess sulfates attract the calcium ions from the clay structure and in time combine to form gypsum. When the calcium ion leaves the clay structure the lattice structure (layer spacing) decreases from the Illite of 15 angstroms to 10 angstroms. A loss of 6 water molecules in the clay structure was also associated with this reaction. The volume change associated with such a reaction could be as much as 50%. The pressure of many clay forms simultaneously makes it very difficult to isolate this reaction.

A second hypothesis could be that very small gypsum crystals were interspersed throughout the clay and dissolve very slowly due to the low permeability of the clay. The salts may somehow affect the physical strength of the clay, allowing it to compress more when the salt were gone, possibly through lack of weak grain to grain cementation.

In order to evaluate either of these hypothesis it was necessary to develop precise time vs. solubility (relationships) for both the pure salt and salt-clay solutions.

SOLUBILITY

The solubility of a salt mixture was difficult to compute, so a direct measuring program was initiated. Tests show that the mudstones contain an average of 4-5% semi-soluble salt by weight. The salt consisted primarily of gypsum and magnesium sulfate. The sandstones consist of less than 0.5% salt. Solubility was measured by using a modified form of USDA Technique 226. This procedure makes use of the conductivity vs. time behavior. If the pure salt has the same general behavior of the clay salt mixtures, then it could be assumed that the clays were not affecting the chemical reactions taking place.

The salt clay mixtures yielded some erratic behavior. The rate of solution was apparently slowed by the clay structure. It appeared the clay breaks down and the salt is released. The salt was either chemically or physically bound to the clay, but there was some interference with the solution taking place.

It also appeared that the addition of lime to the system affects the soluble salt content. The addition of 2% of lime increases the total dissolved solids while larger amounts (5%) causes a net decrease in dissolved solids. Apparently, when the solution was saturated with calcium, precipitation of magnesium sulfate occurs to lower the total dissolved solids.

The acid, caustic soda, oil, cleaning chemicals all penetrate the groundwater throughout the Plant. The groundwater chemistry was created by these contaminants and causes localized variations in settlement. Physical voids up to 1.5 feet thick has been measured in areas where caustic soda leaks have occurred. These areas of high settlement also showed high pH. Testing showed that water chemistry created by the soil was drastically altered by the Plant associated chemicals. Settlement was occurring only in the presence of water. The extremes of pH in the water samples generally ranged from 6.54 - 11.5 with the electrical conductivity ranging from 1000-8000 micromhos/cm. This conductivity corresponds to a total dissolved solids of 650

to 5200 ppm. One sample was saturated and tested in the consolidometer for 100 days and measured afterward at 6.5% salt while an identical sample un-saturated was found to have 10% salt. It was believed that this evidence indicates that some salt was dissolved but once the solution reached equilibrium, solutioning stopped. Except for selected areas of the Plant where fresh water leaks exist nearby, all the groundwater has reached this equilibrium condition.

Based on field observations, the groundwater in the grouted areas appeared to have more dissolved salts. The addition of the calcium creates a small increase in the gypsum content, creating a new, more stable equilibrium condition. With large concentrations of lime in the range of 4-5%, the total soluble salts decrease and exhibit stable behavior. There was no long term solutioning occurring in the lime treated system. Apparently the gypsum was the only salt remaining in solution, with all others precipitated.

The total dissolved salts in the lime-rich system were approximately 35% lower than the natural condition. What was more important was the dissolved solids no longer tend to increase with time indicating that stable chemical behavior can be expected with neither crystal growth nor solution occurring. The solution has become saturated with calcium and magnesium ions.

Weathering

The present geologic conditions are one of residual weathering or gradual wearing away of the many layers of rock which had formed during the depositional period. When this process occurs in the clays, it is called "degradations". Degradation is the reverse of transformation and often is accompanied by a loss of substance. The degradation sequence generally appears to be as follows:

Kaolinite ↔ Illite ↔ Vermiculite mixed layer
 ↔ Vermiculite ↔ Vermiculite-Montmorillonite
 mixed layer ↔ Montmorillonite

The clay minerals degrade when the interlayer cations are removed; the addition of water allows movement of these cations (see Figure 3). The small amount of water from rainfall makes the process very slow but the raising of the water table by artificial means can tremendously accelerate the process.

Millot (1970) states, "When solutions are sufficiently unsaturated in cations to dissolve the soluble elements of clay minerals, they are attacked by three different ways; by the defects, the inclusions and the holes in the crystals, by oxidation of ferrous iron if present and by the interlayer joints. This brings about a division, then a micro-division of the minerals. As the size decreases, action on the joints increases and the release of interlayer cations is accelerated."

Clay minerals can maintain their existence in a progressively changing form up to the point where these minerals were of the order of 10

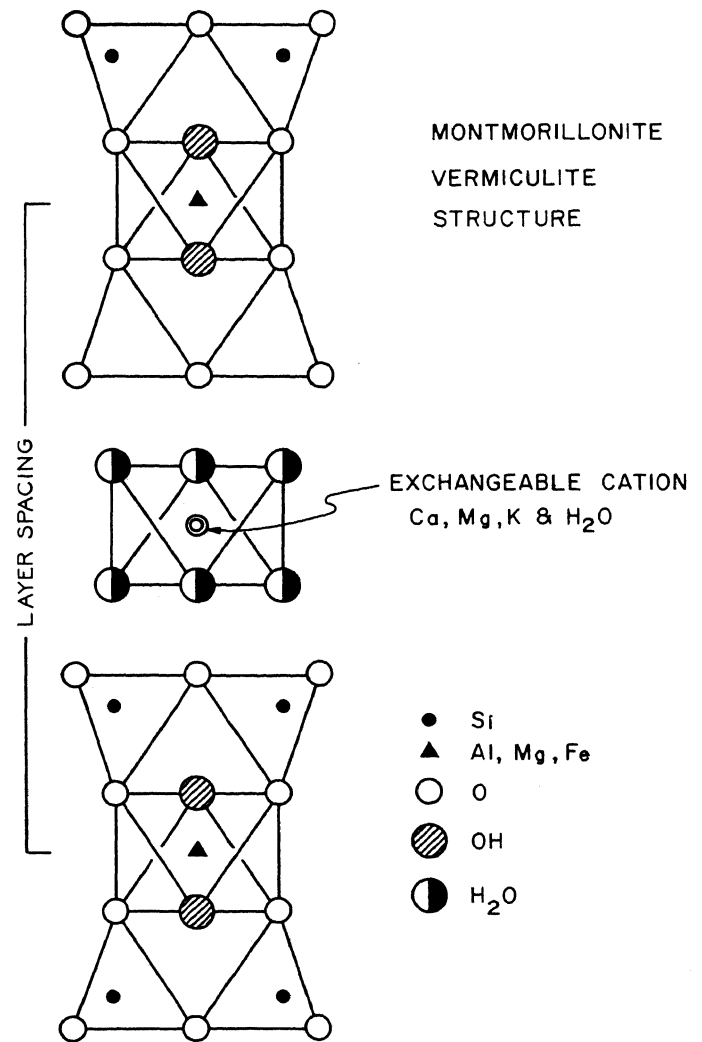


FIGURE 3
CLAY LATTICE STRUCTURE

angstroms and similar to montmorillonite.

The currently existing thin gypsum (salt) lenses found in the bedding planes in the upper 30 feet were a result of deposition of leached out salts from the overlying clay lenses. The rainfall infiltrates the soil slowly, picking up the soluble cations as it travels downward. As the clay gives up its cations, it shrinks in volume, leaving the cracks and bedding plane separations identified earlier. As the moisture content decreases, the crystals precipitate or grow in the cracks and bedding planes.

Apparently no crystals exist in the unweathered blue-grey materials located at a depth of 30 feet. The reddish brown color of the mudstones was associated with the crystalline salts in the bedding planes.

As the cations are leached out, the clays tend to weather toward the montmorillonite end of the transformation series. This trend was confirmed

by testing. The samples were lumped by depth into various zones to arrive at an average. The variability was generally high within these zones. The zones were chosen 0-7, 7-14, and 14-21 feet because of obvious changes in the soil properties. The 0-7 foot samples were all above the present water table and so reflect natural conditions. The average percent montmorillonite was highest in this group at 40.59%.

The 7-14 foot zone showed very large grout takes during all grouting programs. This zone showed lesser weathering but was very soft. After 9 years of saturation, it showed 31.32% average montmorillonite content.

The 14-21 foot zone is harder than the previous and shows average 27.9% montmorillonite. This zone has been saturated approximately 20 years.

If the degradation sequence hypothesized were in effect, the trend identified would have been as predicted. While it was not practical to quantify this sequence to perfectly predict the expected montmorillonite proportion, there was little doubt that the trend is real.

Reversal of Transformation

Several lab samples were treated with type S lime which consists of approximately 60% calcium hydroxide, 40% magnesium hydroxide. The lime immediately stopped the settlement behavior in laboratory consolidation test. The mechanism by which this occurred is called Aggradation. George Millot states in his book, "Aggradations are transformations that reconstruct normal clay minerals from degraded minerals provided by weathering. They occur under the influence of solutions that are rich in mineral cations and silica in sedimentary environments and under the influence of the successive early and late stages of diagenesis" (1970).

The Aggradation process consists of replacing the magnesium cation in the clay structure by supplying all the magnesium required to saturate the solution. The clay lattice returns to a 15 angstrom spacing, thereby stopping further volume change. In this case, a mixture of Type V cement and Type S lime was used. The combination of these supply a quick source of magnesium from the cement and a long term source from the slow solution of lime. Theoretically, the lime should dissolve at approximately the same rate as the clay degrades providing an equilibrium condition. In addition, the excess of calcium ions provides weak bonds to the clay material, attaching themselves to the edges in a calcium silicate reaction similar to Portland cement. This reaction should further stabilize the clay system.

GROUTING

The first test was conducted in May, 1976. A switchgear room existed between the two turbine pedestals which had undergone considerable settlement. The structure was isolated from the turbine mats and the equipment not sensitive to settlement, so it was chosen as a test location.

A calcium-magnesium-silicate rich grout consisting of 50% lime and 50% fly ash was injected into the middle of the room. Approx-

mately 13 CY of material was injected into two grout points. The same grout was mixed with 50% soil in the lab and loaded to 16 KSF in the consolidometer. The grout was mixed with 50% soil in the lab and loaded to 16 KSF in the consolidometer. The grout in the field and lab showed slight evidence of expansion. No post-injection expansion was allowed due to the critical alignment criteria for the turbine-generator structures, so a second grout was developed. The second generation grout consisted of (per cubic yard):

4 Sacks Type V cement
400 Lbs. Type S Lime
Water and Sand to Desired
Pumping Consistency

Unit 4 was preparing for an overhaul in October, 1977 and the pulverizers were badly out of alignment. This opportunity was used to field test the new grout. 120 day consolidation tests had shown no adverse expansion. Approximately 96 cubic yards of grout were injected beneath foundations in September, 1977.

The data collected after grouting shows no movement in the grouted area while it continued in the rest of the site. The settlement data indicates that the settlement was totally arrested in the area. Subsequent coring gave nearly 100% recovery, even though grout was not apparent in all core holes.

Figure 4 shows typical settlement plots of areas that have been grouted. As can be seen on these figures, long term straight line settlements stopped after being grouted. Figure 5 shows a settlement plot typical of an area which was generally down gradient from the grouted areas. However, this area was not grouted itself. As can be seen, the settlement stopped here also although it took a longer time.

CONCLUSIONS

A case was presented for degradation of clay shales at the Plant site. The use of a lime rich grout apparently neutralizes the chemical reactions involved, halting further settlement. The remedy was demonstrated to be effective in both the laboratory and in the field. It is also reasonable to assume that in other areas of the world where similar geologic and climatic conditions exist, and water tables are artificially raised, a similar scenario may result. It is therefore suggested that in these areas where there is no previous construction history, some long term consolidation tests be performed in order to identify any long term effects which may be taking place and may not be obvious from short term laboratory testing.

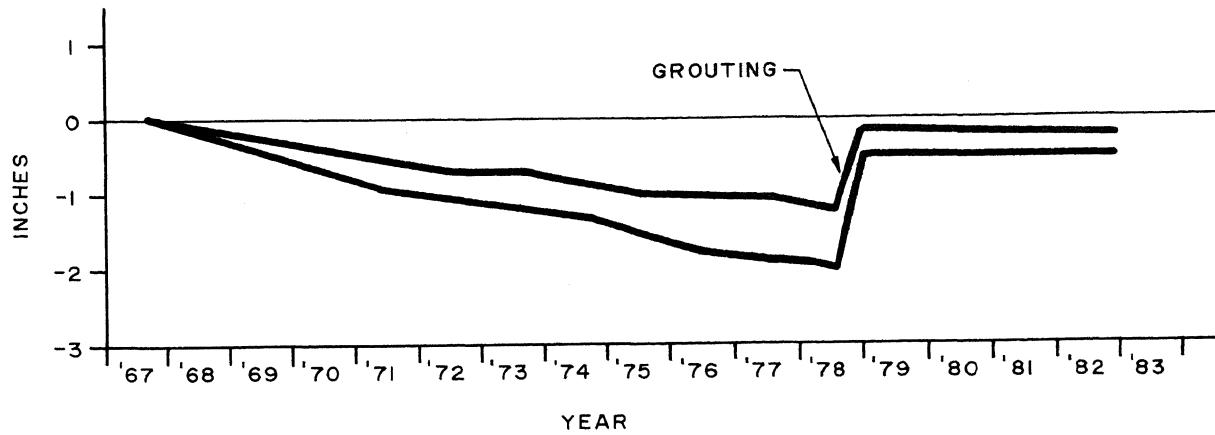


FIGURE 4
SETTLEMENT OF TURBINE PEDESTAL UNIT 5

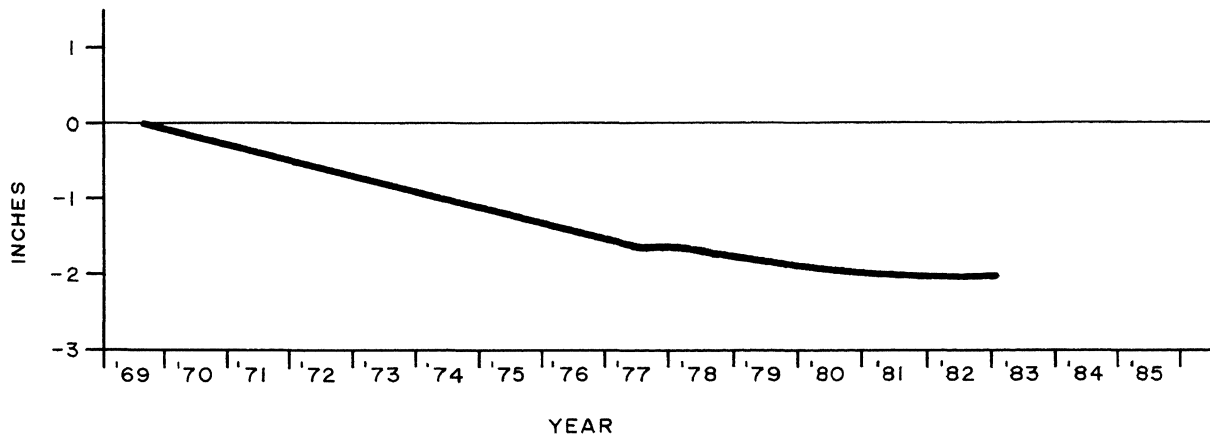


FIGURE 5
SETTLEMENT OF PRIMARY AIR FAN FOUNDATIONS UNIT 4

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