GEORGIA INSTITUTE OF TECHNOLOGY

Engineering Experiment Station

CORRECTED

PROJECT INITIATION

Date September 17, 1965

Project Title: Development of a Water Repellent Treatment for Elbert County Granite

Project No.: A-892

Project Director: J. N. Harris

Sponsor: Elberton Granite Association, Inc.

Effective: 9-20-65 Estimated to run until: 9-19-66

Type agreement: Standard Industrial

Amount: $12,275.00

Reports: Interim Reports #1 - due 12-31-65
#2 - due upon completion of artificial aging study

Informal Reports - as appropriate
Final Technical Report - upon completion

Contact Person: Mr. William A. Kelly, General Manager
Elberton Granite Association, Inc.
P.O. Box ~~694~~ 640
Elberton, Georgia 30635

Assigned to High Temperature Materials Branch
Chemical Sciences & Materials Division

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GEORGIA INSTITUTE OF TECHNOLOGY
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PROJECT TERMINATION

Date October 24, 1967

PROJECT TITLE: Development of a Water Repellant Treatment for Elbert County Granite

PROJECT NO: A-892

PROJECT DIRECTOR: J. N. Harris

SPONSOR: Elberton Granite Association, Inc.

TERMINATION EFFECTIVE: 10-24-67

CHARGES SHOULD CLEAR ACCOUNTING BY: All charges have cleared

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300. A-892

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GEORGIA INSTITUTE OF TECHNOLOGY
ENGINEERING EXPERIMENT STATION
ATLANTA, GEORGIA 30332

December 14, 1966

Elberton Granite Association, Incorporated
Post Office Box 640
Elberton, Georgia 30635

Attention: Mr. William A. Kelly
General Manager

Subject: Letter Report No. 1, Project A-892
"Development of A Water Repellent Treatment for Elbert County Granite" for the Period April - December 1966

Gentlemen:

It is the purpose of this letter report to summarize the work covered in the report period and to provide the Elberton Granite Association with advance information on the cleaning of granite prior to publication of the detailed final report.

During the contract period of April to October the majority of work conducted was concerned with the accelerated weathering of granite in the artificial weathering study. This work consisted mainly of periodically changing the atmospheric conditions in the artificial weathering chamber and observing changes in the appearance of the granite test specimens. The information obtained during this artificial aging period was not considered to be sufficient or conclusive enough to warrant preparation of an interim report prior to completion of the study.

An investigation was made, during the period of the artificial aging study, to adapt the techniques and treatment methods developed by Dr. S. Z. Lewin of New York University. However, due to the differences in chemical and physical make-up of limestone and granite, Dr. Lewin's preservation methods do not appear feasible for use with granite.

In mid-September the funds allotted for this contract had not been expended. Therefore, it was mutually agreed that the work would be extended for a three month period to further investigate methods of cleaning applicable to the granite industry.

A. Accelerated Weathering Studies

The blocks placed in the artificial weathering chamber at 3:30 PM on December 2, 1965 were removed for the final observation on the afternoon of October 6, 1966. This represents a period of 308 days for the total weathering cycle. However, the granite specimens were out of the chamber for periods of 1 to 3 days several times during the study for purpose of observation cleaning and drying. During the weathering cycles the test specimens were subjected to conditions of high humidity, and high concentrations of the oxides of carbon, nitrogen, and sulfur. The specimens were periodically covered with layers of soot (carbon black) to act as an absorber to hold the acid created by the reaction of moisture and the above named oxides in contact with the granite.

On several occasions the stones were cooled from a condition of 100 per cent relative humidity at room temperature to at least - 20° F. This cycle usually required 2 to 3 days to go from room temperature to - 20° F and back to room temperature.

Periodically the stones were removed from the chamber and observed. They were then washed gently using only running water and very gentle scrubbing with a bristle brush. The stones were then allowed to thoroughly dry at temperatures no higher than 120° F. After drying they were observed, the results of the observation recorded, and the stones returned to the aging chamber.

The original schedule for this program called for the conclusion of the aging study in the month of June. However, the appearance of the stones had changed very little by June. Therefore, the test was extended into October. The effects of the weathering study on each granite specimen is shown in Table I.

TABLE I

EFFECT OF ACCELERATED WEATHERING ON ELBERT COUNTY GRANITE

	Treatment				
Granite Number	Plain (Control)	Bond-Dri	Ethyl Silicate 40	G. E. SC-50	Sodium Silicate
206	2	3	4	5	5
211	2*	4	3	2	2
227	3	3	2	5	4*
245	3	3	4	5*	2
268	4	1	2	5*	2

(Continued)

TABLE I (Continued)

EFFECT OF ACCELERATED WEATHERING ON ELBERT COUNTY GRANITE

	Treatment				
Granite Number	Plain (Control)	Bond-Dri	Ethyl Silicate 40	G. E. SC-50	Sodium Silicate
282	3**	3**	2	3	4
299	2	3	3	5*	3

Note: (1) Indicates no change from original color.

(2-5) Indicates increasing darkness of specimens.

*Stain approximately 3/4-inch in diameter.

**Stain generally covering a large area.

All observations made on washed and dried specimens.

In addition to the overall darker color the specimens marked with an asterisk had stains which can best be described by the industry's terminology "sap." These are yellowish-brown stains which are not readily removed by cleaning and are more visible on polished than on unpolished surfaces. At least one block from each type showed these stains except for granite 206.

The small and somewhat subtle changes that occurred in the color of the stones is not sufficient justification to say that any of the various treatments to make the granite water repellent either did or did not improve the weathering characteristics. It was evident that the two silicone treatments, Bond-Dri, and G. E. SC-50, did become less effective with time. Early in the weathering cycles water applied to stones treated with these materials beaded up and would not wet the stone. As time progressed the amount of water beading on the treated surfaces became less and less. Near the end of the test program water beading on the silicone treated stones could not be observed. The ethyl silicate treatment did not seem to affect the characteristics of the granite specimens at all except for a possible slightly more darkening in color. The initial sodium silicate treatment drastically darkened the stones but as time progressed these stones lightened in color. A fully detailed description of the weathering effects on each treated specimen will be given in the final report. Also, the meaning of the artificial weathering tests in relation to actual conditions will be discussed.

In May a visit was made to the New York University Institute of Fine Arts to discuss the work of Dr. S. Z. Lewin in preserving limestone and marble. Essentially Dr. Lewin replaced a portion of the calcium carbonate in the structure with barium carbonate. Calcium carbonate is the major component of limestone and marble and is fairly soluble under acidic conditions. Barium carbonate is less soluble in acids. Dr. Lewin is able to deposit barium carbonate in the pores of a "sound" stone to protect it from deteoriation and also to rebuild badly deteoriated stone by growing crystals of barium carbonate within the structure of the existing stone, thus, "knitting" the stone structure together. Dr. Lewin grows the carbonate crystals by saturating the stone with a barium hydroxide solution then slowly converting the hydroxide to the carbonate. This is accomplished through reaction with the compound urea, which slowly decomposes in water to form ammonia and carbon dioxide.

Unfortunately this mechanism does not readily adapt to use with granite. Limestone is more porous than granite and is subject to deterioration both from internal pressures and by solubility under acidic conditions. The components of granite are resistant to acid attack. The silica (quartz) is almost totally immune and the alkalies in the mica and feldspar are only slightly soluble. However, this slight solubility can lead to deterioration of the stone through mechanical pressures. Calcium and magnesium leached out are deposited in the pores as the sulfate and the growing crystals exert tremendous pressures within the pores. Also, water in its many forms can exert tremendous pressures rupturing the stone. For these reasons it is desirable in a granite to leave "breathing" space, i.e. expansion space for the water and any deposited crystalline material.

The above reasons notwithstanding an attempt was made to deposit barium carbonate within the pores of several granite specimens using the techniques of Dr. Lewin. Attempts to measure the pick up of barium carbonate were made by weighing and measuring porosity before and after treatment. After two treatments weight increase varied from 0.08 to 1.22 per cent with the different specimens. Measured porosity readings varied so much that no confidence could be placed in them. But, in general, there appeared to be a slight decrease in porosity. These treatments were begun too late to include them in the artificial weathering study. However, it is believed that this treatment would have no benefit and could have possibly been detrimental to the stone because of the possibility of barium sulfate crystal growth.

A material developed by the Research group at the Lockheed-Georgia Company for waterproofing windshields is being investigated for its possible applicability for use on granite. This material when applied to a polished stone surface according to directions gives a high lustre to the surface in much the same manner as the common household silicone waxes for use on floors and furniture. This material protects the surface from water, however, mild solutions of inorganic acids will penetrate this protective coating in a matter of days. This coating does not give any protection from water when applied to unpolished surfaces.

B. Cleaning Techniques and Materials

A considerable number of cleaning materials have been considered for cleaning of granite. These include: organic and inorganic acids, proprietary acid cleaners sold under trade names, fluoride compounds, commercial detergents, and organic solvents. Of the materials investigated the best cleaning materials appear to be those already in use by a number of the granite producers in Elbert County. However, the methods used with these cleaning materials are as equally important as the materials used.

To evaluate the capabilities of the various cleaning materials it was necessary to duplicate in the laboratory the type of stains encountered in the fabrication operations involved from quarry to finished monument.

Iron shot was placed on various granite specimens on both polished and unpolished surfaces wet down with water. A damp cloth was placed over these areas to retain the moisture and facilitate the rusting of the shot. For deeper stains and to simulate the discoloration known in the industry as "sap," crystals of iron chloride were placed on polished and unpolished granite surfaces and wet down with water. The iron chloride produced a yellow-brown stain which penetrated deeply into the granite. This type of stain proved impossible to clean without removing the surface layers of the granite. Oil stains were obtained by dripping lubricating oil onto the surface of the stone. Difficulty has occurred in obtaining the "board stains" sometimes occurring from the packaging material, however, work is still progressing on this phase of the cleaning study.

Attempts were made to remove stains caused by rusting of iron shot with a commercial detergent and a scrub brush. The major portion of the rust stain was removed from polished surfaces but was very difficult to remove from the unpolished surfaces. A slight trace of rust remained on the polished surface and could be removed with little effort using dilute room temperature solutions of almost any acid; these include: oxalic, hydrochloric, sulfuric, nitric, phosphoric, and Liquid Zit. The removal of the steel shot rust stains from the unpolished surfaces was a little more difficult. The best acid cleaner, a room temperature saturated solution of oxalic acid, required about 10 minutes to completely remove the rust stains.

Deep iron stains such as those caused by the iron chloride or such as "sap" cannot be readily removed by any acid cleaner, and if such stains are present the only effective method of removal is to remove the exposed granite surface.

The detergent will remove excess oil but it will not take it out of a polished surface. Organic solvents vary in their effectiveness to completely remove all traces of the oil. No organic solvent was found, which could be wiped on then rinsed away or allowed to evaporate, which would completely remove oil stains. Of the common organic solvents available, naptha came closest to removing the oil. A method already being employed by a majority of the plants in Elbert County was found to be the best way to remove stubborn oil stains.

This was to make a plaster paste with natha and place this mixture over the spot for several days. Upon removal of the plater-naptha paste no trace of the oil remains.

Methods of removing stains caused by moisture and rosin from wooden crating material and by Kraft paper in conjunction with moisture has not yet been evaluated because of difficulty in preparing these stains.

The use of fluoride compounds such as ammonium bifluoride, Vapor X-crystals, and Bac-2-Nu on any polished surface is not recommended. Although they remove iron stains rapidly and will lighten weathered or acid darkened stones, they etch the polished surface rapidly. Tentatively, they may be satisfactory for non-polished work.

C. Recommendation and Conclusions

Of the presently known water repellent materials none appear to be capable of completely protecting granite in high humidity areas which have air pollution problems. Presently water proofing material may offer protection for a few years but there is no way of determining the exact life of such treatments except for an "in service" test. The results of the accelerated weathering tests would indicate that the yellowish-brown stains sometimes referred to as "sap" are caused by the effects of acidic moisture leaching iron from within the granite over a period of time. The exact time for these spots to appear would be related to the severity of the environment in which the monument is placed. It also could be partly related to the treatment of the monument during fabrication.

The fact that an acidic atmosphere causes yellow-brown stains to appear on granite casts doubt on the effects of acid cleaning. The acid cleaning may form colorless compounds with iron which are brought to the surface or near the surface and left there upon evaporation of the liquid. Weathering could breakdown the organic compound leaving free iron which is then subject to oxidation producing the characteristic stains. Because of this possibility the use of acid cleaning agents should be kept to a minimum or eliminated entirely.

Possibly sawed slabs should be taken directly to the finishing operation with no cleaning. If the finishing operation does not eliminate the stains through mechanical removal of material the monument could then be cleaned. If the use of an acid cleaner appears to be absolutely essential to remove stains the following procedure should be considered.

The granite to be cleaned should be thoroughly wet down and scrubbed with a good detergent and stiff bristle brush. It should then be rinsed with cool water and scrubbed with a saturated oxalic acid solution which is at the same temperature or slightly cooler than the granite block. The acid solution may be left on as long as is necessary to remove the iron stain but should not be allowed to evaporate to dryness. The next two steps could be the most important. This should consist of a thorough rinsing with water including scrubbing with a stiff brush to remove all possible traces of acid. The monument should then be moved away from the acid wash rack to include removing it from any wooden base upon which it might have been resting. It should then be thoroughly dried with an air hose before allowing it to rest on any wooden base for crating or storage purposes.

If solvent cleaning is necessary to remove oil stains and organic stencil material it could be done at the wash rack after the acid cleaning and before moving. However, any solvent wash should be followed by water and detergent scrubbing and then a clear water rinse. The solvent cleaner if not completely removed from the monument can contribute as much to water marking as any oils or other organics left on the stone.

At the present time there is no indication that the use of Kraft paper can cause marking of the stone. Therefore, the use of wrapping material is a decision for the individual dealer.

Respectfully submitted,

J. N. Harris
Project Director

Approved:

J. D. Walton, Jr., Head
High Temperature Materials Branch

JNH/jw

INTERIM REPORT NO. 1

PROJECT A-892

DEVELOPMENT OF A WATER REPELLENT TREATMENT FOR ELBERT COUNTY GRANITE

J. N. HARRIS

December 1965

Prepared for
Elberton Granite Assoc., Inc.
Elberton, Georgia

1965

Engineering Experiment Station
GEORGIA INSTITUTE OF TECHNOLOGY
Atlanta, Georgia

[redacted]

GEORGIA INSTITUTE OF TECHNOLOGY
Engineering Experiment Station
Atlanta, Georgia

INTERIM REPORT NO. 1

PROJECT A-892

DEVELOPMENT OF A WATER REPELLENT TREATMENT FOR ELBERT COUNTY GRANITE

By

J. N. HARRIS

December 1965

Prepared for
ELBERTON GRANITE ASSOCIATION, INC.
ELBERTON, GEORGIA

TABLE OF CONTENTS

This report contains 25 pages.

LIST OF TABLES

I. SUMMARY

Fabrication operations from gang saw to finished and crated monuments were observed in twelve Elberton Granite Association Member Firms. The greatest differences were found in cleaning after gang sawing, polishing, final cleaning, and crating.

At gang saw operations a large variation was found in concentration of oxalic acid solution and temperature at which the solution is used. All facilities used steel drums to contain the acid solutions. This practice may contribute to the iron stain problem.

Various plants used different grit size and polishing time for slab polishing. However, quality of polish seems to depend more on the skill of the man operating the polishing mills. It was noted that those plants using a five step polishing operation produce a better final product than those trying to short-cut the polishing operation. Also, no observed correlation could be made of the influence of polishing techniques on the staining of monuments.

The greatest differences observed among the plants were in the materials and techniques used in the final cleaning operation. Only one or two plants had any measure of quality control over the solutions used at the wash rack. No attempt can be made at this time to describe "best cleaning" procedure. It is recommended, however, that all plants use a detergent wash after cleaning with a solvent and that monuments should not be washed on the same wooden base that is to become part of a crate.

Two materials are in prevalent use for wrapping finished monuments. These are kraft paper and clear polyethylene plastic. No recommendation as to the best material can be made at this time.

Laboratory work has been initiated to investigate a number of candidate "pore sealing" materials; among these are, the sodium methyl siliconates, ethyl silicates, sodium silicates and colloidal organo-silicates. Seven different Elberton granites have been treated with these materials and are now being subjected to accelerated weathering tests under the influence of water and the oxides of carbon, sulfur, and nitrogen.

Investigation of cleaning materials and techniques used in the trade is underway. It has been discovered that some granites are more sensitive to color change under the action of harsh acid solutions. Water transmission rate studies have been initiated in an attempt to determine the causes for granite color changes and to aid in determining the best method for application of a pore sealant to all granites of the district.

An investigation of the applicability of the Photovolt reflection and gloss meter to determine the gloss of a polished granite surface was made. This instrument will be used as an aid in determining the reduction of the gloss of a polished surface by the acid cleaners.

II. PURPOSE

The objective of this project is (1) to develop "pore sealing" techniques in granite to prevent discoloration or staining, and (2) to develop standardized cleaning agents and techniques to be recommended for use throughout the Elberton Granite Association.

III. INTRODUCTION

In the marketing of cemetery memorials there have been popularly held beliefs that "Elberton granite does not withstand the ravages of time," and that "Elberton granite absorbs too much moisture." In recent work conducted by Georgia Tech for the Elberton Granite Association and the Area Redevelopment Association, Elberton granite was not found to absorb any more moisture than granites from other origins. Nevertheless all granites and other natural building stones are susceptible to moisture damage.

Moisture problems range from the unsightly appearance of a monument which remains partially "wet" for several days after a rain, showing a moisture line on polished surfaces near ground level or adjacent to carved portions, to more serious problems due to atmospheric pollutants. There is great concern today over the possible loss of much of the world's stone art due to rapid deterioration caused by air pollution in this industrial age.

Great quantities of gases such as carbon dioxide, sulfur dioxide and nitrogen dioxide have been released into the atmosphere by industrial processes and the automobile. When these gases combine with moisture, they form strong acids. If this acidic moisture gets into the pores of a stone, it can leach out soluble components and then deposit these materials on the surface of the stone as the moisture evaporates. It can also react with a component of the stone to form a crystalline compound within the stone. These crystalline compounds can grow and exert tremendous pressures within the pores. This internal pressure eventually causes flaking of the surface of the stone.

An older problem associated with moisture is the freezing of water with its accompanying increase in volume which can cause rupture of a stone. Although actual damage to granite caused by freezing has been questioned by many investigators.

To prevent moisture damage of any kind in granite, a method must be found to keep moisture from reaching the soluble components. Many attempts have been made to seal granite for preventing moisture damage. Organic sealers have been used, but these sealants are worn away by the weather in a few short years. Inorganic materials have been investigated which completely seal the pores of a stone. However, these sealants have been unsuccessful. It is almost impossible to remove all the moisture from a stone, thus, subsequent exposure to changes in temperature can cause rupture of any coating by the increased vapor pressure of the entrapped water or by the volume increase if the moisture freezes.

The best approach appears to be one which allows the stone to "breathe." In this case the pores of the stone are lined with an insoluble material so that moisture cannot reach soluble components, yet can enter or leave without being trapped. During the last ten years, this line of thought has been applied with success to masonry and with some limited success to granite. These treatments have incorporated the use of siliceous materials, usually a silicone. Early efforts used a solution of silicone in an organic solvent. This material worked well with masonry but has had little success on materials such as limestone marble and granite. Early uses of this type of treatment on granite by several Elberton Area firms produced disappointing results. The difficulty with this treatment may have come about because of the incompatibility of the organic solvent with moisture that remained in the granite after cleaning. The moisture below the surface of the granite may have kept the silicone from penetrating deeply enough or may have kept the silicone from covering all areas of the stone. More recently a water based material, sodium methyl siliconate, has been used with a limited degree of success. Some groups have used this type of material, and after seven or eight years no defects have occurred with these treated stones. However, sufficient time has not passed to fully assess their value as "lifetime" water repellents.

Both of the silicones described above depend on decomposition of the siliconate by exposure to the atmosphere. The siliconate combines with carbon dioxide (or sulphur dioxide) in the air, releasing the silicone and forming sodium carbonate (or sulphate) as a by-product.

Another type of system does not depend on any other source for completing the required reaction and should deposit material evenly on all pore walls. This is a solution which can be pre-catalyzed and then applied to a stone with a reaction depositing the desired materials in the pores of the stone after a certain pre-determined time. Regardless of the final material used as a "sealer," the technique used should be inexpensive, easy for unskilled labor to apply, permanent in nature, and uniformly applicable to all blue-gray granites in the Elberton district.

At the present time there is no standard method of polishing, cleaning, and packaging the granite for finished monuments. Each plant uses its own techniques and materials. Therefore, if a satisfactory "pore sealing" method is developed, it will be necessary to establish standardized cleaning and preparation techniques throughout the industry. Even if the pore sealing efforts are unsuccessful, standardized preparation, cleaning, and packaging techniques along with standardized instructions to retail monument dealers on the best method of installation for the finished monument can go a long way towards minimizing moisture caused defects on the monuments.

IV. EXPERIMENTAL PROCEDURE

A. Observation of Granite Finishing Operations

Early in the contract period several days were spent in Elberton observing the operations in twelve finishing plants and in talking with key personnel of the Elberton Granite Association and the various finishing plants. In some cases every step in monument fabrication was observed from removal of the stone from the quarry to the finished and packaged monuments ready for shipment. In other plants only the polishing operations, the final wash rack and packaging operations were observed. In addition, stains and water markings on stones in storage yards and on monuments in the local cemeteries were observed.

The purpose of these observations and conferences were two-fold:

1. To determine the cause and nature of stains on monuments.
    a. Those occurring in the plant and on storage yards.
    b. Those occurring on monuments installed in the cemetery.
2. To help in formulating at a later date standard washing and cleaning procedures throughout the industry.

All plants in general follow the same steps in processing granite from the quarry to finished monuments, however, they differ quite a bit in their polishing, cleaning, and crating operations.

1. Cleaning of Gang Sawed Slabs

The majority of operations visited use an oxalic acid solution for cleaning gang sawed blocks. All manufacturers have a problem of rust stains from steel shot left on the granite from the sawing operation unless the sawed slabs are to be immediately taken to the polishing mills. If the slabs are to be immediately polished they are hosed down with water to wash off excess steel shot and any water containing iron particles that may have remained on the stone. If the slabs are to be stored after sawing they are thoroughly wet down with water then scrubbed with an oxalic acid solution.

This oxalic acid scrubbing appears to be a major variable with the different plants and at the same plant at different times of the year. Almost all plants mix their oxalic acid solution in an unlined 55 gallon steel drum. Various foremen stated that they used from 10 to 30 pounds of oxalic acid crystals in 50 gallons of water.

At 60° F it is possible to dissolve approximately 40 pounds of oxalic acid crystals in 50 gallons of water. Water at 194° F will dissolve approximately 500 pounds of oxalic acid crystals per 50 gallons. At one plant a 55 gallon drum was heated over an open fire. From the amount of vapor leaving the surface the solution temperature was estimated to be at least 140° F, yet there were undissolved oxalic acid crystals in the bottom of the drum. This would indicate a concentration very much greater than 30 pounds of crystals per 50 gallons of water. This higher concentration apparently came about from the practice of replenishing the quantity of acid solution by indiscriminately adding water and acid crystals to the container as the solution evaporates and/or is used.

Some manufacturers do not heat their solutions but still use a saturated solution. In this case the concentration of the solution varies with the diurnal temperature. Manufacturers using wire saws do not use an acid cleaner on sawn slabs.

2. Polishing Operations

In the polishing operations the majority of the finishing plants use similar equipment but there is some variation in the grit sizes used for polishing. Table I shows the particle size of silicon carbide and aluminum oxide used in each of the plants in their polishing operation. The majority of the plants use steel shot as the first step in polishing gang sawed slabs but start with silicon carbide on wire sawed slabs. In Table I those plants shown starting with silicon carbide grits rather than steel shot generally are polishing wire sawed material.

Estimates by the polishing men of the time required for polishing a slab run from 45 minutes to 2 hours and 45 minutes. The quality of polishing in some plants is definitely better than in others but this does not seem to be related to the time of polishing but rather to the skill of the machine operator.

3. Wash Rack Operations

The greatest variance in procedures in the Elberton granite district occurs at the wash rack. At this stage in the 12 plants visited cleaning procedures varied from nothing more than a wash down with hot water to cleaning with concentrated Zit. The major portion of the plants use "crystal cleaner" (Vapor X) on steeled finish work and a dilute solution of Liquid Zit on polished surfaces. A few plants use oxalic acid on the finished memorial.

Two organic cleaners are in general use to remove dope and cement left from the stencils applied to the monument during sand blasting operations. These are white gasoline and industrial naptha. The naptha type cleaner in most general use is Gulf's Stoddard solvent. Some plants use a detergent followed by a clear water rinse to remove the organic solvent. Others only use hot water followed by an acid cleaner, and a final rinse with water.

A major difference between the plants is the concentration of the acid cleaners used on the wash rack. Table II shows the type of cleaner used by

TABLE I

PARTICLE SIZE OF MATERIALS USED AT EACH STAGE OF POLISHING

	Polishing Step				
	1	2	3	4	5
Plant	Material	SiC mesh	SiC mesh	Al_2O_3 grit size	Material
1	Steel shot & muck	- 60 + 120	- 180 and - 320		SnO_2
2	- 16 + 60 SiC	- 100	- 320 (3F)	600	SnO_2
3	Steel shot	- 60 + 120	- 320 (3F)	600	SnO_2
4	Steel shot	- 60 + 120	- 400 (4F)	600	SnO_2
5	Steel shot	- 60 + 120	- 400 (4F)	600	SnO_2
6	Steel shot	- 60 + 120	- 400 (4F)	600	SnO_2
7	Steel shot	- 60 + 120 or wire saw muck	- 400 (4F)	600	SnO_2
8	Steel shot & muck	- 70 + 90 or wire saw muck	- 400 (4F)	600	SnO_2
9	Muck	- 60 + 120	- 320 (3F)	600	SnO_2
10	Muck	---	- 400 (4F)	---	CeO
11	Steel shot	- 60 + 120	- 400 (4F)	600	SnO_2
12	- 46 + 70 SiC	- 180	- 320 (3F)	600	SnO_2

each plant visited and the approximate concentration of the cleaner used on "steeled" work.

Table III shows the type and concentration of cleaner used on polished work in each plant and Table IV shows the materials used in order for cleaning carved work on the wash rack.

TABLE II

TYPE AND APPROXIMATE CONCENTRATION OF CLEANER USED ON "STEELED" FINISH MONUMENTS

Plant	Oxalic Acid	Crystal Cleaner	Other
1***	---	---	---
2	---	10 oz.	---
3	---	---	water**
4	weak†	---	---
5	---	---	water
6	32 oz.	---	---
7	---	4-8 oz.	---
8	---	8 oz.	---
9	weak†	---	---
10	---	2-4 oz.	---
11	saturated	---	---
12***	---	---	---

*Concentration equals ounces of cleaner per 12 quart bucket of water.

**Concentrated Liquid Zit used directly on bad stains.

***Cleaning procedures not observed.

†Actual concentration could not be stated by wash rack men or foremen.

The bottom of the die (joint) was cleaned by only one plant of the 12 visited. All others neglected this operation. The majority wash dies on the wooden base that later becomes the bottom of the crate. Most plants set the die directly on the wood, however, one plant insulates the granite from the wooden crate by the use of plastic strips stapled to the top of the crate spacers.

TABLE III

TYPE AND APPROXIMATE CONCENTRATION OF CLEANER USED ON POLISHED MONUMENTS

Plant	Oxalic Acid	Water to Liquid Zit Ratio	Others
1**	---	---	---
2	---	9.1	---
3	---	---	water*
4	weak	---	---
5	---	---	hot water
6	weak	---	---
7	---	dilution unknown	---
8	---	---	water
9	weak	---	---
10	---	---	2 oz. Vapor X in water
11	saturated	---	---
12**	---	---	---

*Concentrated Liquid Zit directly on bad stains.

**Cleaning procedures not observed.

If oil stains have occurred on a monument during finishing two methods are in general use for the removal of such stains. The first method consists of covering the stain with dirt for several days followed by an acid wash. The second consists of mixing white gasoline and plaster of paris and applying to the stain. At least one plant sets the plaster-gasoline mixture on fire to burn out the oil stain. Another plant volatilizes the oil from the granite by carefully heating with an oxy-acetylene torch.

TABLE IV

CLEANING PROCEDURES USED FOR CARVED WORK

Plant	Solvent	Detergent	Water Rinse	Acid	Water Rinse
1	not observed				
2	(1)	yes	hot	yes	hot
3	(1)	yes	hot	---	---
4	(1)	no	no	yes	cold
5	(2)	no	hot	---	---
6	(1)	no	no	yes	cold
7	(2)	no	no	yes	cold
8	not observed				
9	(1)	no	no	yes	cold
10	(2)	no	no	yes	cold
11	(1)	no	no	yes	cold
12	not observed				

(1) Gulf Stoddard solvent.
(2) White gasoline.

4. Crating of the Finished Monument

All plants but one used wooden crates to package the larger monuments. One plant ships its wares uncrated. Of the 11 using wooden crates, one covers the monument with newsprint, two use polyethylene plastic, and eight use kraft paper.

The plants using polyethylene are doing so because of previous bad experiences with staining attributed to the kraft paper. At least two of the plants using kraft paper have used plastic and did not like the results, because the monuments "sweat" under this impervious film.

B. Observation of Elberton Granite Monuments in Local Cemeteries

Stains and "wet monuments" were pointed out by employees of the Elberton Granite Association in two local Elberton cemeteries. Close observation of these monuments showed improper setting on concrete bases and no setting-compound between the stock and die. Three identical small slant markers in one family plot were observed. The two outside markers were completely dry. The marker in the center had a "wet" zone over approximately one-half of the marker. The only apparent difference in these three markers was the fact that the monument in the center had no setting compound under it, whereas, the other two were well set.

C. Laboratory Work

1. Pore Sealing Techniques

An air tight Plexiglass chamber was constructed for use in artificial accelerated weathering studies of treated and untreated granite specimens. Two sets of the seven different six-inch granite cubes provided were split into six-by six-by three-inch blocks. These smaller blocks were treated with candidate "pore sealing" materials. One set of these blocks was left untreated and one set each of the other three sets were treated with a hydrolyzed ethyl silicate solution, Bond-Dri and General Electric's SC-50 masonry water proofing material respectively.

The set of stones treated with the ethyl silicate was immersed in the hydrolyzed solution for 14 hours at which time the solution had gelled. The excess gel was scraped off the stones and the stones allowed to dry for several days at room temperature. The stones treated with Bond-Dri and SC-50 were coated by painting the solutions onto the stones evenly on all sides. The three sets of coated stones and the control set were placed in the air tight chamber along with materials to release high concentrations of sulfur dioxide and nitrogen dioxide into the chamber atmosphere. These stones have been subjected to this atmosphere for approximately three weeks at the time of this report. No noticeable effects on these stones by this atmosphere have been observed during this short period. Additional stones are being treated with other candidate "pore sealing" materials and will be placed in the accelerated weathering test chamber as soon as treatment has been finished.

In the previous work under the Area Redevelopment Administration Contract conventional porosity and absorption tests were carried out which did not indicate that there was any great difference between absorption of the Elberton granites and the Barre Vermont granites with which they were compared. Another possible reason for some granites retaining a "wet" appearance would be through water transmission by capillary action. A test similar to that used by the National Bureau of Standards in their 1940 physical studies of domestic granites has been set up* to determine if the seven Elberton granites have similar water transmission rates. Specimens 3/4-by 3/4-by 3-inch in length have been cut from each granite. Samples with the same code numbers which were left from the ARA work and which were close to the above stated size have been utilized for this purpose to minimize the amount of cutting necessary. These samples have been sealed in two ounce jars filled with distilled water so that the top inch of these specimens pass through the jar lids and are exposed to the atmosphere. Weighings are made daily to determine weight loss. Results of this study will

*D. W. Kessler, et al, "Physical, Mineralogical, and Durability Studies on the Building and Monumental Granites of the United States," Research Paper RP 1320, J. Res. NBS, Volume 25, August 1940, pp 161-206.

help to determine if a pore sealing technique is uniformly applicable to all Elberton granites. It may also help to determine the susceptibility of some Elberton granites to retain a "wet" appearance.

2. Cleaning Techniques

Work has been initiated to determine cleaning materials and techniques best suited for all Elberton granites. Two granite blocks numbers 227 and 268 were deliberately stained with iron oxide by placing iron chloride crystals on the polished surfaces of the stone then dropping sufficient water on the crystals to dissolve them. The water and crystals were left on the stone overnight to allow the excess water to evaporate. The polished surfaces of the two granites were examined under a binocular microscope. They were then cleaned with a room temperature solution of oxalic acid made by dissolving 71.3 gm of oxalic acid crystals in water. The stained surfaces of both stones were wet down with water, scrubbed with the oxalic acid solution, then thoroughly flushed with water. This treatment had very little, if any, effect on the stains. Re-examination of the polished surfaces under the binocular microscope did not reveal any change.

The same treatment as above was repeated except a hot, (194° F) strong solution of oxalic acid containing 360 gm of crystals in 300 ml of water was used. This treatment removed the majority of the stain from both stones but a noticeable yellow stain still remained on the polished surfaces. Re-examination under the microscope revealed no change in structure but comparison with the untreated granite of the same numbers revealed quite a difference. After both 227 and 268 blocks had been blown dry with an air hose they were compared for color with blocks that had not been treated. No apparent difference in color could be seen between the acid treated and the untreated blocks of granite 268. However, the acid treated block of 227 was much darker in color than the untreated blocks of 227.

The stains on the two blocks were next treated with a solution of 113.4 gm of Vapor X crystals in 3.785 liters of water (4 ounces per gallon). This solution did not remove the remaining iron stain from each block but neither did it change the appearance and color of the granite.

The anomaly of the oxalic acid darkening granite 227 without changing the color of 268 was investigated further. One-half of a polished face of a block from each of the other granites was covered with polyethylene plastic taped in place. The other half of the face was first wet with water then scrubbed with the hot oxalic acid solution then finally rinsed with water. Each block was air dried, the plastic covers stripped off, and the surfaces visibly examined for darkening. Results of this examination are shown in Table V. These stones were allowed to air dry untouched for several days then re-examined. Some stones had visibly lightened after several days indicating moisture retention as a probable cause of part of the surface darkening. However, after one week's drying at least three of the stones still showed definite color differences.

The same procedure as outlined above is now being performed with a solution of Vapor X crystals and with Liquid Zit. The results of these studies are not yet complete.

Vapor X crystals were examined by x-ray diffraction. The diffraction pattern obtained corresponded to that of ammonium bifluoride (ammonium acid fluoride $NH_4 \cdot HF_2$). The x-ray fluorescence equipment is not yet in working order, therefore, it has not been possible to analyze the contents of Liquid Zit. However, a chemically pure solution of silver nitrate was reacted with

TABLE V

EFFECT OF ACID CLEANING ON COLOR OF POLISHED FACES
OF ELBERT COUNTY GRANITE

Immediately After Cleaning	After One Week Drying
211	211
299	206
227	227
206	245
282	282
245	299
263	268

Granites arranged in order of decreasing color change.

the Liquid Zit and a white precipitate formed. This precipitate was examined by x-ray diffraction and found to be silver chloride. This would indicate that Liquid Zit contains hydrochloric acid but does not rule out the possibility that other materials may also be present in the solution. The practice of preparing and storing oxalic acid solutions in steel drums may be adding iron to the oxalic acid solution. To check this possibility a fresh solution of oxalic acid saturated at room temperature has been prepared with distilled water in a steel can. At the same time a similar solution was prepared using oxalic acid crystals from the same lot in a glass container. After one week and two week periods, samples of these solutions will be analyzed spectrographically for iron content. The remaining oxalic acid solution in the steel can will be heated to at least 160° F and will be kept saturated by adding more oxalic crystals. The solution will be kept hot during working hours and allowed to cool at night. After an additional week a spectrographic analysis will be made of this solution and compared with the previous analyses.

3. Techniques for Measuring the Degree of Polish on a Granite Surface

Several small hand samples of polished granites from Elberton and Barre Vermont were obtained and visually examined and rated under office conditions (good lighting). The technique used was to reflect a fluorescent light in the polished surface and then examine visually for sharpness of the reflected image. The five samples representing two different Elbert County granites and one Barre granite were rated for polish as shown in Table VI.

TABLE VI

GLOSS RATINGS OF POLISHED GRANITE SURFACES

Granite Sample	Visual Rating*	Photovolt Meter Reading* (%)
Elberton HL	5	98
Barre	4	95
Elberton HW	3	94
Elberton O	2	94
Elberton H	1	89

*Decreasing numbers indicate decreasing polish

These pieces were then examined using a Photovolt reflection and gloss meter with a 60° search unit.

A black glass "standard" rated at a value of 94 was used to calibrate the instruments then readings were made on each of the polished granite specimens previously rated visually under ideal office lighted conditions.

The readings obtained with the meter are also included in Table VI.

The Photovolt readings were in excellent agreement with the visual observations made under ideal conditions. Therefore, this device will be used to help determine if acid cleaners damage the gloss of a polished granite surface.

V. DISCUSSION

A. Observation of Granite Finishing Operations

1. Cleaning of Gang Sawed Slabs

It is not possible at this stage of the work to say whether oxalic acid cleaning after gang sawing is beneficial or detrimental to the sawn slab. If the granite can be cleaned without damage by a mild acid solution, yet damaged by a more concentrated solution, it is safe to say that some stones are being damaged while others are not being hurt even at the same quarry. The practices observed indicate that a wide variation exists in concentration of oxalic acid solution used depending on the temperature at which it is applied and the length of time since the last fresh solution was prepared. A tremendous difference exists in the concentration of a saturated oxalic acid solution at 60° F and the concentration of a saturated solution at 140° F. If it is found necessary to use a saturated solution above ambient temperature a carefully prepared solution should be made in small batches and heated to the proper temperatures just at the time it is needed. A very hot solution evaporates rapidly and would quickly increase in concentration if not already saturated.

The use of steel drums for preparing and storing oxalic acid solutions is questionable. This practice may be adding large quantities of iron to the solution which if put on the stone hot could find its way into the pores of the stone, especially in summer weather when the stone is hot and the crystalline crevices are open. Flushing with cold water could cause a contraction of the stone closing these crevices and locking the oxalic acid solution in before it could be flushed away. As the stone dries and gradually heats up, the crevices would again open and oxalic acid solution would slowly evaporate. This would leave behind any iron which had been in solution in the oxalic acid. A laboratory test is now underway to determine the amount of iron added to the solution from a steel drum. This test should determine if the steel drums are contributing sufficient iron to the oxalic acid solutions to cause staining of granite washed with the solution.

2. Polishing Operations

No cause for staining or discoloration was found in the polishing operations. The quality of polish obtained appeared to be due to the skill of the polisher rather than to a particular combination of polishing grits. It was noted, however, that the plants using a full five step polishing procedure produced better polished stones than those using fewer steps.

3. Wash Rack Operations

Sufficient laboratory data is not yet available to assess the merits of the acid cleaners or techniques used by the various plants in removing stains from the finished monuments. Here as in the oxalic acid cleaning of gang sawed slabs, wide variations in concentrations of acids used were noted. It was encouraging to note that one manufacturer has good quality control of the acid solutions used on the wash rack. Also, it was noted that all but one manufacturer was exercising good practice by using plastic buckets rather than steel for acid solutions.

No assessment of the merits of using industrial naptha or white gasoline for removing organic adhesives left from the sand blasting operation can be made except the higher flash point of the naptha makes it safer for indoor use than gasoline.

The use of soap or detergent for removing the solvents is a recommended step. This will be an especially important step if a satisfactory pore sealer is developed. Comments by the foreman in one facility which previously had done some water proofing with Bond-Dri indicated that "a definite line appeared on the water proofed stone where the masking materials from the stencil had been located." This is an indication of improper removal of the stencil organic adhesives or the solvents used to remove them before water-proofing the monument.

Perhaps the worst condition noted at the wash rack was the practice at some plants of washing the finished die on the wooden base that then becomes the bottom of the crate. During the cleaning operation this base becomes saturated with water and acid solutions which can migrate into the stone by capillary action. Some plants have recognized this problem and transfer the washed and dried monument to a dry base before crating. Others are trying to circumvent this problem by insulating the monument from the wooden base with strips of impervious plastic sheeting.

4. Crating of the Finished Monuments

There are three materials in use for protecting the finished faces of the monument in transit. These are newsprint, kraft paper, and clear polyethylene plastic. Many foremen recognize a problem called "board stains" which are found on monuments at the time of uncrating. The users of polyethylene plastic blame the kraft paper for these stains. The users of kraft paper say that the impervious plastics cause monuments to "sweat" during transit and that this is responsible for board stains. The merits of these two materials have not been assessed at this time. However, it is suspected that the acid and water-soaked bases of the crates may be partially responsible for such stains.

B. Observation of Elberton Granite Monuments in Local Cemeteries

Of the wet and stained monuments observed in the local cemeteries almost all could have been corrected by proper design of carvings to allow for drainage and by proper setting of the monuments. Where wet dies appeared there was always very little or no setting compound between the die and the stock, or the stock was partially buried in the ground.

Elberton wholesalers need to "educate" the retail monument dealers in proper methods of setting monuments and need to establish policies to guarantee that franchised dealers properly install all monuments. Proper installation and design should stop much criticism of Elberton Granite even without the development of a "sealing material."

C. Laboratory Work

1. Pore Sealing Techniques

The accelerated aging tests on granites treated with the candidate "pore sealing" materials have not progressed sufficiently to a point where any observations can be made.

2. Cleaning Techniques

During cleaning studies it was observed that at least three of the Elberton granites were badly darkened when treated with a hot oxalic acid solution. The same identical treatment had little effect on the next two stones and almost no effect on two other stones. It is interesting to note from Table V that except for granite 282 the darkening effect followed the same order as the transverse strength reported under the previous ARA work.* The higher the transverse strength, the less darkening occurred. The water transmission rate studies now being

*Lewis, J. L. and J. N. Harris, "A Program of Research and Technical Assistance for the Granite Industry in Elbert County, Georgia," Engineering Experiment Station, Georgia Institute of Technology, U. S. Department of Commerce Contract Cc-6033, p 82.

conducted may help to reveal a reason for the darkening of these three stones.

Studies of other cleaning materials to include removal of iron stains from unpolished surfaces will be conducted during the next report period.

3. Techniques for Measuring the Degree of Polish on a Granite Surface

Although the scope of this contract work is not directly concerned with polishability of Elberton granite or the ability to effectively measure this polish, it was planned to use the Photovolt reflection and gloss meter as an aid in determining the effect of acid cleaning agents on the polished surfaces of Elberton granite. Therefore, it was necessary to determine if this meter could discriminate between slight differences in gloss of polished surfaces.

The Photovolt reflection and gloss meter can be used to effectively measure the gloss of a polished surface on a granite monument. Such a meter could aid the EGA inspector in the Certified Monument Program. Poor plant lighting conditions would not affect the meter reading since it contains its own light source, can be battery operated, and the sensing head can be operated in any position. Because of the wide range of color and texture (grain size) of the various Elbert County granites, it would be necessary to establish a standard for each type of granite in the district. Once these were established, the meter could be used to evaluate the polish on any monument and a value could be established below which a polished monument would not be acceptable.

[redacted]

INTERIM REPORT NO. 2

PROJECT A-892

DEVELOPMENT OF A WATER REPELLENT TREATMENT FOR ELBERT COUNTY GRANITE

J. N. HARRIS

April 1966

Prepared for
Elberton Granite Assoc., Inc.
Elberton, Georgia

1966

Engineering Experiment Station
GEORGIA INSTITUTE OF TECHNOLOGY
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This report contains 15 pages.

I. SUMMARY

Investigations were continued on a number of candidate "pore sealing" materials by artificial weathering of granite specimens treated with these materials. Several different Elberton granites treated with four candidate "pore sealing" materials have been subjected to accelerated weathering tests under the influence of water, and oxides of carbon, sulfur, and nitrogen. Solid materials such as lampblack (soot) have been allowed to settle on the granites for intermittent periods of time and have then been washed away. All stones are beginning to show evidences of darkening in color and staining. It is anticipated that six to eight additional weeks of accelerated weathering tests should be sufficient to evaluate the relative value of each candidate pore sealant.

An entirely different approach to the preservation of limestone and marble monuments has been made by a New York University professor. He has expressed interest in adapting his techniques and materials to granite. This is presently being explored.

Water transmission studies did not reveal a relationship to a granite's tendency to retain a "wet" apperance for a long period of time.

Liquid Zit, an acid cleaner containing HCl, causes the same order of darkening of individual granites as does hot oxalic acid.

Gloss measurements on polished granite surfaces before and after acid cleaning reveal that acid cleaning causes a dulling of the gloss of the polished surface.

Although a saturated oxalic acid solution may contain more than one per cent iron, this iron in solution does not appear to cause immediate staining of the granite. However, since the oxalic acid could tie up iron in a color-

less complex the definite absence of iron penetration of the granite surface at this time cannot be proved. If an iron complex does penetrate the surface the action of weathering over many years might break down the complex causing future stains.

Attempts to remove oil stains from granite were unsuccessful except by the use of light organics such as naptha and gasoline. Future work will be undertaken to develop procedures to insure complete removal of all organic materials.

II. PURPOSE

The objective of this project is (1) to develop "pore sealing" techniques in granite to prevent discoloration or staining, and (2) to develop standardized cleaning agents and techniques to be recommended for use throughout the Elberton Granite Association.

III. INTRODUCTION

The first interim report under this contract discussed the methods and processes involved in producing a finished granite memorial. The areas in the finishing process which might contribute to the development of stains and other defects in the granite memorial were examined and some possible problem areas suggested for further study.

Equipment was constructed and artificial aging studies were begun using untreated and "pore sealed" granites. This study was continued during the second interim report period and is still in progress. Work was continued concurrently on a cleaning study.

III. EXPERIMENTAL PROCEDURE

A. Accelerated Weathering Studies

During this period treated stones and a control set (untreated) have been subjected to an atmosphere containing high concentrations of the oxides of carbon, sulfur and nitrogen. These concentrations have been intermittently varied. The concentration of water vapor in the atmospheric chamber has also been varied from a relative humidity of less than 20 per cent to more than 95 per cent at temperatures of 75° to 80° F. The temperature in the chamber was varied from +80° F to less than -70° F. Solid materials which are found in industrial atmospheres, such as carbon (soot), have been allowed to settle on the stones in the chamber.

Every two to four weeks the stones were removed from the chamber and examined visually. Each set of stones was rated visually from darkest to lightest according to the treatment given the stones. Also each stone was examined carefully for the appearance of yellow or rust colored stains. The results of the latest examination are shown in Table I.

Each stone was then thoroughly scrubbed with a Tampico brush and tap water then placed in a 130° F room for 24 hours. After this treatment the stones were again visually examined, rated from darkest to lightest, and any unusual stains noted. No changes in darkness ratings were noted and stains were slight.

After completion of each such examination the stones were returned to the Plexiglass chamber along with fresh chemicals to generate high concentrations of gaseous oxides.

TABLE I

EFFECTS OF ACCELERATED WEATHERING ON ELBERT COUNTY GRANITE

Granite Number	Treatment: Plain (Control)	Bond-Dri	Ethyl Silicate 40	GE SC-50	Sodium Silicate	Remarks
206*	3	1	4	2	5	Polished surfaces uneven in color on sodium silicate and ethyl silicate treated stones.
211*	4	1	4	2	5	Large brown stains on unpolished surfaces of plain and sodium silicate treated stone.
227*	5	1	4	2	5	Yellow stains on unpolished surface of plain stone. Large brown stains on unpolished surfaces of plain and ethyl silicate treated stones.
245	3	2	5	2	4	Dark green-yellow stains on unpolished surface of plain stone yellow stains on unpolished surfaces of SC-50 and ethyl silicate treated stones.

NOTE: 1 indicates lightest color 5 indicates darkest.

*Color change from 1 to 5 covers a wide range on these stones.

(Continued)

TABLE I (Continued)

EFFECTS OF ACCELERATED WEATHERING ON ELBERT COUNTY GRANITE

Granite Number	Treatment: Plain (Control)	Treatment: Bond-Dri	Treatment: Ethyl Silicate 40	Treatment: GE SC-50	Treatment: Sodium Silicate	Remarks
268	5	1	2	3	4	Dark green-yellow stains on unpolished surface of plain stone.
282*	5	2	4	1	3	Untreated stone has developed a large blue-green stain on polished surface and a yellow-brown stain on unpolished surface. The Bond-Dri treated stone has developed a small brown stain on an unpolished surface.
299	4	1	5	2	4	Small brownish stains on unpolished surfaces of Bond-Dri stone.

NOTE: 1 indicates lightest color 5 indicates darkest.

*Color change from 1 to 5 covers a wide range on these stones.

B. Pore Sealants

Information was obtained from the Linde Corporation on their product Y-1059 which had been previously used in Elberton to some extent. This material is now considered obsolete and they are not actively pursuing the development of any new "waterproofing" materials. Their experience with Y-1059 was unsatisfactory as a material for "waterproofing" granite.

Water transmission rate studies, described in the previous interim report, were completed. The water transmitted through each granite in a period of six days is shown in Figure 1. The area of each granite specimen exposed to the atmosphere was approximately 3.6 in^2. Table II shows air porosity and water absorption rates obtained in the previous ARA work as a supplement to the data in Figure 1.

TABLE II

AVERAGE ABSORPTION AND POROSITY
OF ELBERT COUNTY GRANITES

Bar No.	Air Porosity (%)	Water Absorption (%)
206	1.35	0.38
211	1.27	0.36
227	1.36	0.36
245	1.27	0.35
268	1.23	0.27
282	1.58	0.42
299	1.67	0.38

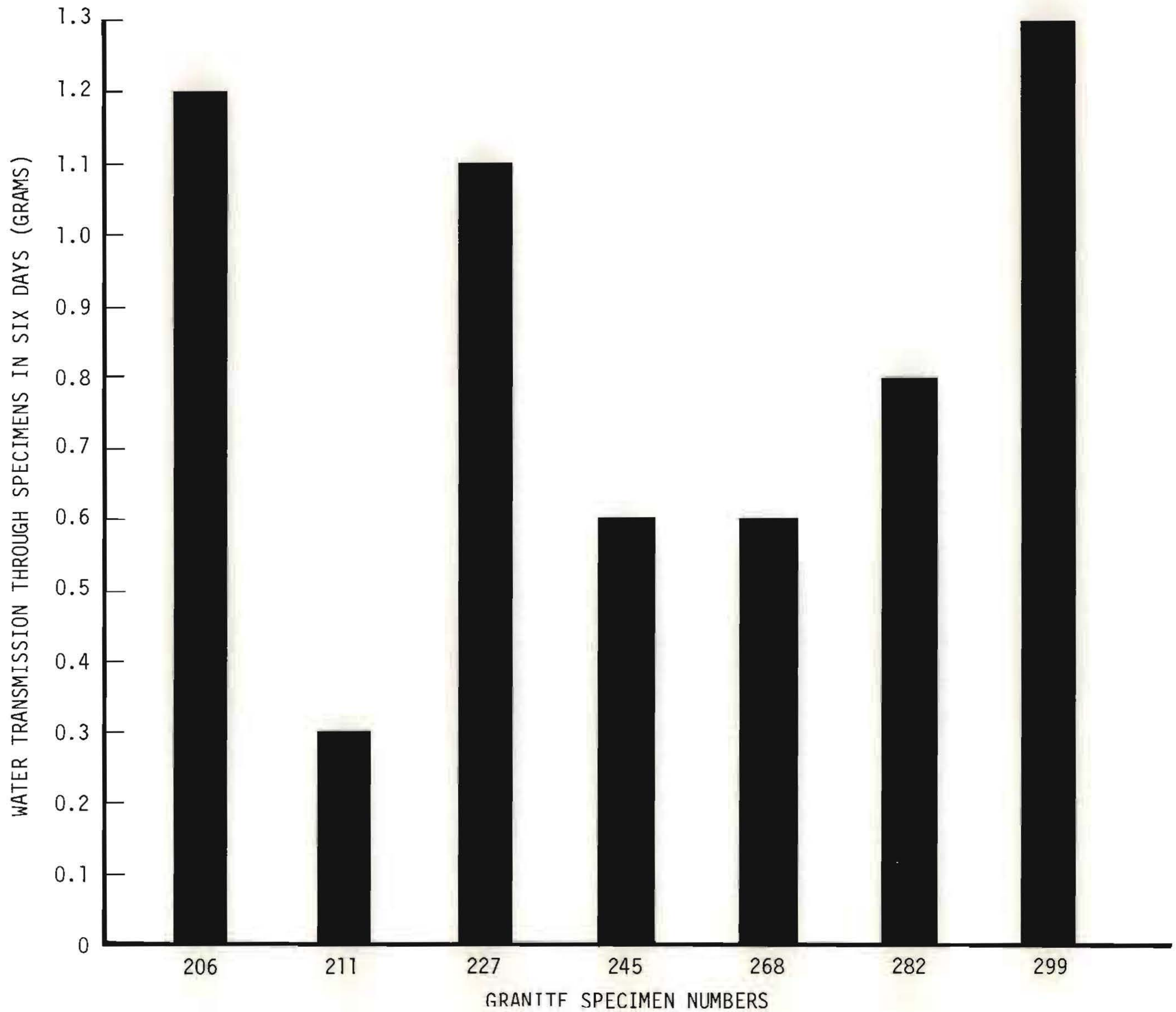

Figure 1. Water Transmission of Elbert County Granite.

C. Cleaning Techniques

Liquid Zit was used to clean one-half of a polished face of each different granite. The other half of the polished face was covered with polyethylene plastic taped in place to prevent any of the Liquid Zit from reacting with the granite under the covered portion. The Liquid Zit was applied after first thoroughly wetting the stone with water. The Liquid Zit was allowed to remain on the surface for ten minutes and was then thoroughly flushed away with tap water. The wet surface was then dried with high pressure air and the tape and plastic film stripped off. A visual examination of the treated and untreated surfaces of each block was made. The results are shown in Table III. These results are identical with those obtained with the oxalic acid treatment as reported in Table V of Interim Report No. 1.

TABLE III

EFFECT OF CLEANING WITH LIQUID ZIT ON COLOR OF POLISHED FACES OF ELBERT COUNTY GRANITE

Immediately After Cleaning	After One Week Drying
211	211
299	206
227	227
206	245
282	282
245	299
268	268

Granites arranged in order of decreasing color change.

The Photovolt Reflectometer was used to measure the effect of acid cleaning on a polished surface. A set of granite blocks was prepared, as before, by covering one-half of each polished surface with plastic film. The other half of one polished face was cleaned with oxalic acid. The opposite half face was cleaned with a solution of Vapor-X crystals. After thoroughly flushing with water the plastic films were stripped off and the stone dried thoroughly at 130° F for 48 hours. Photovolt Reflectometer measurements were made on each treated and untreated polished surface of each stone. These readings are shown in Table IV.

TABLE IV

GLOSS RATINGS OF POLISHED GRANITE SURFACES BEFORE AND AFTER CLEANING WITH ACID CLEANERS

Granite	Control Surface	After Cleaning With Vapor-X	Control Surface	After Cleaning With Oxalic Acid
206	75	64	89	82
211	92	88	90	80
227	90	88	82	64
245	91	85	94	87
268	93	87	75	42?
282	79	82	87	87
299	81	82	94	85

The following work was undertaken to determine the effect of iron, taken into an oxalic acid solution from a steel container, on staining of stones cleaned with the acid solution. A room temperature saturated solution of oxalic acid was prepared in a steel container. The container was covered with a lid to prevent evaporation of the solution and left undisturbed for one week. At the end of a week the solution was stirred and a small sample removed for spectrographic analysis. The lid was replaced and the solution allowed to remain undisturbed for another week. At the end of this period a second sample was removed for spectrographic examination. The oxalic acid solution in the can was then heated to boiling and additional oxalic acid crystals added to saturate the solution. The solution was boiled for 70 minutes then cooled and a sample taken for spectrographic analysis.

Spectrographic analysis showed the room temperature saturated solution had picked up 0.1 per cent iron after one week, and 1.0 per cent iron after two weeks. Boiling of the solution caused a further pick up of only a slight additional percentage of iron.

Polished and rough surfaces of the Elbert County granites were cleaned with the oxalic acid solution from the steel container. The solution was applied to the granites in various ways, i.e. hot solution on cold stones (70°), hot solution on hot stones (130° F), cold solution on cold stones, and cold solution on hot stones. In some cases the acid solution was wahed off the stones before it had a chance to dry. In other cases the acid was allowed to dry on the stone overnight. The dried acid left a yellow stain on the surface of the granite, but this stain was easily removed by flushing with water.

Attempts were made to observe any changes in the surface of the granites after the various acid cleaning treatments. Before application of the acid the surfaces of the granites were observed under a microscope. After each acid treatment the same area of each treated surface was again observed. No changes in grain structure were observable by this technique.

Since subtle changes might not be detected by this technique micrographs were made from a small polished section of granite. A small section of granite 268 was hand polished to a high luster using 0.5 micron diameter aluminum oxide as the final polishing step. A 6.5X micrograph was made of this surface. The polished surface was then cleaned with oxalic acid, flushed with water, dried and a micrograph made of the same area as previously photographed. No noticeable differences were found between the two micrographs.

Attempts have been made to duplicate in the laboratory the type of stains found at the quarry and in finishing operations. Iron stains were obtained by allowing steel shot to rust while in contact with the surface of granite blocks. Grease spots were obtained by mixing iron filings left on a power hacksaw with water and pouring this suspension onto the granite surface. The iron did not rust but the grease on the filings was absorbed into the granite. This offered an opportunity to examine methods for removing the grease spot without resorting to organic liquids such as naptha or gasoline. Attempts were made to remove the spot with water, detergent and scrub brush. This treatment did not remove the spot. It was then found necessary to resort to an organic liquid to completely remove the grease. Work is now progressing on the best methods to remove rust stains and oil spots and to determine if the removal treatment is in anyway detrimental to the surface of the granite.

V. DISCUSSION

The accelerated weathering studies are beginning to show results by the darkening and staining of some of the untreated stones and a few of the treated stones. At this time it is felt that an additional 6 to 8 weeks is needed to fully assess the effects of the artificial weathering of the treated stones and to determine which, if any, of the treatments will be most beneficial to all Elbert County granites.

Should none of the present treatments prove beneficial there is still a possibility of an entirely different type of treatment. A New York University professor has developed a successful treatment for limestone and marble. He has expressed an interest in examining samples of Elberton granite and would be glad to make his materials available should they prove beneficial. This possibility is now being actively investigated.

The water transmission rate studies show quite a difference in rate of transmission for the seven different Elbert County granites in this study. However, there is no apparent relation between water transmission rate, porosity, or the tendence to retain a "wet" appearance on polished surfaces. For instance, after being wet, granite 211 retains a darker appearance longer than any other granite, yet is has a low porosity and low water transmission rate. Granite 299 has the next "wettest" appearance, yet it has a high porosity and high water transmission rate. On granites 268 and 245 both the water transmission rate and porosity are average for the Elberton area granites, yet these two stones lose their "wet" appearance faster than any of the other granites.

The tendency of a granite to darken when treated with an acid solution seems to be a combination of the stones tendency to remain "wet" and its composition. Stones cleaned with Liquid Zit and dried with high pressure air exhibited the same order of darkening as did the stones cleaned with hot oxalic acid. These values were reported in Interim Report No. 1.

The use of an acid cleaner on a polished granite surface dulls the polish as can be seen by the Photovolt Reflectometer results shown in Table IV.

The iron picked up in the oxalic acid solution from the steel drums used at the gang-saw operations has no visibly apparent effect on the cleaning ability of the solution. A visible iron stain does not result even when an iron bearing oxalic acid solution is allowed to dry on the surface of a stone. On the other hand, an iron bearing hydrochloric acid solution allowed to dry on the surface of a stone produces an iron stain which penetrates the polished surface. This stain is impossible to remove without removing the granite surface.

This difference can be attributed to one of two reasons. The hydrochloric acid holds the iron in solution as long as there is liquid present. In the presence of moist air this material is oxidized to iron oxide (rust). While in the liquid state this material disassociates into iron, hydrogen and chloride ions. The ions of iron are roughly the same size as an atom of iron and hence, can penetrate the smallest crevice or pore in the granite surface. As the liquid evaporates iron is left behind in the crevices. Oxalic acid is a chelating agent, this means that iron in an oxalic acid solution is tied up in a complex molecule. This molecule; (1) may be too large to penetrate the small crevices or pores of the granite surface, or (2) the molecule penetrates the surface of the granite but upon evaporation of the liquid is left in the granite as an unseen colorless complex. If the latter is the case, a granite memorial might be put into service and many years later, through the action of weathering, the complex molecule might be broken down releasing the trapped iron. This iron could then oxidize producing iron stains. The use of an oxalic acid cleaner on surfaces which are to be removed later in polishing operations should not be detrimental. However, the use of oxalic acid on the final polished surface could possibly cause stains at a later time.

Attempts to remove organic oil stains by methods other than those already in use in Elbert County have been unsuccessful. One problem still to be investigated is to determine what is necessary to be sure that all of the light organic cleaner (naptha, gasoline, etc) that is used to remove the oil is also thoroughly removed from the stone.