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BONDING PROPERTIES OF MILL WASTE

TAILINGS

By

Jozef R. Roos

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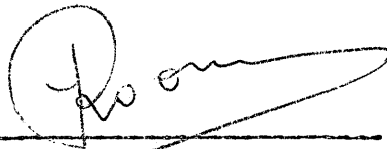
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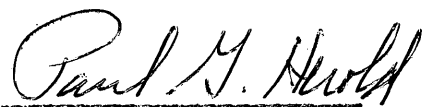
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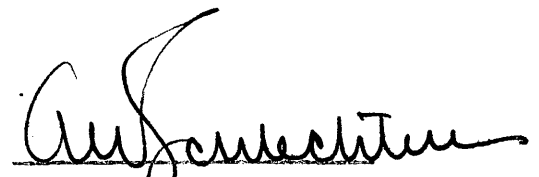
A thesis respectfully submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Metallurgical Engineering.

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ABSTRACT

The United States Bureau of Mines sponsored this work in the area of solid waste disposal. This work was aimed at trying to utilize mine dump and mill waste tailing piles, which are so abundant in the state of Colorado.

The waste materials were studied as a raw material for the production of building products formed by the use of low - temperature bonding action.

The materials from fourteen different tailing piles were analyzed to determine their constituents. Atomic absorption spectrophotometry was the most important analyzing technique used.

The relative solubilities of silica in saturated solutions of calcium hydroxide and of magnesium hydroxide in water were determined. Test bars were made with tailings and calcium hydroxide as bonding agent. The bars were aged under various conditions and their strength measured. It was found that aging in steam at 125 C speeded up the strengthening mechanism greatly.

It was also found that the two mechanisms for cementitious bonding, carbonation and formation of hydrated calcium silicates, contributed in the same amount to the strengthening.

Construction bricks could be formed from tailings and lime, using a steam curing treatment.

Also test bars were formed with tailings and a petroleum - based binder. On aging at 110 C for ten days, the bars developed appreciable strength. In this way, building blocks of equal quality to commercial concrete blocks could be produced. Such blocks also would be less expensive to manufacture.

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ACKNOWLEDGEMENTS

The author wishes to express his appreciation to Dr. P. G. Herold for his interest and guidance during this study. Also the author is indebted to the United States Bureau of Mines for sponsoring this research.

INTRODUCTION

Mine waste dumps and tailing piles are very abundant in the state of Colorado. When the gold rush came to an end late in the nineteenth century hundreds of mines closed down and left a considerable amount of the waste materials behind.

Mining and milling operations today are producing thousands of tons of tailings each day, thus adding unsightly material to the scenery. For example: American Metal Climax, Inc., at Climax, Colorado, rejects forty thousand tons of tailings each day. Not only is the scenery marred, but also the mining companies have to invest huge amounts of capital in the disposal of their tailings.

The present study was aimed at trying to utilize these mill and mine waste tailing materials. This study was conceived as preliminary theoretical work for actual forming of various types of ceramic ware. The portion of the problem covered by this thesis was detailed as a study of the waste materials as a raw material for the production of building products formed by the use of low - temperature bonding action.

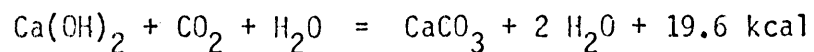
This would be similar to the methods presently used in the concrete block industry, with or without steam curing.

The study was also intended to include bonding by water - soluble materials such as calcium hydroxide and magnesium hydroxide.

REVIEW OF LITERATURE

To our knowledge the present study is new in its purpose: trying to utilize mine dump and mill waste tailings. Certainly limited studies have been done by several mining companies, but these investigations were aimed primarily at stabilizing the tailing piles.

The literature review which follows refers to the lime - soil and lime - silica reactions. Zalmanoff (1, 2) and Taylor (3) considered carbonation and formation of hydrated calcium silicates as the mechanisms for strengthening lime - silica materials. Zalmanoff (1) described the general conditions for the carbonation of lime. The carbonation reaction is given as follows:



The reaction is heterogeneous inasmuch as a solid, a gas, and a liquid are on the left hand side of the equation. The precipitation reaction is most likely to occur in the liquid state, due to the ionic characteristics of the participants. If the reaction takes place in the liquid state, the gaseous CO_2 must undergo a solutioning process which is another complex step. In the above reaction, the reaction rate is controlled by the availability of CO_2 and by the rate at which water can be removed from the system. Since the natural CO_2 content of the air is so low - only 0.05 % by weight (4) - the reaction proceeds rather slowly.

Hall (5) found that calcium hydroxide mixed with a clay and cured in a steam atmosphere at 100 C developed very quickly the strength obtained only after allowing the carbonation reaction to take place in air for several weeks. Hall proved that this was due to the formation of hydrated calcium silicates. This reaction also is likely to take place in the liquid state. However, here water has to be provided for the hydration reaction to take place. The hydrated calcium silicates formed in this way were found to be amorphous or very poorly crystalline.

For a more detailed description of the mechanisms involved in carbonation and formation of hydrated calcium silicates, which is beyond the scope of this work, see references 1, 2, and 4.

It should also be noted that calcium hydroxide is used for the production of silica brick which is a refractory material. The calcium hydroxide takes silica in solution and forms calcium silicate liquid which, on drying, acts as a glue (6).

MATERIALS USED AND EXPERIMENTAL PROCEDURE

Tailings investigated and method of sampling

The designation of the tailings used, their location, the type of tailing, their age (estimated time on the pile), and the date they were taken are given in Table 1.

Some of the tailings were taken by the author, others were received from the Companies mentioned. The samples were taken at different places on the piles so that a fairly representative sample was obtained. To get a better representative sample of a pile, drilling would have been necessary. Indeed the composition of the material at the bottom of the pile can vary somewhat from the composition of the material at the top. This variation in composition could be caused by a change in milling or mining procedures and/or by weathering.

However since the primary aim of this study was to investigate the materials in the tailing piles as a preparation for the production of structural products, these relatively small variations in composition become unimportant.

Table 1: Tailings investigated in this study.

Designation	Location	Type	Age(years)	Date taken
Old Climax	Climax, Colo. Amax, Inc.	Flotation tailing	40	October 20, 1966
Young Climax	Climax, Colo. Amax, Inc.	Flotation tailing	0	October 20, 1966
Naturita	Naturita, Colo. Vanadium Corp. of America	Flotation tailing	0	November 18, 1966
Durango	Durango, Colo. Vanadium Corp. of America	Flotation tailing	0	December 15, 1966
Idaho Springs	Idaho Springs, Colo.	Mine waste dump	80	October 20, 1966
Lead Slag	Leadville, Colo.	Smelter slag dump	10	April 10, 1967
Silverton	Silverton, Colo.	Mine waste dump	80	April 10, 1967
Ouray	Ouray, Colo.	Flotation tailing	50	April 10, 1967

Table 1 (continued): Tailings investigated in this study.

Designation	Location	Type	Age(years)	Date taken
Sawach	Leadville, Colo.	Mine waste dump	80	July 20, 1967
Lower Denaro	Leadville, Colo.	Mine waste dump	80	July 20, 1967
Iron Mask	Leadville, Colo.	Mine waste dump	80	July 20, 1967
Little Jonny	Leadville, Colo.	Mine waste dump	80	July 20, 1967
El Capitan	Leadville, Colo.	Mine waste dump	80	July 20, 1967
F. T. E. *	Leadville, Colo.	Flotation tailing	50	July 20, 1967

* Flotation Tailings East of Leadville, Colo.

Chemicals used

Penepriime: inexpensive petroleum-based binder, commercial product from Empire Petroleum Company, Denver, Colorado. No analysis.

Perchloric acid (HClO_4): Baker Analyzed Reagent, No. 9652.

Contains less than 0.003 % impurities.

Hydrfluoric acid (HF): Baker and Adamson Reagent A. C. S., Code 1100.

Contains less than 0.006 % impurities.

Potassium pyrosulfate ($\text{K}_2\text{S}_2\text{O}_7$): Baker and Adamson Reagent A. C. S.,

Code 2094. Contains less than 0.008 % impurities.

Calcium carbonate (CaCO_3) used for test bars: commercial product

from Mallinckrodt. No analysis.

Calcium carbonate (CaCO_3) used for solubility measurements:

Mallinckrodt Analytical Reagent 4071. Contains less than 0.001 % silica.

Magnesium oxide (MgO): Mallinckrodt Analytical Reagent 6015.

Contains less than 0.04 % silica.

Calcium hydroxide was produced by calcining calcium carbonate at 1000 C and reacting the resulting calcium oxide with distilled water. Magnesium hydroxide was produced by reacting magnesium oxide with distilled water.

The purity of the chemicals was checked before use by X-ray diffraction analysis.

The standard solutions used for atomic absorption spectrophotometry were supplied by Fisher Scientific Company and by Aztec Instruments, Inc.

Moisture content of the tailings

250. g of each tailing sample was weighed and dried overnight at 110 C. The moisture content was calculated by the following expression:

$$\% \text{ Moisture content} = \frac{250.0 - \text{dry weight}}{250.0} \times 100.0$$

Sieve analysis of the tailings

In order to determine the sieve analysis of each tailing, 200 g of the dry materials were weighed and stirred in water for one hour. By washing the material through one sieve after the other, the materials on Tyler sieves 8, 10, 14, 20, 28, 35, 48, 65, 100, 150, 200, and 325 mesh were obtained.

The particles that passed the 325-mesh sieve were classified into different size fractions by means of a settling test in 14-in.-high glass cylinders.

The Lead Slag tailings were extremely coarse and were crushed to -8 mesh before the sieve analysis test was made.

Analysis by X-ray diffraction

A Horelco X-ray diffraction apparatus was used with the copper-target tube operating at 50 kV and 35 mA. The X-rays generated were filtered by means of a nickel filter, and the results were recorded as line intensity versus the diffraction angle on a chart.

The patterns were recorded between 2θ values of 10 and 80 degrees at a speed of 1 degree 2θ per minute.

The principles on which the diffraction technique is based are well known (7, 8). Bragg's law ($n\lambda = 2d\sin\theta$) gives a relationship between the wavelength λ of the X-rays, the diffraction angle θ , and the interplanar distance d . Thus each compound has its own characteristic peaks on a recorded pattern.

Chemical analysis by X-ray fluorescence

A Horelco X-ray fluorescence apparatus with the copper-target tube operating at 40 kV and 30 mA was used for qualitative analysis, and also for quantitative analysis of silicon and titanium.

The method is as follows (9): A high capacity exciter tube irradiates the unknown sample, removing electrons from the L- and K-levels and thus causing the various types of atoms in the sample to emit their characteristic radiations. These characteristic X-rays are then analyzed by means of an analyzer crystal separating them into their respective $\sin \theta$ values according to Bragg's law, $n\lambda = 2d\sin\theta$. Since each element has its own characteristic radiation an identification can readily be made on a qualitative basis.

For each tailing sample, two complete patterns were taken between 5 and 110 degrees of 2θ , recording line intensity versus angle 2θ . One pattern of each tailing was taken at standard atmospheric pressure, using a lithium fluoride crystal and a scintillation counter. This allowed the detection of the elements above titanium in the periodic table, present in the sample. Another pattern was taken with the system under vacuum and with argon flushing through, using an A. D. P. analyzer crystal and a gas flow counter. This allowed the detection

of the elements between sodium and vanadium of the periodic table, present in the sample.

The technique was also used to obtain a quantitative analysis for silicon and titanium. Standards were used with compositions slightly lower and higher in silicon and titanium than the unknown sample, and with a matrix similar to the sample matrix. The line intensity was measured at a fixed angle of 2θ for standards and samples, both for silicon and titanium. The amount of unknown in the samples was determined by linear interpolation. The sensitivity of the apparatus used was not very high for the determination of silicon; the results for silicon analysis need to be considered as $\pm 2\%$ silicon.

Chemical analysis by atomic absorption spectrophotometry

A Techtron AA-4 atomic absorption spectrophotometry unit was used for the quantitative analysis of iron, calcium, magnesium, sodium, potassium, aluminum, silver, and gold.

With this technique the element which has to be determined may be a major component or a "trace". In this instance "trace" metal concentration is in the order of one part per million (1 ppm).

Some elements can be determined at levels below this, e. g. 0.003 ppm zinc, - but there are others which are difficult to determine even at the 10 ppm level, e. g. vanadium (9).

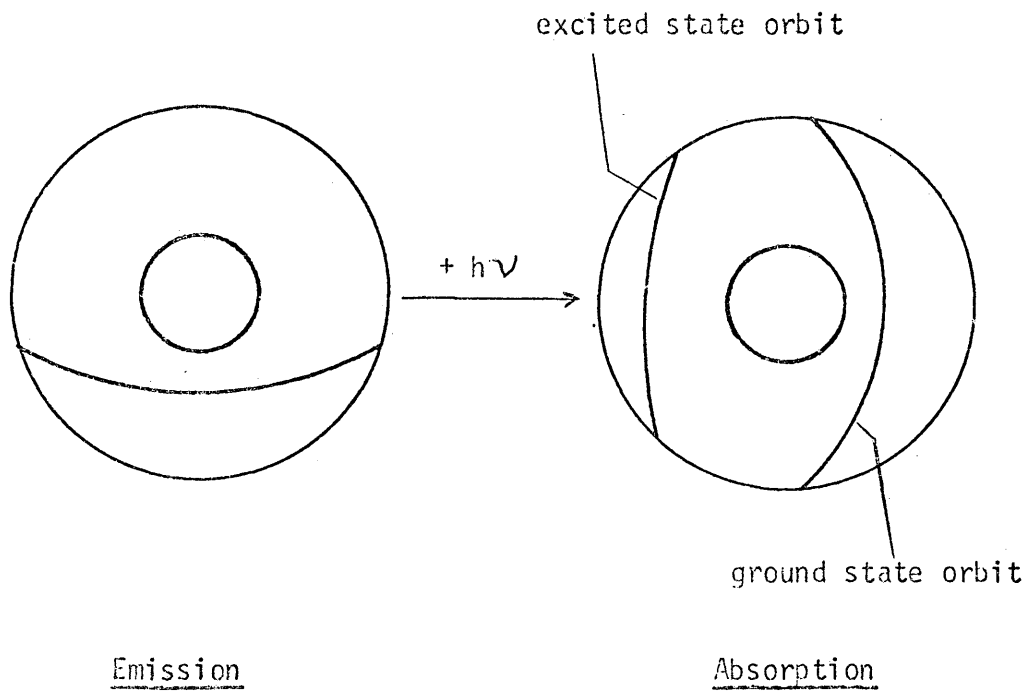
With the present commercially available equipment the sample should be a liquid. For solids and gas samples conversion to a liquid is required; the ease of this step depends on the sample under consideration. The method used in this study to convert the solid samples into liquids is given in a following paragraph under the heading, Preparation of samples for atomic absorption spectrophotometry.

The basis for the atomic absorption analyzing method is as follows (10, 11, 12): The element being analyzed is atomized in a flame. The atoms strongly absorb radiant energy at their resonance frequencies. Measurement of how much energy is absorbed indicates how much of the metal was in the sample. The process is the reverse of emission spectrophotometry as can be seen from Figure 1 (10). Atomic absorption spectrophotometry looks at unexcited atoms; emission spectrophotometry detects energies from excited atoms returning to the ground state.

Because of the nature of the procedure, there are certain advantages inherent in this method:

1. It is very sensitive. Because of the intensive absorption at the resonance wavelength, determinations at the ppm level can be done easily for most elements.

Figure 1: The emission and absorption processes.



2. It is relatively free from interferences by other elements.

Because the wavelength band absorbed by a particular element is so narrow, other elements will not absorb even though they are in the light path. Unfortunately the element itself usually emits at the identical wavelength at which it absorbs. However,

this side effect has been overcome by modulating the equipment.

3. It is very versatile. As of today about fifty metals can be determined by this method. The concentration level of components which can be directly analyzed can be varied simply by changing to a different absorption wavelength, or by changing the length of the absorption optical path. This can be seen from the Beer-Lambert law (13):

$$\log I = \log I_0 - K l c$$

in which I_0 = initial intensity of the beam of radiation,

I = reduced intensity,

K = extinction coefficient of the vapor at
wavelength ,

l = length of the absorbing medium, and

c = concentration of analyte.

Some of the inherent difficulties of the method which have not been overcome as yet are listed below:

1. Elements must be determined one at a time.
2. Only liquid samples can be analyzed by the presently available equipment. Without doubt the future will provide us with the facility of atomizing solids directly (14).

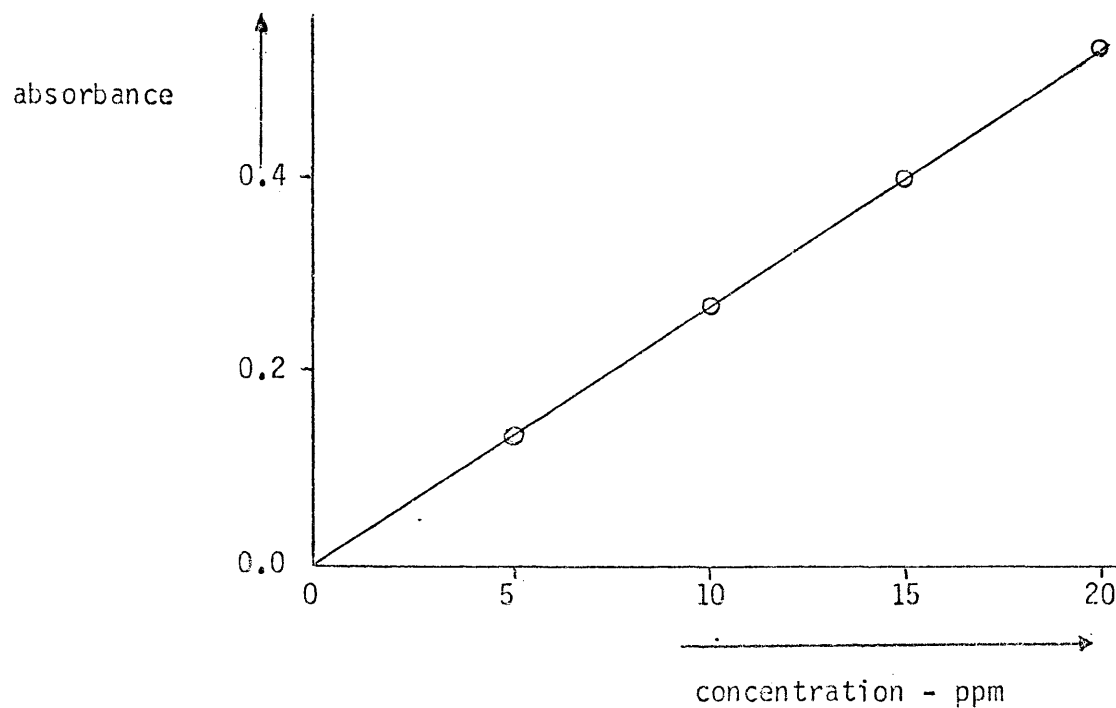
3. Cations often cause interference by controlling the rate of reduction of molecules to atoms.
4. About fifty percent of the known elements cannot yet be analyzed by this method.

The determination of the unknown concentration of a certain element in an aqueous solution was done as follows: The samples were diluted so that the concentration of the analyte was in a definite range. This concentration range was 1 to 20 ppm for the elements iron, calcium, magnesium, sodium, and potassium, 50 to 300 ppm for aluminum, and 0.05 to 1 ppm for silver and gold. Standards were prepared for each element covering the appropriate concentration range.

In the case of aluminum, chemical interference by sodium was observed. To overcome this problem 1000 ppm of sodium was added to the standards and samples, establishing in this way the same amount of interference for standards and samples.

The atomic absorption unit used in this study indicates percent transmittance (T) or absorbance (A) directly, where $A = \log 1/T$. Absorbance was plotted versus concentration. A calibration curve which is typical for iron, calcium, magnesium, silver, and gold is shown in Figure 2. For silver and gold, only the section of the curve below 5 ppm should be considered.

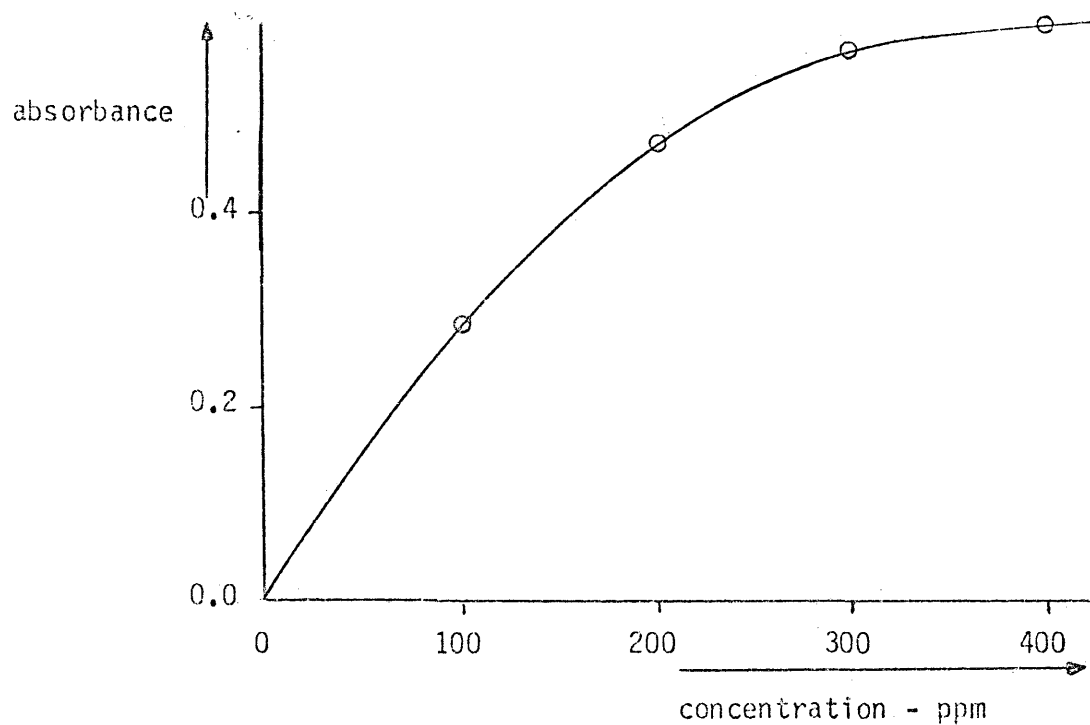
Figure 2: Typical calibration curve for iron, calcium, magnesium, silver, and gold.



A typical calibration curve for aluminum is represented in Figure 3. Note that the Beer-Lambert law is not obeyed at these high concentrations.

In the case of sodium and potassium, a definite interference was observed which was primarily not chemical; all kinds of elements were added to standards and samples to test this.

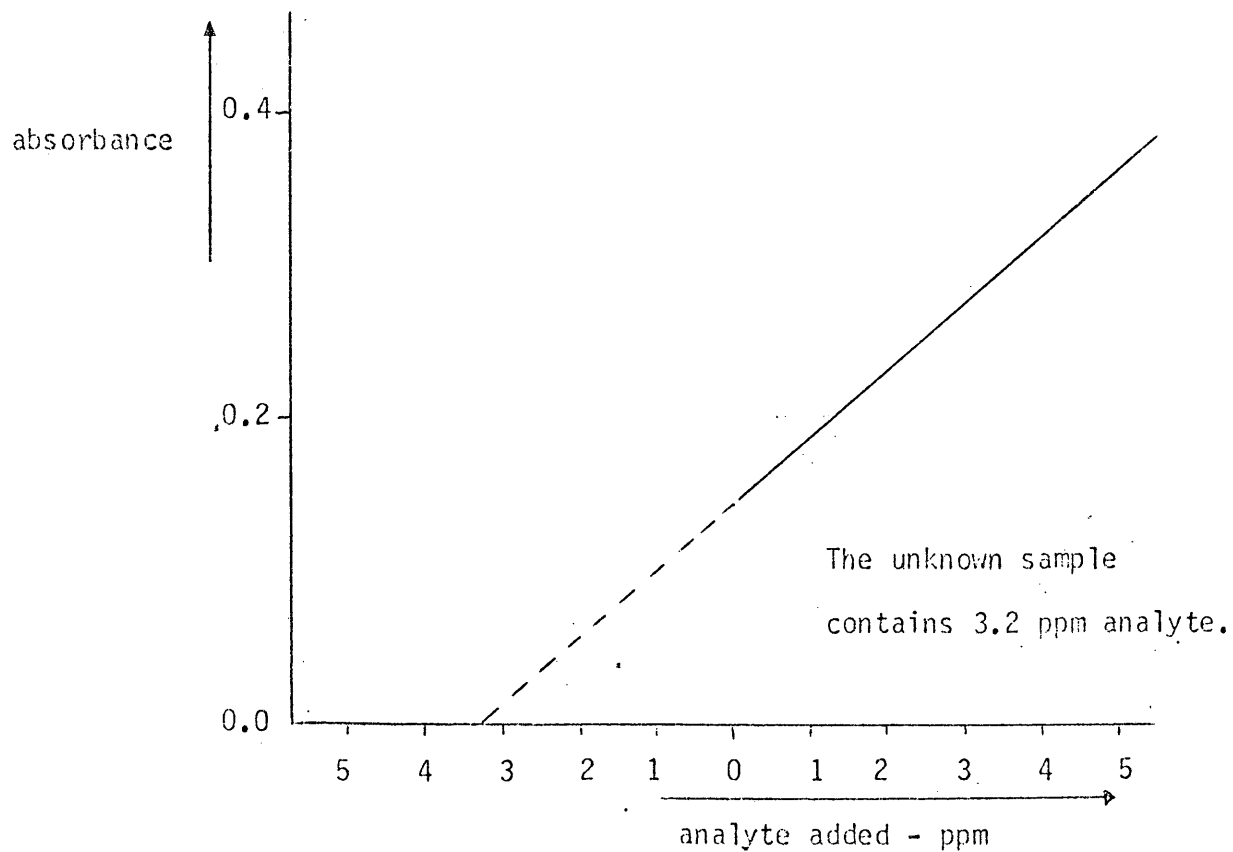
Figure 3: Typical calibration curve for aluminum.



For the determination of sodium and potassium the so-called method of additions or autostandardization method was used (13). In this technique, increasing amounts of the analyte itself are added to the unknown sample, being careful to establish the same dilution volume for all the final solutions. A plot of absorbance against unknown concentration X , $X + 1$ analyte unit, $X + 2$ analyte

units, etc., will establish an absorbance slope. Intersection of this curve with the negative portion of the concentration co-ordinate will indicate the concentration of analyte in X. See example in Figure 4.

Figure 4: The autostandardization method.



For the determination of iron, sodium, potassium, silver, and gold, the solutions were atomized in air-acetylene flame. Typical gas pressures were 2.5 psi acetylene and 15 psi air. The air-acetylene flame temperature averages 2300 C (13).

Since calcium, magnesium, and aluminum form refractory oxides, atomization of these elements at 2300 C is rather poor. Therefore, for the determination of calcium, magnesium, and aluminum, the solutions were atomized in an acetylene-nitrous oxide flame. Typical gas pressures were 9 psi acetylene and 16 psi nitrous oxide. The acetylene-nitrous oxide flame temperature averages 2955 C (13).

Preparation of liquid samples for atomic absorption spectrophotometry

The following procedure was used for the preparation of samples used for the determination of iron, calcium, magnesium, sodium, potassium, aluminum, silver and gold by atomic absorption spectrophotometry: 500 mg were weighed in a platinum crucible. The crucible had a capacity of 25 ml. Five drops of perchloric acid and ten to twelve ml of hydrofluoric acid were added. The mixture was then heated to dryness on a hot plate. Ten ml of perchloric acid were then added and the mixture was heated for ten minutes. The crucible was allowed to cool down and the content

of the crucible was placed in a 400-ml beaker and about 200 ml distilled water added. The aqueous, slightly acid, solution was then allowed to boil for five minutes. The eventual residue was filtered off and fused with potassium pyrosulfate and added to the main solution.

Determination of the ignition loss of the tailing samples

The samples were powdered and dried overnight at 110 C. Then 200 g of each tailing sample were weighed in a porcelain crucible and calcined in an electric furnace at 1000 C for one hour. The weight of the calcined sample was then determined. The ignition loss was determined from the following expression:

$$\% \text{ Ignition loss} = \frac{\text{dry weight} - \text{calcined weight}}{\text{dry weight}} \times 100.0$$

Density measurements

The density of the tailings was determined by pouring a known weight of material in a 100-ml glass cylinder and then a reading was taken of the volume it occupied.

The packed density was determined by pouring a known weight of material in a 100-ml glass cylinder and determining the volume it occupied after shaking the glass for five minutes.

Preparation of test bars

The specimens in which calcium hydroxide was used as the bonding agent were prepared by thoroughly mixing, utilizing a mortar and a pestle, the proper amounts of the desired powders with enough moisture to hold the specimens together after forming. The specimens were formed by pressing in a rectangular brass die using a Carver Laboratory hydraulic press having a 20,000-lbs capacity. The pressure exerted by the Carver press on the specimens was 15,000 lbs. The formed bars were 6 x 1 x 0.4 in. in size, which resulted in a forming pressure of 2,500 psi.

The specimens in which Peneprime was the bonding agent were prepared by thoroughly mixing the proper amounts of taling and Peneprime liquid. The specimens were formed by pressing in a rectangular brass die using hand pressure or a Carver Laboratory hydraulic press, using various pressures up to 6,000 lbs maximum, which resulted in a maximum forming pressure of 1,000 psi.

Aging of test bars

The specimens with calcium hydroxide as the bonding agent were aged at different temperatures for different times. Aging at room temperature and atmospheric pressure was done in the air. Aging at 100 C in steam, and aging at 125 C in steam were done in an electrically-heated autoclave. The autoclave was manufactured by Barnstead Still and Sterilizer Company, and was of the type with hinged door and double wall.

The specimens with Peneprime as the bonding agent were aged at 110 C in a dryer for different time periods. After 10 days of aging the strength did not increase any more; therefore an aging time of 10 days was chosen for all tests.

Strength determinations

The normal method of measuring the strength of a ceramic material is by either a crushing test or a modified tensile test which measures the modulus of rupture. Of the two tests the modulus of rupture test is more acceptable because it gives more accurate data.

The determination of the modulus of rupture of the specimens was done according to the method described for testing fireclay-base castable refractories after firing (14). In practice the test consists of supporting the sample on two knife edges and applying a load on another knife edge at the center of the bar until fracture occurs. In this study the sample was supported by two 1/8-in.-diameter hardened-steel rods and the load was applied on a similar-size rod. The modulus of rupture of each specimen was calculated according to the following expression:

$$M = \frac{3 P L}{2 b d^2}$$

where M = modulus of rupture in psi,

P = load in lbs at which the specimen failed,

L = distance in in. between the centerlines of the lower bearing edges,

b = width of the specimen in in., and

d = depth of the specimen in in.

The load was applied at a speed of 0.11 in. per min and was held the same in every test. This is necessary since the rate of application of load has a very decided effect on the results. The modulus of rupture values increase for increasing rates of load application.

The width and the depth of the specimens was measured by means of a micrometer near the fractured surface.

The testing machine used for this work was a Baldwin-Emery SR-4 testing machine, model FGT.

Determination of the water of absorption

The water of absorption was determined for each specimen with Penepriime as the bonding agent.

The method was as follows: The dry weight of the sample was determined. Then the sample was boiled in water for one hour and

the wet weight was determined. The water of absorption was calculated from the following expression:

$$\% \text{ Water of absorption} = \frac{\text{wet weight} - \text{dry weight}}{\text{dry weight}} \times 100$$

Solubility measurements by means of optical emissionspectroscopy

Silica in the form of tailings or in the form of potters flint was added to saturated solutions of calcium hydroxide in water, and to saturated solutions of magnesium hydroxide in water. The mixtures were brought in contact for one hour at different temperatures. The different reaction conditions used were the following:

1. At 25 C and atmospheric pressure, and stirred magnetically.
2. At boiling temperature of the solution (about 100 C) and atmospheric pressure, using a reflux condensor.
3. At 125 C and 19.4 psi overpressure, in an autoclave.

The solutions were then filtered and the filtrate was heated to dryness. The residue of the drying operation was then analyzed for silicon by means of optical emission spectroscopy.

It is well known that the solubility of calcium hydroxide and of magnesium hydroxide in water changes with temperature (16). However our object is not to measure absolute quantities of silicon going into a certain volume of saturated solution, but to measure the quantity of silicon going into solution for a certain amount of calcium hydroxide or magnesium hydroxide in solution.

The technique of optical emission spectroscopy is as follows: The sample mixed with an equal amount of graphite powder is excited in a D. C. arc, and a characteristic spectrum of all the elements present in the sample is obtained on a photographic plate. An optical densitometer is used to identify the lines in the spectra and to determine their relative intensity. In this way a qualitative analysis for silicon could be established.

EXPERIMENTAL RESULTS AND DISCUSSION

Moisture content of the tailings

The values obtained for the moisture content of the different tailings are represented in Table 2.

The variation in moisture content is due to the different constituents in the tailings, and especially to the degree of dryness of the tailings as they came in.

Results of sieve analysis tests of tailings

The grain size distributions obtained for the different tailings are represented in Table 3.

Several tailings were not suited very well for a settling test. Note the difference in grain size distribution of the two Climax tailings.

Table 2: Moisture content of the tailings

<u>Tailing</u>	<u>Percent moisture</u>
Old Climax	2.56
Young Climax	0.00
Naturita	0.00
Durango	4.80
Idaho Springs	4.56
Ouray	11.00
Silverton	5.33
Lead Slag	0.00
Savach	3.81
Lower Denaro	6.05
Iron Mask	2.24
Little Jonny	2.82
El Capitan	3.75
F. T. E.	4.42

Table 3 (continued): Sieve analysis of the tailings (percentages).

	Silverton	Sawach	Lower Denaro	Iron Mask	El Capitan	Little Jonny	F. T. E.
+ 8 mesh	52.30	47.67	43.00	51.05	76.51	33.70	0.26
- 8 + 10 mesh	2.90	4.13	3.44	2.69	1.71	3.91	0.29
- 10 + 14 mesh	4.25	6.23	4.81	3.79	2.16	4.38	0.77
- 14 + 20 mesh	3.73	6.81	5.77	4.71	2.29	5.32	2.63
- 20 + 28 mesh	2.38	4.88	4.49	3.78	1.65	4.89	6.09
- 28 + 35 mesh	1.94	4.42	3.95	3.36	1.40	4.97	11.17
- 35 + 48 mesh	1.56	3.80	3.21	3.41	0.58	5.23	14.12
- 48 + 65 mesh	1.45	3.36	2.75	3.01	1.12	4.85	13.27
- 65 + 100 mesh	1.22	2.21	2.92	3.17	1.38	5.41	14.11
- 100 + 150 mesh	1.14	2.47	2.24	2.65	0.89	4.40	9.98
- 150 + 200 mesh	1.10	0.74	0.48	0.06	0.21	2.53	0.41
- 200 + 325 mesh	2.10	3.45	4.23	6.19	2.45	5.58	14.94
- 325 mesh + 10 μ	10.00	2.09					10.52
- 10 μ + 5 μ	12.11						1.30
- 5 μ + 2 μ	1.05	6.70	18.71	12.14	7.64	14.85	0.26
- 2 μ + 1 μ	0.54						0.05
- 1 μ	0.00						0.00

Results of X-ray diffraction analysis

X-ray diffraction patterns were run on all the tailing samples. The following compounds were found to be present in detectable amount in all the samples except the Lead Slag:

1. Alpha quartz (SiO_2),
2. Muscovite, natural 3T-type, $(\text{K,Na}) (\text{Al, Mg, Fe})_2 (\text{Si}_{3.1} \text{Al}_{0.9}) \text{O}_{10} (\text{OH})_2$, and
3. Orthoclase (Feldspar), $\text{K} (\text{Al, Fe}) \text{Si}_3\text{O}_8$.

Since this analysis is qualitative rather than quantitative, it is impossible to state the amount of these compounds present in the sample. However it was clear from the obtained patterns that alpha quartz was the most abundant component.

The diffraction pattern of Lead Slag did not show any decided peak, which indicated that it was primarily an amorphous glass.

Chemical analysis results

The results of the quantitative analysis of the tailings are represented in Table 4.

Table 4: Chemical analysis of the tailings.

	Old Climax	Young Climax	Idaho Springs	Naturita	Durango	Lead Slag	Ouray
% SiO ₂	84.15	78.25	69.50	85.74	83.05	45.01	72.09
% Al ₂ O ₃	7.22	11.01	10.11	6.16	7.10	6.51	10.40
% FeO	1.23	1.82	5.77	1.03	1.54	30.90	5.79
% TiO ₂	0.14	0.18	0.61	0.16	0.27	0.81	0.47
% CaO	0.22	0.36	0.11	1.00	1.08	12.84	0.28
% MgO	0.39	0.80	0.94	1.17	1.08	1.60	1.26
% K ₂ O	2.97	3.22	2.13	0.75	0.95	0.90	2.18
% Na ₂ O	0.13	0.21	1.23	1.09	1.42	0.74	0.54
% Ag	< .002	< .003	< .002	< .002	< .002	< .002	< .002
% Au	< .002	< .002	< .002	< .002	< .002	0.005	< .002
% Ign. loss	1.23	1.85	8.74	0.91	1.71	0.00	6.01
% total	97.68	97.71	99.15	98.01	98.21	99.31	99.02

Table 4 (continued): Chemical analysis of the tailings.

	Silverton	Sawach	Lower Denaro	Iron Mask	EI Capitan	Little Jonny	F. T. E.
% SiO ₂	63.10	79.09	71.75	78.15	69.26	58.00	68.75
% Al ₂ O ₃	17.76	10.33	13.56	4.26	15.61	7.93	7.41
% FeO	5.69	2.80	3.64	5.48	4.62	12.77	10.24
% TiO ₂	0.82	0.27	0.30	0.34	0.26	0.40	0.36
% CaO	0.13	0.06	0.13	0.10	0.13	3.58	1.96
% MgO	0.38	0.64	0.85	0.12	0.70	3.40	1.96
% K ₂ O	2.61	2.27	1.90	0.57	1.73	0.90	1.02
% Na ₂ O	0.38	0.09	0.08	0.04	0.09	0.09	0.10
% Ag	0.003	0.011	0.015	0.010	< .002	0.002	< .002
% Au	< .002	< .002	< .002	0.003	< .002	0.004	< .002
% Ign. loss	7.73	3.64	5.81	9.41	5.96	12.80	6.17
% Total	98.60	99.19	98.02	98.47	98.36	99.87	97.97

The X-ray fluorescence method was used for the determination of silicon and titanium. All other elements were determined by atomic absorption spectrophotometry. Except for silver and gold the results were expressed in percentage of the oxide.

The values obtained for silver and gold cannot be taken as truly representative for the content of these elements in the tailing piles. This is due to the sampling method.

In order to check the analytical methods used in this study, a clay named "Johnson Red Shale" was analyzed by wet chemical analysis at the Wood Laboratories, and also in this work by the methods cited above. The results of both analyses are represented in Table 5.

Results from solubility measurements

A quantitative analysis for silicon could not be obtained by optical emission spectroscopy, because of the very small amount of silicon present in the samples. However most important are the qualitative results. It was found that the higher the temperature of reaction, the more silicon went into solution for a certain amount of calcium hydroxide or magnesium hydroxide in the solution.

Table 5: Comparison between wet chemical analysis by Wood Laboratories and the author's analysis.

	Wood	This study
% SiO ₂	42.40	43.70
% Al ₂ O ₃	15.37	15.22
% FeO	3.60	3.61
% TiO ₂	0.41	0.45
% CaO	11.95	12.00
% MgO	1.78	1.70
% K ₂ O	1.18	1.31
% Na ₂ O	0.89	0.85
% Ignition loss	19.33	19.46
% Total	97.80	98.30

Since the formation of hydrated calcium silicates is likely to take place in the liquid state (see above), the reactants have to go into solution before the reaction can take place.

The results thus indicated that a larger amount of hydrated calcium silicates, and hence a higher strength could be expected for the test bars, cured at the higher temperature.

Strength results for test specimens with calcium hydroxide as bonding agent

Calcium hydroxide was selected as bonding agent. Magnesium hydroxide was not considered because it is relatively expensive, and also because the water solubility of magnesium hydroxide is much smaller than that of calcium hydroxide. However it is believed that similar results could be obtained using magnesium hydroxide.

The compositions used for the test bars were as follows:

Series C: 100 g Young Climax tailing
 35 g calcium hydroxide
 25 ml water

Series P: 100 g Young Climax tailing
 35 g calcium hydroxide
 10 g Portland cement
 25 ml water

The specimens after forming had no measurable strength. The specimens showed a considerable increase in strength after various air curing times, and also after various steam curing treatment times. The strength of the air-cured specimens as a function of curing time is given in Table 6 and represented in Figure 5. The strength of the specimens cured in 100 C steam as a function of curing time is given in Table 7 and shown in Figure 6. The strength of the specimens cured in 125 C steam as a function of curing time is given in Table 8 and shown in Figure 7.

The values for the modulus of rupture given in Tables 6, 7, and 8, and represented in figures 5, 6, and 7 are average values calculated from 15 different tests.

It is clear from Figures 5, 6, and 7 that steam curing is a much faster strengthening method than air curing. A comparison of Figures 6 and 7 also shows that the higher the steam temperature the faster the strengthening takes place. This is in perfect agreement with the results from the solubility measurements, confirming that the strengthening in a steam atmosphere primarily occurs with the formation of hydrated calcium silicates. Hydrated calcium silicates could not be detected in the steam-cured specimens by X-ray diffraction analysis because these compounds are mostly amorphous. However Hall (5) detected them by electron microscopy studies.

In the air-cured specimens the presence of calcium carbonate was detected by X-ray diffraction analysis of the bulk of the sample. By powdering the samples the calcium carbonate peaks disappeared from the pattern almost completely. This indicates that the carbonate was probably being formed at the surface of the solid hydrate in voids between particles.

More calcium carbonate was found at the surface of the specimens than on the inside which was soft and chalky compared to the relatively hard surface.

From a comparison of the modulus of rupture values for the longest curing times in the three cases, it can be estimated that if longer curing times were allowed, the maximum strengths obtained would be of the same magnitude for air-cured specimens and for steam-cured specimens. This confirms that both low-temperature cementitious reactions, formation of calcium carbonate and formation of hydrated calcium silicates result in the same amount of strengthening.

Also it can be seen from Figures 5, 6, and 7 that the effect on the strength of adding Portland cement to the specimen composition is rather small, and in the order of 0 to 5 %.

Table 6: Modulus of rupture (in psi) of air - cured specimens,
versus air - curing time.

<u>Air curing time</u>	<u>Series C</u>	<u>Series P</u>
3 days	180	185
1 week	331	336
2 weeks	512	515
3 weeks	565	571
4 weeks	591	595
5 weeks	605	606
6 weeks	618	620
7 weeks	620	624

Figure 5: Modulus of rupture of air - cured specimens,
versus air - curing time.

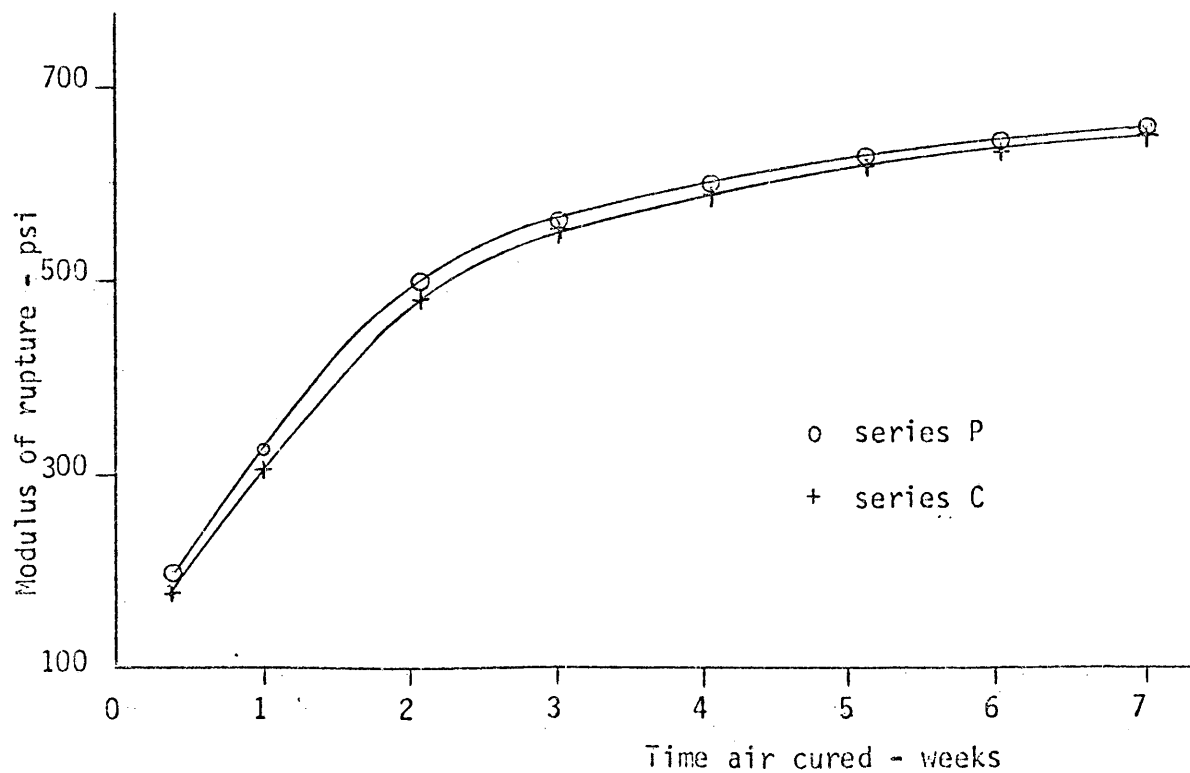


Table 7: Modulus of Rupture (in psi) of 100 C - steam - cured specimens, versus steam - curing time.

<u>Steam - curing time</u>	<u>Series C</u>	<u>Series P</u>
1 hour	176	179
2 hours	305	303
4 hours	426	437
8 hours	549	561
12 hours	632	647
16 hours	668	679

Figure 6: Modulus of rupture of 100 C - steam - cured specimens, versus steam - curing time.

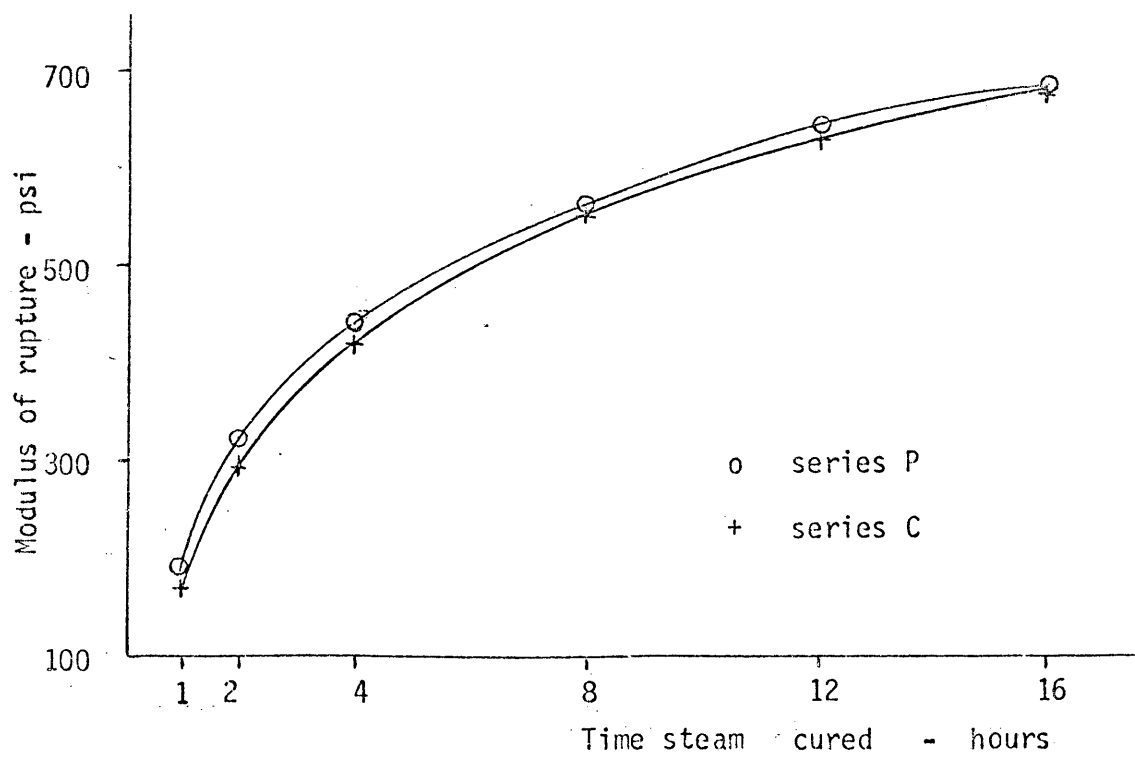
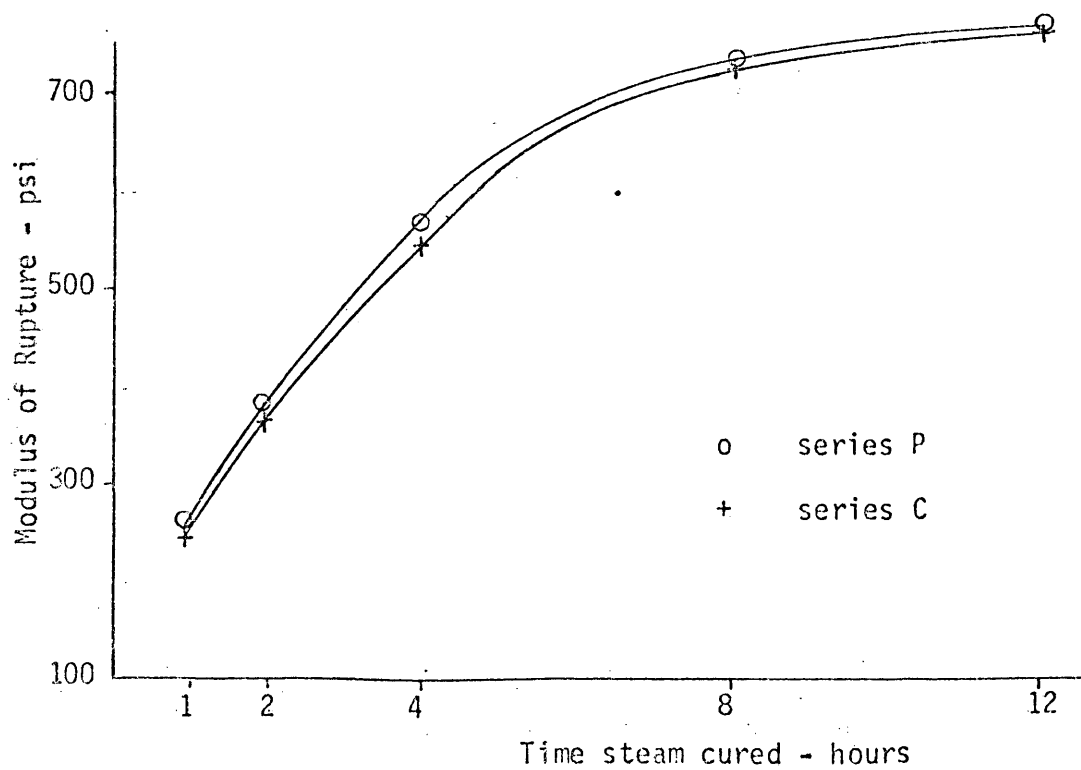


Table 8: Modulus of Rupture (in psi) of 125 C - steam - cured specimens, versus steam - curing time.

<u>Steam - curing time</u>	<u>Series C</u>	<u>Series P</u>
1 hour	242	245
2 hours	387	392
4 hours	559	570
8 hours	705	725
12 hours	745	749

Figure 7: Modulus of rupture of 125 C - steam - cured specimens, versus steam - curing time.



These tailings, except the lead slag, could thus well be used for the production of sand-lime brick, economical factors not taken into consideration.

No attempt was made in this study to optimize the amount of calcium hydroxide used.

Results from density measurements

Density measurements were made for the following tailing samples: Old Climax, Young Climax, Naturita, and Durango. The results for the unpacked density and the packed density are given in Table 9.

Table 9: Unpacked density and packed density for four tailings.

Tailing	Unpacked density (g/cc)	Packed density (g/cc)
Old Climax	1.36	1.61
Young Climax	1.25	1.54
Naturita	1.44	1.62
Durango	1.40	1.59

Because of its high packed density, the Naturita tailing was then chosen for a more detailed study of the packed density.

The Naturita tailing was divided into the following grain size fractions:

a = -4 mesh + 48 mesh

b = - 48 mesh + 65 mesh

c = - 65 mesh + 100 mesh

d = - 100 mesh + 200 mesh, and

e = - 200 mesh.

By making combinations in 20 % steps with these five fractions, a maximum packed density of 1.71 g/cc was found for the following composition:

80 % of grain size fraction a, and

20 % of grain size fraction e.

Complete results for the packed density are given in Appendix A.

Strength results for test specimens with Penepriime as bonding agent

The composition of the mixture used for the test bars was:
80 % Naturita a + 20 % Naturita e, since this composition had shown

the highest packed density (see above).

Six different series of test specimens were prepared using a different ratio of Penepriime to batch for each series. In each series bars were formed at different pressures, up to a maximum of 1,000 psi forming pressure. The specimens were aged at 110 C in a dryer. The specimens did not have any measurable strength after one day, and reached their maximum strength after six to ten days. All the specimens were aged for ten days and their strength measured. The highest strength in each series was observed with the bars made at 1000 psi pressure. Table 10 represents the values obtained for the modulus of rupture of the bars formed at 1000 psi pressure, for each different ratio of Penepriime to batch. Complete results are given in Appendix B. The ratio's are expressed in gallons of Penepriime per square yard of batch for one inch penetration. These are the units used in soil-stabilization calculations. The highest strength obtained was 675 psi for 1.50 gallons of Penepriime per square yard of batch.

The water of absorption was measured for each specimen and found to be higher than 10% in every case.

It was estimated that under more ideal conditions: better forming at higher pressures, the use of better petroleum-based bonding agents, the maximum strength could be brought up to 1000 psi, and the water of

absorption brought down to 5 %. This estimate has been confirmed by recent developments in industry. On August 22, 1967, Esso (18) presented a "Revolutionary Building Block".

Table 10: Strength (in psi) of test specimens with Peneprime as bonding agent.

Ratio of Peneprime to batch (gal/sq yd)	Modulus of rupture* for bars formed at 1000 psi and aged for ten days at 110 C (psi)
1.20	600
1.35	620
1.50	675
1.60	650
1.70	645
2.00	610

* The values for the modulus of rupture represented here are average values of fifteen different tests. The maximum deviation observed was ± 45 psi.

The manufacture of Esso's so-called BIX blocks is as follows: Soil is mined, screened and mixed with an inexpensive asphaltic binder and an appropriate chemical additive. Then the blocks are shaped at approximately 2,000 psi pressure and cured at a relatively low temperature. An estimated one-third of the world's soil is suitable for the process, with the additive varied to suit the specific soil being used. Non-agricultural soils are preferred. The brick so produced is claimed to be equivalent in quality to the conventional concrete block and less expensive than these.

In the case of the tailing materials, the "soil" is already mined and often screened. The local production of these bricks could be profitable if a local market were developed. However, a large - rather psychological - disadvantage of these bricks is their black color.

CONCLUSIONS

Test bars made from a dense tailing composition and Peneprime, an inexpensive asphaltic binder, showed enough strength to be used as building blocks. This could well become a major use for the many tailing piles if a local market were established. Recent investigations by a major oil company confirm this. The black color of these blocks however is a major disadvantage to their marketing value.

Measurements of solubilities of silicon in saturated aqueous solutions of calcium hydroxide and of magnesium hydroxide showed an increase in solubility of silicon per unit hydroxide in the solution with increasing temperature. Test bars made from tailing and calcium hydroxide as bonding agent were cured at room temperature, at 100 C in steam, and at 125 C in steam. It was found that with air curing, formation of calcium carbonate was the principal mechanism of strengthening, and that with steam curing, formation of hydrated

calcium silicates was the principal mechanism of strengthening.

The two mechanisms responsible for low-temperature cementitious bonding, carbonation and formation of hydrated calcium silicates, were found to develop strengths of the same magnitude. This agrees with the results obtained by Hall (5).

It was also found that the higher the steam temperature for curing the faster the strength was developed. This is in agreement with the results from the solubility measurements. It indicates that silicates are more soluble at higher steam temperatures and pressures, thus forming a high strength bond more rapidly. This could become an economical consideration.

Since the maximum strength obtained reached well above 700 psi, and since no attempt was made to optimize the amount of calcium hydroxide used, it can be concluded that most of the tailings could be used for the production of sand-lime brick.

If a study were done with magnesium hydroxide replacing calcium hydroxide as bonding agent, probably analogous conclusions could be expected.

APPENDIX A

Packed Density for the Naturita Tailing

<u>Batch composition</u> *	<u>Packed density</u>
100 % a	1.58 g/cc
100 % b	1.53
100 % c	1.53
100 % d	1.51
100 % e	1.38
20 % a + 80 % b	1.55
40 % a + 60 % b	1.55
60 % a + 40 % b	1.57
80 % a + 20 % b	1.58
60 % a + 40 % c	1.58
60 % a + 40 % d	1.66
60 % a + 40 % e	1.70
80 % a + 20 % e	1.71
60 % a + 20 % b + 20 % d	1.64
40 % a + 40 % d + 20 % e	1.65
60 % b + 20 % c + 20 % d	1.69
40 % a + 20 % b + 20 % c + 20 % d	1.63
40 % a + 20 % c + 20 % d + 20 % e	1.69
40 % a + 20 % b + 20 % d + 20 % e	1.66
20 % a + 20 % b + 20 % c + 20 % d + 20 % e	1.67

* For legend see page 44.

APPENDIX B

Strength of Specimens with Penepime as Bonding Agent

<u>Ratio of Penepime to batch (gal/ sq yd)</u>	<u>Forming pressure (psi)</u>	<u>Modulus of rupture (psi)</u>
1.20	hand formed	303
	250	427
	500	495
	750	556
	1000	600
1.35	hand formed	317
	250	424
	500	502
	750	577
	1000	620
1.50	hand formed	342
	250	417
	500	486
	750	588
	1000	675

<u>Ratio of Penepime to batch (gal/ sq yd)</u>	<u>Forming pressure (psi)</u>	<u>Modulus of rupture (psi)</u>
1.60	hand formed	327
	250	400
	500	475
	750	581
	1000	650
1.70	hand formed	299
	250	377
	500	480
	750	589
	1000	645
2.00	hand formed	284
	250	342
	500	460
	750	542
	1000	610

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