RESEARCH ON THE USE OF WASTE SILICA FROM THE CERRO PRIETO GEOTHERMAL FIELD, MEXICO

John W. Lund, P.E. and Tonya L. Boyd

Geo-Heat Center
Oregon Institute of Technology

ABSTRACT

The Geo-Heat Center has been investigating the utiliza-tion of waste silica from the Cerro Prieto geothermal field for several years. The main objectives of the research were to com-bine silica with various additives to (1) form bricks for low cost housing, and (2) to produce a suitable road surfacing material. The various additives that were tested included hydrated lime, portland cement, plastic fibers, asphalt cement and emulsified asphalt. The silica-cement combination produced the strongest bricks and had the best weather resistance, whereas, the silica-lime combination produced the bricks with the lowest thermal conductivity and specific gravity density. The addition of plastic fibers to the silica-lime mixture improved both strength and weather resistance. The combination of asphalt and silica is not suitable as a road surfacing material, however, silica-cement appears promising.

INTRODUCTION

The Geo-Heat Center has been investigating the utiliza-tion of waste silica from the Cerro Prieto geothermal field for several years (Lund et al., 1994, 1995a, and 1995b). The main objectives of the research was to combine silica with various additives to (1) form bricks for low cost housing, and (2) to produce a suitable road surfacing material.

The impetus behind this project was the large quantities of silica being produced from waste brines at the power plants in the Imperial valley of Mexico and California, and a cooperative agreement between the U.S. Department of Energy (USDOE) and Comision Federal de Electricidad (CFE) of Mexico.

Of specific interest was the Cerro Prieto geothermal field in Mexico which has an installed capacity of 620 MW, and in the process generates 6,400 tonnes/hr (7,000 tons/hr) of brine consisting of about 6 tonnes/hr (6.6 tons/hr) of silica (927 ppm average). Since the geothermal fields of the area extend into the Imperial Valley of California where waste silica is produced from an additional 420 MW of geothermal power generation, it is hoped that this research would also be applicable to the U.S. side of the border.

The residual waste brine, after evaporation is reduced to 5,600 tonnes/hr (6,200 tons/hr) at Cerro Prieto. It is then disposed of into large surface evaporation ponds covering 18.6 square km (4,600 acres) in area. The volume of silica in these ponds is unknown, however the field has been operating since 1973, and thus there should be approximately half a million tonnes of silica in the ponds.

Some attempts have been made by UNOCAL at their Imperial Valley plant (now owned by Magma Power) to use their waste silica stabilized with cement for roads and dikes around the plant. However, concern over low levels of radio-activity, has curtailed this work. They are now disposing of the waste, extracted by a crystallizer-clarifier system to control scaling, to a separate disposal site.

CFE has done testing on various mixtures of silica and additive for building blocks and roofing tiles. Samples of their results are displaced at the museum at Cerro Prieto. Unfort-unately, no documentation of this testing was every prepared, thus the results and many of the additives are unknown.

RESEARCH OBJECTIVES

The objectives of the research were to:

1. Produce low specific gravity bricks that were suitable for low-cost building construction using the waste silica with various cementing additives (i.e. have adequate strength, low thermal conductivity and high resistance to weathering).

2. Produce a mixture of silica with either cement or asphalt that would be suitable for a low-volume road surfacing (i.e. has adequate strength and stability, and resistance to traffic abrasion).

The testing procedure would include:

1. Mixing the silica with lime, cement, pozzolan and fibers to mold bricks and cubes, and then cure them under various conditions of temperature and moisture.

2. Test molded specimens after various curing times (7, 14 and 28 days) in flexure (bricks) and compression (cubes).

3. Test dried samples for thermal conductivity and weathering.

4. Test silica-asphalt mixtures by Marshall stability and immersion-compression.

SILICA CHARACTERISTICS

The term "silica" is used here to describe material that is mainly silica, but does contain other chemical species. Three separate samples of silica waste were taken and shipped from Cerro Prieto during the two years of the study. The initial sample, unknown to us, was from an evaporite deposit at a silencer, whereas the later two samples were actually taken from the evaporation ponds. The evaporite deposit had a specific gravity of 2.29 and was extremely fine grained (over 90% passed the #200 sieve (0.075 mm). The two pond samples had specific gravities of 2.27 and 2.18, and were much coarser with visible amorphous particles (Figure 1). These latter samples had approximately 75% and 30% passing the #200 sieve (see Figure 2 for the complete mechanical analysis). Since the initial sample results were not typical of what could be obtained from the larger source in the evaporation ponds, the results were not considered significant, but are documented in (Lund, et al., 1995a).

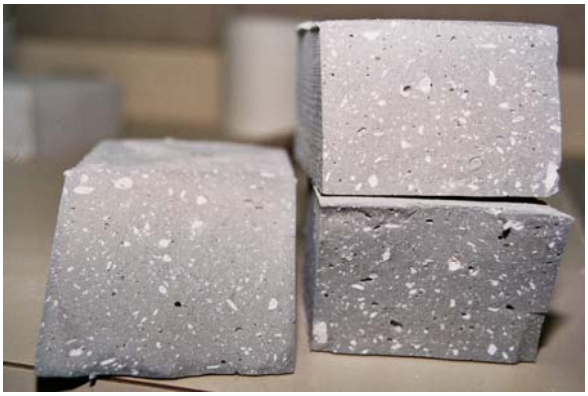


Figure 1. Cross-section of silica-cement bricks showing silica gradation.

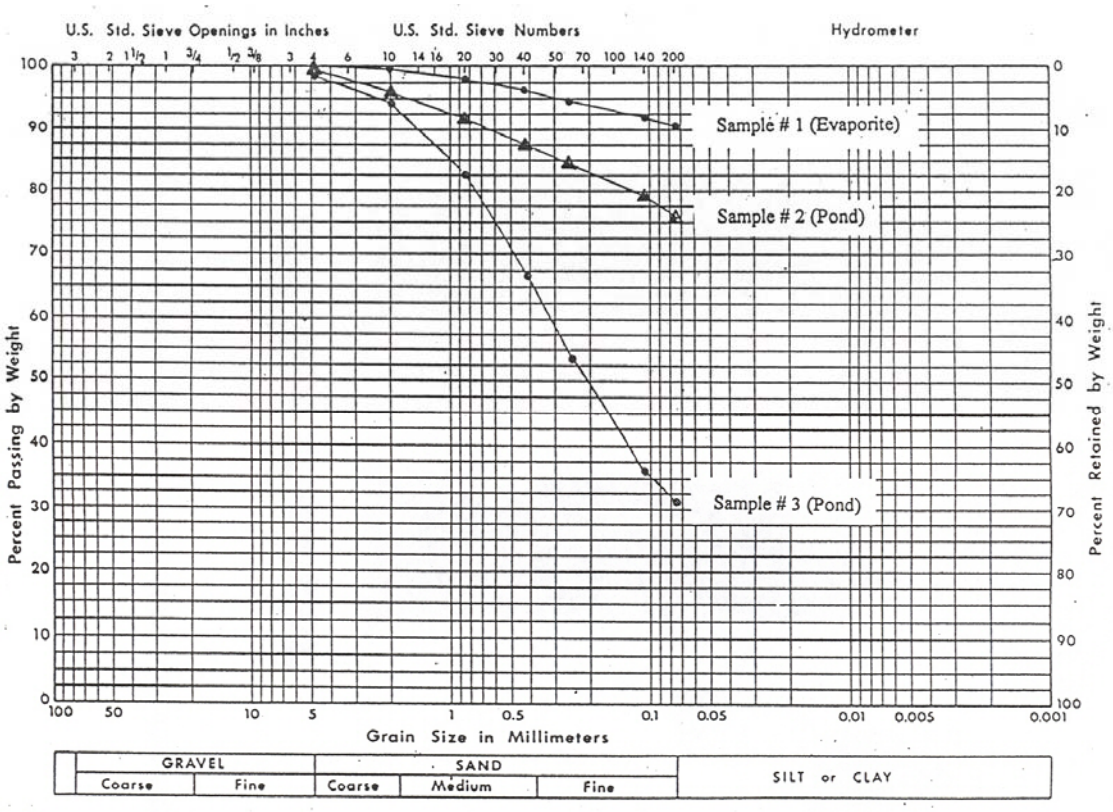


Figure 2. Mechanical analysis of Cerro Prieto silica waste.

According to work done at Cerro Prieto in 1993 (Residencia General de Cerro Prieto, 1994), the typical chemical analysis of the brine is shown in Table 1.

Table 1. Chemical Analysis of the Brine (mg/1 – ppm)	
Total dissolved solids	28,286
Chloride	15,638
Sodium	8,510
Potassium	1,971
Silica	927
Calcium	388

Work done for us by Brookhaven National Laboratory (personal communication, Dr. Eugene T. Premuzic, 1996) on the two pond waste silica samples are shown in Table 2 (with over 100 ppm concentration). The two sample appeared to be composed primarily of silica (over 80%) and varying amounts of potassium, calcium and chloride. They were very low in barium and no thorium or radium were detected by Energy Dispersive Spectroscopy (EDS) or the counting procedure. The results were obtained by both EDS x-ray analysis and by Scanning Electron Microscopy (SEM).

Table 2. Chemical Analysis of Waste Silica (ppm)		
Isotope	Sample #2	Sample #3
Silicon	3745.4	4308.5
Iron	1521.8	1749.2
Calcium	815.4	823.2
Aluminum	294.8	645.9
Zinc	390.9	89.8
Phosphorus	321.0	0
Boron	230.5	229.4
Manganese	156.1	241.2
Magnesium	20.2	120.6

TESTING PROCEDURE

Bricks and Cubes

The bricks were formed in 7.60 cm wide by 5.10 cm high by 15.2 cm long (2 in. x 3 in. x 6 in.) molds with removable sides. These would then be cured under various conditions of moisture and heat and finally tested in bending (flexure) by three point loading (Figure 3). The test procedure closely followed ASTM C 293-79 (Standard Test Method for Flexural Strength of Concrete), and were tested after 7, 14 and 28 days of curing. This was later modified and only 7 days of curing was used.

Figure 3. Flexure testing of silica-mixture bricks.

Cubes were formed in 5.10 cm (2.00 in.) square molds and then tested in unconfined compression following ASTM C 109-90 (Test Method for Compressive Strength of Hydraulic Cement Mortars). Some difficulty was experienced in determining the maximum strength of these specimens, producing variable results, thus this test procedure was later suspended.

Asphalt Mixtures

The asphalt cement (AR-4000) mixtures were compacted into 10.2-cm (4.00-in.) diameter by 5.1-cm (2.00-in.) high specimens and then heat cured. They were then tested in compression according to the Marshall Stability Test (ASTM D 1559-82). This test procedure would determine if the material was suitable for use as asphalt concrete structural pavement surfacing material. Emulsified asphalt (CRS-2H) mixtures were tested in immersion-compression (ASTM D 1074-83 and D 1075-81) to determine its suitability for surface treatment of roads in the form of a slurry seal.

Thermal Conductivity

Samples of all the bricks were mailed to USGS in Menlo Park for thermal conductivity testing. In conjunction with these test, the dry specific gravity of each brick was determined to see if there was a significant correlation between the two measurements. The thermal conductivity was determined using the conventional needle probe in a half-space mode (Sass, et al., 1984).

Weathering

The more promising mixtures for the bricks were subjected to a weathering test. Since time was not available for an extended outdoors test, an accelerated laboratory test procedure was developed. This involved a wet-dry test where a dried brick was first sprayed with water, then soaked overnight (about 12 hours), then oven dried at 60°C (140°F) for 12 hours, before repeating the cycle. A total of 10 cycles were performed and the initial dry weight was compared to the final dry weight to determine a percentage loss. The greater the loss, the less suitable the mixture is for construction use where it will be exposed to weathering.

TESTING RESULTS

A summary of the flexural strength, specific gravity, thermal conductivity and weather percent loss are show in Table 3. The type of sample indicates the weight proportions of silica to cementing material. The sample numbers indicate which sample of silica was used (1 = original silencer sample, 2 and 3 = pond samples).

The silica-hydrated lime mixtures produced the lowest specific gravity, thus indicating that they would have the best insulating values (low thermal conductivity). These mixtures also produced the lowest strengths of all the various additive combinations. Initially the samples were cured in a water bath with poor results, and then heat cured in an oven at 60°C (140°F) for 7, 14 and 28 days. The heat curing was to simulate accelerated curing in the field. Flexural and compression testing produced lower strengths with increased curing time, contrary to what was expected. Upon a detailed investigation, it appeared that the samples were drying out in the oven which prevented adequate curing and produced minute thermal cracks in the bricks (Figure 4). The longer the curing time the more thermal micro-cracks that were produced, since the curing water in the bricks was evaporating. The samples then failed in flexure along these thermal micro-cracks.

Table 3
Summary of Test Results of Hydrated Lime and Silica Mixtures

Sample Name	Type of Sample	7-day Flex (KPa)	14-day Flex (KPa)	28-day Flex (KPa)	Specific Gravity	Thermal Conductivity, W/mK	Weathering Percent Loss
1I	1-Silica/1-Lime	387.8	258.6	86.2	0.64	0.36	73.10
2A	1-Silica/1-Lime	1034.2	861.8	560.2	0.72	0.30	7.60
3HA	1-Silica/1-Lime	732.6			0.96	0.32	2.00
1J	2-Silica/1-Lime	129.3	86.2	86.2	0.58	0.35	100.00
2B	2-Silica/1-Lime	517.1	430.9	344.7	0.67	0.30	47.60
2P	2-Silica/1-Lime	1465.1	1465.1	1335.9	0.65	0.31	6.00
2Q	2-Silica/1-Lime	1637.5	1982.2	1637.5	0.67	0.31	6.00
3IA	2-Silica/1-Lime	517.1			0.96	0.34	2.80
1N	3-Silica/1-Lime	86.2		43.1	0.49	0.29	100.00
2C	3-Silica/1-Lime	430.9	344.7	258.6	0.65	0.31	12.30
3JA	3-Silica/1-Lime	3447.4			0.99	0.35	3.20
3KA	4-Silica/1-Lime	2542.4			0.96	0.30	3.10
3LA	5.67-Silica/1-Lime	301.6			0.95	0.36	5.00
3MA	9-Silica/1-Lime	172.4			0.89	0.34	17.30
3NA	19-Silica/1-Lime	129.3			0.89	0.32	100.00
1K	1-Silica/1-Cement	2930.3	2973.4	2844.1	0.81	0.36	3.70
2D	1-Silica/1-Cement	6334.6	5515.8	5774.4	1.08	0.34	2.30
3T	1-Silica/1-Cement	5946.7			1.47	0.44	10.20
1F	2-Silica/1-Cement	1508.2	1465.1	1809.9	0.73	0.36	9.50
2E	2-Silica/1-Cement	3231.9	3705.9	4438.5	0.88	0.33	6.20
2N	2-Silica/1-Cement	3792.1			0.79	0.31	4.40
2O	2-Silica/1-Cement	3921.4			0.82	0.30	4.30
3U	2-Silica/1-Cement	4912.5			1.24	0.38	6.50
1H	3-Silica/1-Cement	861.8	861.8	818.8	0.57	0.34	7.70
2F	3-Silica/1-Cement	3231.9	3878.3	4524.7	0.80	0.30	7.20
3V	3-Silica/1-Cement	4179.9			1.24	0.39	1.70
3DA	4-Silica/1-Cement	2154.6			1.24	0.40	12.20
3EA	5.67-Silica/1-Cement	1034.2			1.15	0.34	12.20
3FA	9-Silica/1-Cement	517.1			1.04	0.32	10.10
3GA	19-Silica/1-Cement	129.3			0.92	0.29	11.70
1L	1-Silica/1-Lime/1-Cement	3016.5	3059.5	3447.4	0.84	0.36	3.50
2G	1-Silica/1-Lime/1-Cement	3447	4524.7	3361.2	0.96	0.35	6.60
1D	2-Silica/1-Lime/1-Cement	2154.6	1465.1	1637.5	0.81	0.42	17.60
2H	2-Silica/1-Lime/1-Cement	3705.9	4309.2	4697.1	0.84	0.35	10.90
1G	3-Silica/1-Lime/1-Cement	1508.2	1077.3	1206.6	0.67	0.34	6.80
2I	3-Silica/1-Lime/1-Cement	3188.8	2973.4	3533.6	0.80	0.30	4.90
2M	4-Silica/1-Lime/1-Cement	2628.6	4093.8	2844.1	0.71	0.32	5.70
1S	1-Silica/1-Lime/1-Fiber	430.9	711		0.57	0.34	8.40
2J	1-Silica/1-Lime/1-Fiber	1809.9	1508.2	1249.7	0.67	0.27	9.40
1YA	2-Silica/1-Lime/1-Fiber	86.2			0.49		100.00
2K	2-Silica/1-Lime/1-Fiber	1465.1	1120.4	1508.2	0.59	0.28	11.00
1ZA	3-Silica/1-Lime/1-Fiber	86.2			0.44		100.00
2L	3-Silica/1-Lime/1-Fiber	1766.8	1335.9	1292.8	0.62	0.29	12.00

Since, the strength of lime-stabilized mixtures is both time and temperature dependent, it was found that curing temperatures above 50°C (122°F) should be avoided, with 40°C (104°F) recommended without introducing pozzolanic reactive products that significantly differ from those expected during field curing (Transportation Research Board, 1987). Research reveals that the lower curing temperature is equivalent to producing 28-day strength in about 69 hours (Biswas, 1972 and Townsend and Donaghe, 1976). Thus, we felt that 7-days curing was more than adequate to simulate field curing time.

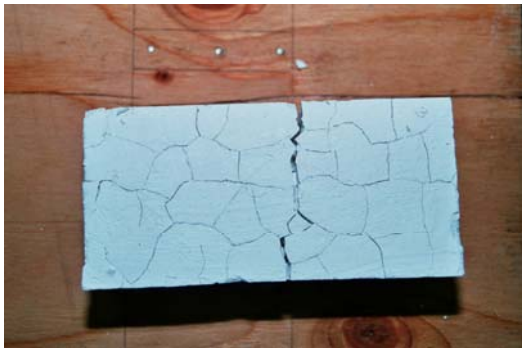


Figure 4. Top view of a silica-lime brick showing micro-fractures (enhanced with a ball-point pen).

Based on the above findings, two changes in our procedure were introduced (1) curing at 40°C instead of 60°C, and (2) curing in moisture-proof plastic bags. As a results, almost no moisture was lost from the bricks and higher strength were produced and these increased with curing time. The results of 7-day flexural strengths are shown in Figure 5. The silica from sample site #3 were mixed with a silica to lime proportion from 1:1 all the way to 19:1 (50% to 5% lime by total dry weight of mix), and cured using the revised procedure. Moisture content of these latter samples varied from 63% to 71% by total dry weight of the mix. These strengths are more indicative of what can be produced in the field.

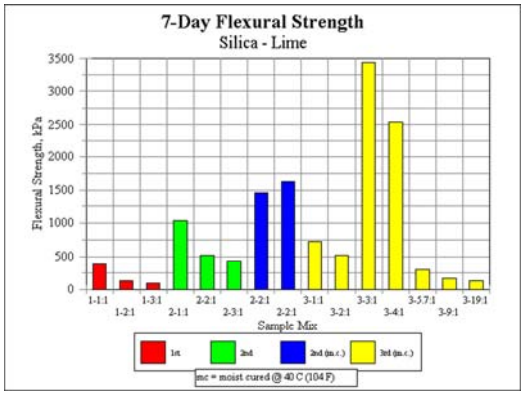


Figure 5. 7-day flexural strength of selected silica-lime mixtures.

Portland Cement

Portland Cement mixtures (using Type II cement) produced flexural strengths that were approximately twice that produced by lime stabilization. The flexural strengths are dependent upon the amount of mixing water used, as the lower water/ cement ratios produce high strengths. Samples were tested using a silica-cement ratio ranging from 1:1 to 19:1 (50% to 5% cement by total dry weight of mix). Specific gravities and thermal conductivities were slightly higher for the cement mixtures as compared to the lime mixtures. Moisture contents varied from 52% to 70% by total dry weight of the mix. The flexural strength results of cement mixtures are shown in Figure 6.

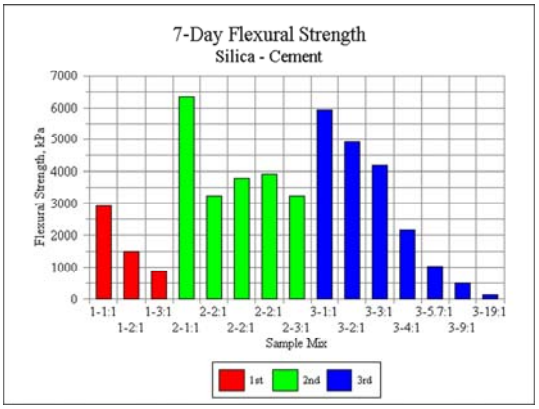


Figure 6. Flexural strength of selected silica-cement mixtures.

Portland Cement and Hydrated Lime

Results from the combined cement and lime stabilization produced strengths between those obtained from just lime and cement alone. There appears to be no strong advantage to using this combination of additives, unless the cost of lime is considerably less than cement, and the strengths higher than those obtained from just lime stabilization are desired.

Hydrated Lime and Plastic Fibers

Approximately eight grams (0.3 oz) of plastic fibers, varying between 1.4 and 2.7 percent by dry weight of sample, were used to provide additional flexural strength to the lime stabilized samples. This produced significantly higher strengths than those samples without fibers cured at 60°C (140°F) and only slightly higher strength when compared with those cured at 40°C (104°F).

Thermal Conductivity

Thermal conductivity was determined for various dry weight samples of bricks using the conventional needle probe in a half-space mode at the USGS laboratory in Menlo Park, California (person communication with Colin Williams). The thermal conductivities varied from 0.27 to 0.44 W/mK. In general, the lower the specific gravity of the mixture, the lower the thermal conductivity. Also, for a particular sample of silica, the thermal conductivity of the bricks decreased with increasing silica content. Specific gravities of the silica-lime samples varied from 0.635 to 0.991 and for the silica-cement samples from 0.571 to 1.244. The silica from sample site #3 produced the highest specific gravities and the highest thermal conductivities. The thermal conductivities compare with values for common brick at 0.72, gypsum or plaster board at 0.17, glass fiber insulation at 0.043 and urethane foam at 0.026 W/mK. Figures 7 and 8 are a plot of specific gravity vs thermal conductivity for selected silica-lime and silica-cement samples.

Figure 7. Specific gravity vs. thermal conductivity of selected silica-lime samples.

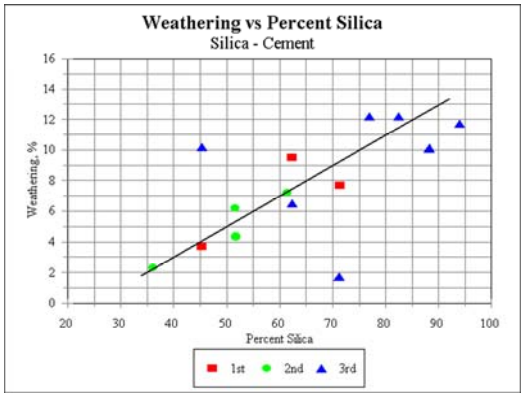
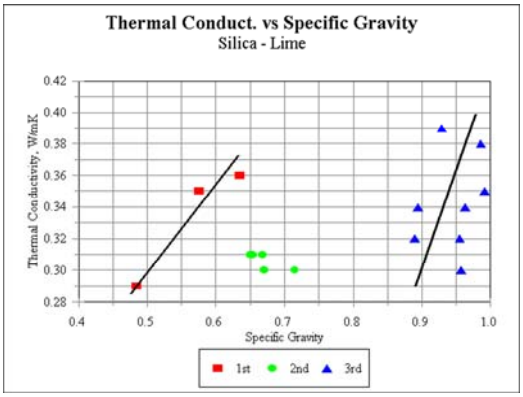


Figure 8. Specific gravity vs. thermal conductivity of selected silica-cement samples

Weathering

In general, the higher the silica content the greater the percentage weight loss due to the simulated weathering cycles. Most of the silica-lime mixtures cured at 60°C (140°F) completely failed (100% loss) before the end of the test period. Silica-lime samples with plastic fibers held together much better, usually with only a 10% weight loss. The silica-cement and silica-lime-cement mixtures fared well, all except one, with less than 12% loss. The silica-lime samples cured at 40°C (104°F) in sealed plastic bags, had less than 12% loss, except for the 10% and 5% lime content samples. Figures 9 and 10 show the relationship between silica content and the percent of weathering for the three silica sources.



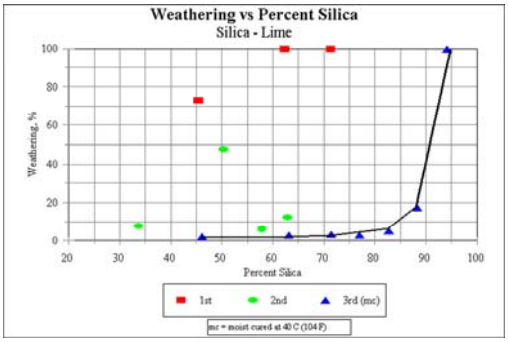


Figure 9. Weathering vs. silica content for selected silica-lime samples.

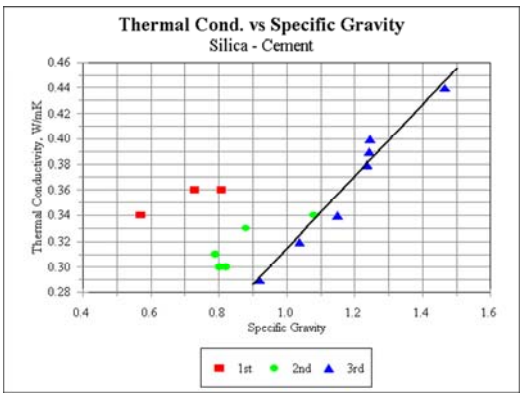


Figure 10. Weathering vs. silica content for selected silica-cement samples.

Asphalt Cement

The Marshall mix design method (ASTM D 1559) was used to evaluate the suitability of the asphalt cement (AR-4000) as an additive for a structural pavement. Various com-bination of aggregate, sand and silica were investigated with the silica content at 10%. Asphalt contents from 4% to almost 20% by

weight of mix were used. The higher percentages were necessary to hold the mix together, as the lower percentages did not provide enough cohesion. In all cases the stability was extremely low and the flow was extremely high. Based on these results, this mix combination was not considered acceptable for use in the field.

Asphalt Emulsion

Immersion-compression tests (ASTM D 1074 and D 1075) were performed on mixtures of silica and emulsion (CRS-2H) to determine their suitability as a road surface treatment. Ten to 18% by weight of emulsion was used. All samples disintegrated during testing and thus failed the test. This use was also rejected for field testing.

CONCLUSIONS

The main conclusions from the testing are:

1. Silica-lime mixtures have low strength and weather resistance. However, they have high insulating properties. With controlled curing conditions, at ambient temperatures up to 40°C (104°F) and without loss of moisture, the strength and weather resistance improves considerably. The addition of fibers to the mixtures increases the strength and weather resistance.
2. Silica-cement mixtures have high strength and weather resistance. However, they have slightly lower insulating properties. These mixtures can better be used in load bearing wall.
3. Asphalt mixtures are not suitable using silica and thus should not be considered for any field construction.
4. Silica-cement mixtures also appear to have application as road surfacing material with the addition of an asphaltic chip seal for erosion protection.

FUTURE INVESTIGATIONS

It is proposed to test several walls constructed of silica-lime and silica-cement mixtures in the Imperial Valley area. This will provide long term field testing of the various types of bricks and determine if they need protective coatings, reinforcing, etc.

During the course of the investigation it was determined that a lightweight roofing tile using portland cement, silica and cellulose fibers is presently being manufactured in Mexico City and sold through outlets in the U.S. under the brand name "Maxitile." Their advertised advantage is that they are lighter weight (60 percent lighter than clay or concrete tile at 20 kg/m^2 [4 lbs/ft^2]). CFE is presently investigating the potential for use of the Cerro Prieto waste silica by this manufacturer.

ACKNOWLEDGMENTS

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