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Recycled Waste-based Cement Composite Patch Materials for Rapid/Permanent Road Restoration

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By

Toshifumi Sugama
Energy Resources Division
Energy Science & Technology Department
Brookhaven National Laboratory
Upton, NY 11973

For
Project Manager
Daniel D'Eletto
Senior Engineer
KeySpan Gas East Corporation
D/B/A
Brooklyn Union of Long Island
445 Broadhollow Road
Melville, NY 11747

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KEYSPAN

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Executive Summary

A chemically bonded cement (CBC) composite system based upon recycled boiler ash (BA) was designed and formulated for use as an all-season, rapid-setting material for repairing road patch at temperatures, ranging from 0° (32 °F) to 40° (104 °F). The optimized formulation of the CBC composite consisted of 36.0 wt% pulverized BA, 18.9 wt% Secar #51 calcium aluminate cement (CAC), 4.6 wt% Type I portland cement (Type I), 5.9 wt% sodium polyphosphate (NaP), 6.5 wt% silica coarse aggregate (CA), 9.7 wt% silica sand aggregate (SA), 0.7 wt% chopped glass fiber, 3.2 wt% acryic-styrene copolymer (ASC, 50 wt% ASC solid state) emulsion, and 14.6 wt% water. The first four components, BA, CAC, Type I, and NaP were mixed together to make dry packed CBC, which has a long-shelf life. This dry CBC was designed for use as the binder for two different repair materials in pit structure, and also for ease of use in the field. One of the material systems needed was a strong, tough capping layer (~ 6 in. thick), which was required to possess a compressive strength of > 4000 psi. The other one was the cementitious backfill underlayment (~ 30 in. thick beneath the capping layer) that requires a compressive strength only of ~ 40 psi because subsequently it will be excavated by hand.

For the capping layer, the glass fiber-reinforced CBC composite developed in this program was characterized by having the following six specific properties:

1) Development of a compressive strength of > 200 psi at an early curing stage of 2 hr in the temperature range of 0° to 40°C,
2) Compressive strength of > 5000 psi after 12 days curing,
3) Bending strength and tensile strength of > 350 psi and > 240 psi by 24 hours, at 25°C,
4) Great freezing-thawing durability accompanying weight loss of < 4% only after 80 cycles,
5) A low liner dry shrinkage of ~ 80 x 10^{-2} mm at 21 days after casting,
6) Outstanding adherence to wet, dry, and icy surfaces of old cement concrete and to the surfaces of epoxy-coated steel reinforcement bars, and also some bonding to asphaltic concrete surfaces.

In addition, the ASC component in the composite not only acted to sequester the vanadium (V) metal present in raw BA, but also imparted a densified composite structure, leading to low water permeability.

A full-scale demonstration of the capping CBC composite was carried out at the KeySpan Energy site in Brentwood to ensure that the results of in-house work were reproducible, and also to validate the technical feasibility of using the composite in the field. A test pit of 2-ft. wide, 8-ft. length and 6-in. depth, was successfully filled with the composite material. About 90 min after placing it, the surfaces of composite cap developed a sufficient strength to be stepped upon, and the required compressive strength of > 4000 psi was attained after ~ 24 hr.

In our work to formulate the CBC-based backfill underlayment material and to develop a technology for placing it, we identified that effective ratios of CBC/wet soil in meeting the material criteria (compressive strength of ~ 40 psi) are 20/80 and 30/70 by weight. We also found that a high concentration of NaCl contaminant in the soil retarded the curing rate of the CBC. The compressive strength of the CBC specimens containing NaCl-contaminated soil gradually increased with an elapsed curing time, subsequently reaching ~ 40 psi after around 12 days. These in-house data were obtained from the specimens placed in accordance with the following sequence:

1) Mixing the excavated soil and dry CBC in a conventional concrete mixer,
2) Placing well-mixed backfill material in the pit,
3) Tamping the surfaces of the placed backfill material to create a densified underlayment structure,
4) Spraying sufficient water over the tamped backfill material to start the CBC curing and to obtain a compressive strength of ~ 40 psi,

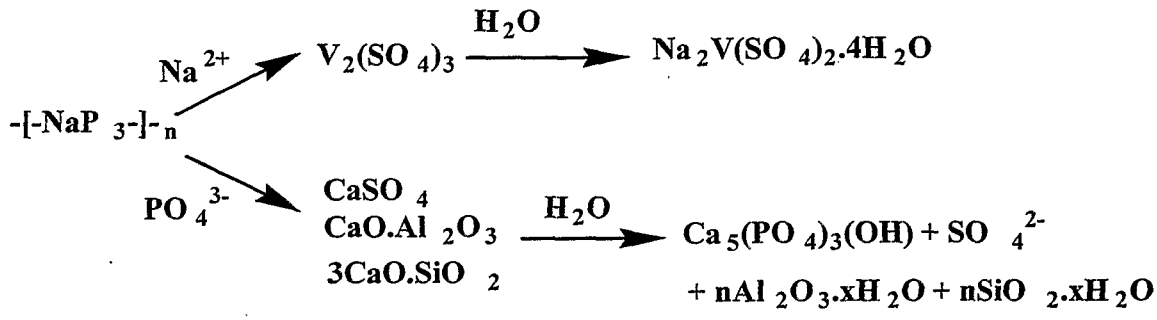
However, there was virtually no suitable field test for evaluating the feasibility of this technology, nor for assessing the extent of congealment and compatibility of the backfill material to the capping layer made with the CBC composite and asphaltic concrete. These factors may be critical in the success of this technology in the field.

1. Introduction

Over the past year, KeySpan Energy sponsored a research program at Brookhaven National Laboratory (BNL) aimed at recycling boiler ash (BA) and waste water treatment sludge (WWTS) byproducts generated from KeySpan's power stations into potentially useful materials, and at reducing concurrent costs for their disposal. Also, KeySpan has an interest in developing strategies to explicitly integrate industrial ecology and green chemistry. From our collaborative efforts with KeySpan (Diane Blankenhorn Project Manager, and Kenneth Yager), we succeeded in recycling them into two viable products; Pb-exchange adsorbents (PEAs), and high-performance cements (HPCs) [1,2]. These products were made from chemically bonded cement and ceramic (CBC) materials that were synthesized through two-step chemical reaction pathways, acid-base and hydration. Using this synthesis technology, both the WWTS and BA served in acting as solid base reactants, and sodium polyphosphate, [$-(-NaPO_3-)-_n$] , known as an intermediator of fertilizer, was employed as the acid solution reactant. In addition, two commercial cement additives, Secar #51 calcium aluminate cement (CAC) and Type I calcium silicate cement (CSC), were used to improve mechanical behavior and to promote the rate of acid-base reaction of the CBC materials.

For the PEAs, not only do the synthesized CBCs remediate Pb-contaminated soils, but also they acted to immobilize and stabilize hazardous heavy metals, such as vanadium (V) and nickel (Ni), which are contained in these raw byproducts. In fact, using a CBC formulation consisting of 54.0 wt% WWTS, 23.0 wt% CSC, and 23.0 wt% [40 wt% $-(-NaPO_3-)-_n$], TCLP tests showed that the concentrations of Pb, Ni, and V metals leached out from the specimens containing ~ 28800 mg/kg of Pb, ~ 6300 mg/kg of Ni, and ~ 11130 mg/kg of V, into the acid extraction fluid, were only 0.15 mg/L of Pb, 0.15 mg/L of Ni, and 4.63 mg/L of V. On the other hand, the BA-CAC-$NaPO_3$ system-based CBCs had a high potential for use as HPCs, offering a high mechanical strength, quick-setting characteristics, and a binding matrix for V and Ni metals present in the BA. Since the CAC additive promotes the rate of acid-base reactions, the incorporation of base reactant with a 70/30 BA/CAC ratio into the $-(-NaPO_3-)-_n$ acid reactant

generated a high exothermal reaction energy, leading to rapid hardening and setting. The cement slurry was converted into a solid state within the first ten minutes after mixing. The 70/30 ratio specimens at 2 hours after mixing had a compressive strength of 1520 psi. Further, an excellent compressive strength of > 4800 psi was attained when the cement specimens were cured by immersing them in 80°C steam for 20 hours. Two important factors played a key role in generating such a high compressive strength: One was the formation of well-crystallized hydroxyapatite [HOAp, $Ca_5(PO_4)_3(OH)$] and sodium vanadium sulfate hydrate [SVSH, $(Na_2V(SO_4)_2.4H_2O)$] in the cement bodies; the other was the development of a densified microstructure. These reaction products may be formed by the following hypothetical reaction mechanisms:



First, the Ca cations liberated from the BA and CAC had a strong chemical affinity for the phosphate anions dissociated from the $-(-NaPO_3-)-_n$ acid solution, leading to the formation of calcium phosphate compounds. Second, Na cations as the counter anions of phosphate ions favorably reacted with $V_2(SO_4)_3$ present in the BA to yield the sodium vanadium sulfate compounds. Finally, the hydration of these reaction products contributed to promoting their crystallization, thereby developing a dense microstructure in the CBC. In this mechanism, three compounds, SO_4^{2-}, $nAl_2O_3.xH_2O$, and $nSiO_2.xH_2O$, may be formed as byproducts in this acid-base-hydration reaction.

Overall, we believed that the CBC derived from these wastes has great potential in the following three applications: First, as a remediating material for soil contaminated with

hazardous Pb metal; second, as a rapid-setting repair patching and filling material for damaged roadways and bridges, and third, was as a high strength precast concrete products, such as building blocks, pipes, and slabs.

2. Project Objective

Based upon the very attractive property of CBC with a quick setting and hardening, the objective of this program is to design recycled BA waste-based CBC composites for use as all-season, rapid-setting patch materials for damaged asphalt roadways. This program also sought to develop paving technologies for permanently restoring roads, as well as techniques for packaging the composites to ensure a long shelf life and easy use in the field. The binder phase in this patch material system is made from BA waste generated as an industrial byproduct at KeySpan's power stations. The integrated material systems to be formulated consist of BA-based CBC binders, aggregates, fibrous reinforcements, and water-borne organic polymer admixtures. The scheme for the structure of the patched hole (about 5 ft. by 5 ft.) mainly involves two distinct layers. One layer, the capping patch, which extends ~ 6 inches deep from the surface must be constructed with composite materials having an ultimate compressive strength of > 4,000 psi. The other layer, a cementitious backfill underlayment of ~ 30 in. thickness beneath the capping layer must be filled with a soil-containing CBC material, which needs to have a compressive strength of only ~ 40 psi so that subsequently, it can be excavated by hand.

To successfully use CBC as a rapid-setting, high strength capping repair material at all seasons over a temperature range of 0° to 4°C, improvements must be made in the following seven properties: 1) fast curing at a freezing temperature; 2) ductility and impact strength; 3) adherence to old cement concrete, asphalt and frozen soil; 4) freeze-thaw durability; 5) mechanical strength at one hour after mixing; 6) impermeability to water and Cl^- ions; and 7) protection of steel reinforcement bars against corrosion. To meet the first requirement, since CBC is prepared by an exothermic acid-base chemical reaction, stronger basic additives, such as CaO-containing compounds, were incorporated into it to promote the rate of the reaction at low

temperatures. The approach to improving the other properties was to incorporate high-modulus fibrous reinforcements, water-born organic polymers, and the chemically inert SiO_2 aggregate into the CBC. Once the work to optimize the formulation of CBC composite materials was completed in the laboratory, a full-scale demonstration under actual traffic conditions was conducted in collaboration with KeySpan (Daniel D'Eletto, Project Manager) to evaluate the material's technological feasibility, and to investigate the performance of the placed patches. Also, KeySpan System Laboratory played a key role in verifying that CBC complied with environmental requirements.

The work described in this final report began in August 1999 and was completed in July 2001. This work consisted of six tasks:

Task 1.	Optimization of Capping BA-based CBC Composite Formulation
Task 2.	Characteristics of Formulated CBC Composite
Task 3.	Formulation and Properties of Soil-containing CBC for Use as Backfill Underlayment
Task 4.	Development of Placement Technology for Backfill CBC System
Task 5.	Lightweight CBC Concrete
Task 6.	Dry Packaging of Capping CBC Composite and Full-scale Field Demonstration.

The success of our research not only alleviates environmental concerns related to the disposal of BA, but also promises the recycle of industrial wastes into usable products.

3. Materials

Raw BA waste, to serve as a base reactant, was supplied from KeySpan's Northport power plant (Figure 1). The "as-received" BA was a rock-like bulky solid, and was pulverized using a portable crusher (Retruch Type BB1A, Brinkmann, Co.). Figure 2 shows the distribution of particle size, and Table 1 lists the chemical constituents for the pulverized BA. A granular polybasic sodium polyphosphate [NaP, $-(-NaPO_3-)-_n$, Aldrich Chemical Company], known as

an intermediate fertilizer, was used as the acid reactant. Two inorganic additives, Secar # 51 calcium aluminate cement (CAC, Lafarge Aluminates Ltd.) and Type I calcium silicate cement (Type I, Lehigh Portland Cement Cop.), were used to improve the mechanical strength and to accelerate the acid-base reaction, respectively. We evaluated the usefulness of three different fibrous materials, E-glass, polypropylene, and carbon fibers, in improving toughness and ductility of the CBC concrete. The dimensions of these fibers were as follows: 1) chopped E-glass (8-μm diam. x 6 mm long), supplied by Owens Corning Fiberglass, 2) collaterally fibrillated polypropylene (18.8 mm long), obtained from Forta Corporation, and 3) chopped carbon fiber (7.4 μm diam. x 3 mm long) derived from a polyacrylonitrile (PAN) precursor, supplied by Asbury Graphite Mills, Inc. A water-born acrylic-styrene copolymer (ASC) emulsion, supplied by the BF Goodrich Corp., was applied to sequester the vanadium (V) metal, which is most dominant of several heavy metal species present in the BA. The properties of the ASC emulsion were as follows: pH of ~ 4.0, total polymeric solid of 50 wt%, and viscosity of ~ 125 centipoise. The aggregate system included a silica-based coarse aggregate (size, 9.5 to 2.4 mm), and a silica sand aggregate (size, 1.2 to 0.15 mm).

4. Results and Discussion

4.1 Optimization of Capping BA-based CBC Composite Formulation

The ultimate goal of this task was to optimize the formulation of a BA-based CBC composite that could be used as a capping material for roads under all weather conditions over a temperature range of 0° to 40°C.

4.1.1. BA-based CBC Concrete

First, our focus centered on designing a formulation for neat BA-based CBC that would display a compressive strength of at least 1000 psi, after curing for 24 hours over a wide range of atmospheric temperature, from 0° to 40°C. Five formulations (Table 2) for the BA-based CBC systems were designed to obtain this information. In preparing the test specimens, a certain amount of water was added to a dry mixture containing BA, CAC, Type I, and NaP. The CBC

slurries then were cast in cylindrical molds (3- in.- diam. x 6- in.- long) and left for 24 hours in an atmosphere. The hardened CBC specimens then were removed from the molds to determine their compressive strength. The designed formulations were characterized by varying the ratio of CAC/Type I additive, while keeping constant the amounts of three other components, the BA, NaP, and water. Table 3 shows the compressive strength of these specimens after curing for 24 hours at 0°, 10°, 25°, and 40°C. The data demonstrated that the two factors are responsible for strengthening the specimens. One factor was the proportion of CAC to Type I additive; increasing the ratio improved the material's strength. The other factor was the atmospheric temperature; namely, the strength of the specimens tends to rise with an increase in curing temperature. The data also showed that at 0°C, specimens made with the formulation No.70 and the CAC/Type I ratio of 100/0 had the highest strength. However, it was very difficult to prepare specimens at temperatures of > 10°C because the setting time of cement slurries is too short to be cast with them into the molds. Consequently, the formulation No. 71 consisting of 42.6 wt% BA, 22.2 wt% CAC, 5.6 wt% Type I, 7.0 wt% NaP, and 22.6 wt% water was recommended as the most effective one in providing a moderate setting time and in developing an appropriate strength. Although the specimens made with this recommended formulation displayed a compressive strength of > 1500 psi at the curing time for 24 hours, two important questions to be resolved still remained. One was 1) what is the maximum strength of the specimens with a prolonged curing time at temperature range of 0° to 40°C? The other was 2) do the specimens develop a compressive strength of > 4000 psi, which is one of the required criteria for a desirable concrete capping ? In answering these questions, the specimens were left for up to 28 days at 0°, 10°, 25°, and 40°C, and were tested to determine the compressive strength at the curing ages of 2 hours, 5 hours, 1 day, 3 days, 7 days, 14 days, and 28 days. For the purpose of comparison, commercial Type I cement specimens also were tested. The results from these specimens are illustrated in Figure 3. Despite preparing the CBC specimens at a freezing point, they developed an initial strength of ~ 200 psi in the first curing period for 2 hours after mixing. As expected, this initial strength increased with an increasing temperature; the strength of specimens made at 40°C was 700 psi, corresponding to 3.5 times more than those made at 0°C. The compressive strength of all the specimens tended to increase with an elapsed curing time. After 28 days, the strength of the 25°C- and 40°C-cured specimens was determined to be > 4000 psi. After the same curing time, the 0°C- and 10°C-specimens had a compressive strength of 3400 and 3200 psi, respectively. In contrast, no strength could be measured from the commercial Type I

cements after 5 hours curing, even though they were cured at mild temperature of 25°C. Thus, the developed CBC pastes appear to have a high potential for use as a binder for rapid-setting repair composites. Further, the strengths of all CBC specimens after 28 days at 0°, 10°, and 25°C, were much greater than those of the commercial Type I cement specimens.

Thus, the most promising formulation of dry CBC mixture for use as a rapid-setting all season cementitious material was 55 wt% BA, 29 wt% CAC, 7 wt% Type I and 9 wt% NaP.

Using this optimized CBC formulation, our study now shifted to developing concrete specimens that would gain a compressive strength of > 3000 psi after leaving them for 24 hours at room temperature. The work to be developed included the following two major objectives. One objective was to design a proper proportion of BA cement to aggregate system consisting of silica-based coarse aggregate (CA, size, 9.5 to 2.4 mm) and silica sand aggregate (SA, size, 1.2 to 0.15 mm), and the other one was to be optimize the CA/SA ratio. The data obtained for the former objective are shown in Table 4 and Figure 4. With a constant CA/SA ratio of 50/50 by weight, the compressive strength of the specimens depended mainly on the amount of CBC in the concrete system. The best specimens in offering improved strength can be made with 68.1 wt% CBC. The compressive strength of 3172 psi obtained from this concrete specimens was ~ 18 % higher than that of the neat cement pastes without any aggregate, suggesting that the most effective ratio of cement/mix aggregate in developing a strength of > 3000 psi was 80/20 by weight.

Next, our experimental work focused on determining the compressive strength of the concrete specimens made by varying the CA/SA ratio. The results from these specimens are given in Tables 5-7. Integrating the information on all these data revealed that the optimum ratio of CA/SA was 40/60 by weight. Additionally, specimen No. 94 made from a CBC/mix aggregate ratio of 80/20 displayed the highest compressive strength of 3200 psi in this test series. However, there is no information on the maximum strength developed after the curing times for at least 28 days. Nevertheless, we recommend a formulation (Table 8) consisting of 68.1 wt% BA cement, 6.8 wt% CA, 10.2 wt% FA, and 14.9 wt% water, as the optimum for using as the capping CBC concrete in the patch material systems.

4.1.2. Vanadium Metal-sequestering Organic Polymer Additive

Since BA contains a substantial amount of vanadium (V) metal, one important consideration is its immobilization and sequestration in the solidified CBC. Although there is currently no EPA regulation for the leaching amount of V, after referring to an EPA safe standard of < 5 mg/l for Pb metal, we decided that the leachability of V should be controlled to no more than 5 mg/l.

One approach to immobilizing V metal was to incorporate a water-borne organic polymer additive into the CBC. Among the various polymeric additives, the acrylic-styrene copolymer (ASC) was employed because of its excellent adherence to metals and cements. The amounts of ASC added to the CBC system were 5, 10, and 15 % of the total weight of BA, CAC, Type I and NaP components. Table 9 shows the formulations of the ASC-modified CBC slurries. Using these formulations, the test specimens were prepared in accordance with the following sequence. First, an appropriate amount of ASC was added to the dry CBC consisting of 55 wt% BA, 29 wt% CAC, 7 wt% type l, and 9 wt% NaP components, and mixed by hand. Second, water was slowly added to the ASC-containing CBC slurry, until it attained a desirable consistency that was determined as zero slump. Finally, the CBC slurry was cast into the molds and left for two weeks at room temperature. The concentration of V ions leached out from the two-week-aged CBC specimens was measured in accordance with the Toxicity Characteristics Leaching Procedure (TCLP) recommended by EPA; the results are given in Table 10. The CBC without any ASC marked as ASC/CBC ratio of 0 % liberated 271.0 mg/l. Since the amount of V present in this original specimens before TCLP testing was estimated as ~ 1350 mg/kg, it appears that even the hardened CBC itself has a great ability to immobilize and sequester V metal. When a 3.3 wt% ASC was incorporated into the control specimens, the concentration of V leached out dropped considerably to 4.3 mg/l. With 6.5 and 9.5 wt% ASC, its leachability was determined to be 6.2 and 3.1 mg/l, respectively. Thus, this information strongly verified that the ASC additive contributes significantly to improve the ability of CBC to immobilize V.

In addition, we investigated the effectiveness of ASC in strengthening the CBC concrete specimens. Formulations with ASC/CBC ratios of 0, 5, 10, and 15 % were made for this assessment (Table 11). We tested their compressive strength after curing for 24 hours at 25°C.

Figure 5 plots compressive strength versus ASC/CBC ratios. It shows that compressive strength tends to increase with an increasing ratio until it reaches 10 wt%; beyond that ratio, strength seems to decline.

Hence, incorporating a proper amount of ASC into the CBC concrete specimens not only alleviates the environmental impact of V metal, but also is responsible for improving the compressive strength of CBC concrete specimens.

4.1.3. Fiber Reinforcement

In seeking the fibrous reinforcements that improve toughness and ductility of the CBC concrete specimens, we evaluated three potential fibrous materials, E- glass, polypropylene, and carbon fibers. In preparing the fiber-reinforced CBC composites, 0.5. 1.0, and 1.5 % of these fibers by weight of the total amount of the CBC was incorporated into the CBC concrete slurry consisting of 65.9 wt% dry CBC, 6.6 wt% coarse aggregate, 9.9 wt% sand aggregate, 3.2 wt% [50 wt% ASC aqueous solution], and 14.4 wt% water. The fiber-containing composite slurries then were cast into cylindrical molds (1.2- in.- diam. x 2.5- in.- length) for tensile splitting test and into 1- in. x 1- in. x 12- in.- beam molds for bending test. Afterward, the composite specimens were left for 24 hours in an atmospheric environment at 25°C for conducting these tests. The bending test for the beam specimens supported on 8.2 in. span was subjected to bending under center loading. Figure 6 shows the changes in bending strength of these fiber-reinforced composites as a function of the amount of fiber. The strength-fiber content curves for all the specimens indicated that the highest value of strength seems to be obtained by adding 1 wt% fibers into the CBC concrete. A further increase in the fiber content to 1.5 wt% reduced its strength.

From comparing the strength values of the specimens, the effectiveness of these fibers in improving the bending strength was in the following order: E-glass > polypropylene > carbon. The bending strength of 360 psi for the 1 wt% glass fiber-reinforced composites was more than three times greater than that of the non-reinforced ones. Similar results were obtained from the tensile strength of these composites (Figure 7). It should be noted herein, in general, the glass fiber is very difficult to use to reinforce the conventional portland cement concrete because of its

high susceptibility to alkaline degradation in the prortland cement slurry at pH ~ 12. In contrast, the pH of CBC slurry is ~ 9.2, allowing the glass fiber to incorporate into the CBC concrete.

4.2. Characteristics of Formulated CBC Composites

From the integration of all the data described above, the optimized formulation of glass fiber-reinforced CBC composites is given in Table 12. With this formulation, our focus moved toward characterizing the cured CBC composites as a rapid-setting road restoration material. The factors to be explored included adherence to dry, wet, and icy surfaces of the cement and asphaltic concrete adherend, freezing-thawing durability, liner dry shrinkage, water permeability, and protection of steel reinforcement bars against corrosion.

4.2.1 Adherence

One dispensable property for path repairing materials is that they must adhere to the old cement and asphaltic concrete adherends. An inadequate adhesion at the interfaces between the repairing materials and these adherends frequently causes a failure of the patched materials because of the penetration of water into the interstices between the adherends and patched materials. Thus, it is very important to obtain information on whether the formulated CBC composite adequately bonds to these adherends.

In this work, the old cement concrete specimens were prepared by mixing four components, 41.0% Type I cement, 20.0 wt% coarse aggregate, 20.0 wt% sand, and 19.0 wt% water. The mixed concrete slurries were cast into 1- in. x 1- in. x 12- in.- beam molds, and then allowed them to cure in an atmospheric environment at 25°C. After curing for 28 days, the beam-shaped concrete aherends were cut in half with a diamond saw. One half of the beam was placed back into the same beam mold as that used in making the concrete adherends. To prepare the adhesive bonding specimens, the CBC composite slurry made with the formula given in Table 12, was poured in the half empty space of the mold, and then left for 7 days at 25°C or at 0°C. For the contact surfaces of adherends, three different conditions, dry, wet, and icy, were employed to assess whether the composite appropriately links to the cement concrete adherend in all seasons. The Type I cement concrete was used as the control specimens. The degree of

linkage between the composite adhesive and the cement concrete adherend was estimated by comparing the values of bond strength computed from the maximum load at the failure of the adhesive/adhered joints by the bending test under the loading at the joint. Table 13 gives the test results from these specimens. Also, the locus of the joint failure for the specimens after the bending test was visually examined to support these findings. The bond strengths at interfaces between the composite and the dry or wet adherends were 26.8 psi and 27.0 psi, respectively. The fracture surfaces for both specimens after testing disclosed that the bond failure took place in the cement concrete adherend. Such a cohesive failure mode can be accounted for the outstanding adherence of the composite to either the dry or wet cement concrete aherend. In contrast, the control Type I cement concrete poorly bonded to both the wet and dry adherend. In fact, the values of the bond strength were ~ three times lower than those of the composite joint specimens. Such low bond strength revealed that the bond failure occurs at the interfaces between the control Type I concrete and the adherend, which can be figured out as the adhesive failure mode. When the composites were jointed to the icy surfaces of adherend at 0°C, the joint specimens had a bond strength of 18.9 psi. A similar value was measured from composite specimens linked to the dry surfaces of adherend at the same temperature. The visual observations of the failed specimens indicated that the failure mode is a mixture of cohesive and adhesive ones. Thus, the composites have some affinity for the icy cement concrete surfaces. Since CBC is cured through two-step reaction routes, exothermal acid-base and hydration, the heat energy evolved by the exothermal reaction may de-ice the frozen adherends at the critical interfacial contact zone, promoting the adherence of the composite to the adherends. As expected, the ability of the control Type I cement concrete in which there is no exothermal reaction, to link to icy surfaces was very poor, and its bond strength was too weak to be measured.

Trying to investigate the ability of the composites to adhere to the cold asphalt patch adherend, the specimens were prepared in the following way. First, the composite slurry was poured into the cylindrical mold (3- in.- diam. x 6- in.- long) to fill half its volume, and then left for 1 hr in an atmospheric environment at 25°C. Second, the cold asphalt patching material was placed directly on a barely cured composite surface to fill the remaining half in the mold. Third, the surfaces of the placed asphalt were tamped with a hammer to compact the asphalt layer, and

then were left for 10 days at 25°C. Finally, the composite specimens linked to the asphalt patch finisher were removed from the cylindrical molds.

However, we encountered difficulties in determining the bond strength of these joint specimens because of the extraordinary elasticity of the asphalt. It was not hard enough to remain on the composite surfaces, and naturally disintegrated shortly after being removed. The visual observations of the broken asphalt/composite joint specimens revealed that some asphalt remained at the BA concrete surfaces. However, there was no clear evidence on how well the asphalt adheres to the composite. Thus, an alternative way is needed to gain quantitative data on the interfacial bond strength. Nevertheless, the remaining asphalt fragments can be taken as evidence that some asphalt clings to the composite.

4.2.2. Freezing-thawing Durability

We next measured the resistance of the CBC composites to rapidly repeated cycles of freezing and thawing in water. For the purpose of comparison, the ordinary portland cement concrete specimens were used as the control. The 7-day-cured composite and portland cement concrete specimens were placed in the freezing and thawing chamber (Figure 8). One freezing and thawing cycle consisted of alternately lowering the temperature of the specimens from 40 to 0°F (4.4 to -17.8°C) and raising it from 0 to 40°F (-17.8 to 4.4°C) within 4 hours. The loss in weight for the specimens after 10, 20, 30, 46, and 82 cycles was measured as the barometer of durability factor. The plots of the loss in weight versus the number of freezing and thawing cycles for these specimens are given in Figure 9. Amazingly, the composite specimens displayed superior durability compared with that of the hydraulic ordinary portland cement concrete specimens. Even if the specimens were subjected to 64 cycles, the loss in weight of the composites was only ~ 3 %. In contrast, the conventional portland concede specimens failed after 46 cycles, with a very high weight loss of ~ 40 %. Figure 10 compares the visual appearance of the composite marked as "BA-based cement concrete" and portland concrete specimens after 46 cycles. As seen, the portland concrete specimens were severely damaged by the rapid freezing and thawing cycles, whereas there was no significant deterioration for the composite specimens. Thus, it appears that the resistance of the CBC composites to freezing and thawing is much greater than that of the conventional hydraulic portland cement concrete.

4.2.3. Linear Dry Shrinkage

Considering the shrinkage of the composite specimens as a function of time after casting, a high extent of shrinkage not only causes failure of the bond structure at the critical interfacial boundary zones between the composite and the patch wall, but also develops the numerous cracks in the composite body. Such undesirable phenomena due to excessive shrinkage allow water to penetrate through the opening spaces created by the separation of the placed composite from the patch wall. The penetrating water is detrimental to the remaining intact patch structure because of its undermining effect beneath the patching layer. Thus, the experimental work concentrated on determining the extent of shrinkage of the CBC composite specimens after casting. For comparison, the conventional portland cement concrete specimens were used. Figure 11 shows the apparatus along with the strain gauge used for measuring the extent of unrestrained linear shrinkage of 2-in. x 2-in. x 11.4- in.- beam specimens. Figure 12 depicts the shrinkage of these specimens plotted as a function of curing time after casting. For the conventional portland cement concrete specimens, there was shrinkage of 84×10^{-2} mm in the first 24 hours curing period. Afterward, shrinkage gradually increased with extended curing time. Its value at an age of 21 days was 99×10^{-2} mm, corresponding to 18 % more than that of the 1-day-aged specimens. In contrast, the extent of shrinking of the composite specimens was lower than that of the conventional concrete specimens; their shrinking value of 70×10^{-2} mm after 1 day curing was ~ 18 % less than that of the conventional concrete specimens at the same curing time. The shrinkage-curing time curve indicates a tendency towards an increase in shrinkage with time up to 14 days; beyond that, it seems to level off at 80×10^{-2} mm. Thus, the composites undergo some degree of shrinkage. However, its magnitude was much lower than that of the conventional cement concrete.

4.2.4. Water Permeability

The rate of water transportation through the cylindrical CBC composites (2- in.- diam. x 2- in.- length) was determined by the Ruska liquid permeameter. The value of water permeability under the pressure of 2 atm was gained from the following equation: $K_a = \mu VL/AP$; where K_a is the intrinsic permeability in Darcys, V (cc/sec) is the rate of flow at the fluid viscosity, μ (cP),

and L and A are the thickness (cm) and the cross section area (cm^2) at the sample under a hydrostatic pressure P (atm). The information obtained was correlated directly with the values of porosity and density of the composite specimens measured by Helium comparison pyconometry (Model, AccuPyc 1330 Micromeritics). Three other specimens, ordinary portland cement, ASC-modified CBC specimens and non-modified CBC specimens, also were prepared as reference specimens to compare with those of the glass fiber-reinforced CBC composite containing ASC. The results from the 7-day cured these specimens are shown in Table 14. The ordinal portland cements (OPC) had a water permeability of 0.92 millidarcys, a porosity of 38.42 %, and a density of 2.27 g/cc. By comparison with those of OPC, the CBC specimens in the absent of ASC and glass fiber showed a lower porosity and an increased density, leading to a 14 % decrease in water permeability to 0.79 millidarcy. A further fall in water permeability to 0.58 millidarcys was observed from the ASC-modified CBC specimens, suggesting that the specimens become densified structure. Thus, incorporating ASC additive into the CBC not only acts to immobilize the V metal, but also appears to minimize the number of free voids existing in the CBC bodies. When glass fibers were added to the ASC-modified CBC specimens, their water permeability and porosity somewhat increased to 0.59 millidarcys and 33.72 %. However, these values corresponded to an ~ 36 % reduction in water permeability and an ~ 12 % decrease in porosity, compared to those of the OPCs. Consequently, the CBC composites have a better water proofing property than do the OPCs.

4.2.5. Anti-corrosion

One important property needed for the CBC composite is an ability to protect the steel reinforcement bars against corrosion. In trying to obtain this information, cut epoxy-coated bars (0.6-in.-diam. x 2-in.-long) were embedded into composite slurries being placed in the molds (1.5-in.-diam. x 3.0 -in.-height), and then left them for 24 hours in atmospheric environment. Afterward, the hardened steel bar-reinforced cement concrete specimens were removed from the molds, and immersed in 15 wt% NaCl solution at 90°C to perform the corrosion-accelerating testing of the embedded steel. For comparison, the coated steel bars also were incorporated into the conventional portland cement concrete. The results revealed that neither the composites nor the conventional portland cement concrete showed any sings and traces of corrosion of the steel

bars after 3 month immersion. However, we note that the composites displayed a great adherence to the epoxy-coated steel bar surfaces. The loss of adhesion at the interfaces between the composite and the bar took place through the concrete layers; in fact, unremovable CBC fragments were observed on the bar's surfaces which had separated physically from the composite matrix (Figure 13). In contrast, the bonding of conventional concrete to the coated steel bar was very poor, demonstrating that the interfacial bond failure occurred at the concrete/bar joints. No fragments of concrete were reported on the dislodged bar's surfaces (Figure 13).

4.3. Formulation and Properties of Soil-containing CBC for Use as Backfill Underlayment

In this task, the first experiment was to design a proper proportion of CBC to soil for use in the underlying cememtitious backfill material systems. The soil used in this work was collected from the grounds near our building, and it contained 7.3 % water. Table 15 shows the mix formulation of these soil cement specimens. The proportion of CBC to soil ranged from 10/90 to 40/60 ratio by weight. The soil cement specimens are required to have a low compressive strength of ~ 40 psi, suitable for a subsequent excavation by hand. Table 16 gives the results of the compressive strength for the 24-hr-aged specimens. The 20/80 and 30/70 ratios seem to meet the material criterion; the compressive strengths of the 10/90 and 40/60 ratio specimens were too low or high to be used.

One concern about the formulated cementitious backfill material system is the contamination of soil by NaCl which originates from rock salt used for deicing roadway surfaces during the winter. Thus, we investigated the effectiveness of NaCl-contaminated soil in the setting time and the development of strength for backfill soil cements. To obtain this information, we made up the backfill specimens with the proportion of 30 wt% CBC to 70 wt% soil containing NaCl at 0, 0.5, 1.0, and 2.0 wt% . Figure 14 shows the changes in compressive strength of the soil cement specimens containing various amount of NaCl as a function of time. The data demonstrated that NaCl retards the setting time of the cement specimens; in fact, the compressive strength of the 1-day-aged specimens tends to decline when NaCl content was

increased. The compressive strength of 10 psi for 2.0 wt% NaCl-containing specimens after 24 hours curing was as much as six times lower than that of unadulterated specimens at the same curing time. However, the strength for all the specimens increased with an extending curing time. Correspondingly, although the 2.0 wt% NaCl specimen after curing for 24 hours had a compressive strength of only 10 psi, its strength rose seven times to 70 psi after 14 days curing. This value fully met the criterion of ~ 40 psi.

4.4. Development of Placement Technology for Backfill CBC Systems

In developing the ideal technology for placing the cementitious backfill underlayment, Daniel D'Eletto (KeySpan) proposed the following sequence. First, excavated soil containing some moisture is mixed directly with an appropriate amount of dry packed CBC in a conventional concrete mixer or with hand mixing tools. Second, the well-mixed backfill material is placed in the pit, and its surfaces are tamped to create a densified underlayment structure. Finally, a sufficient amount of water is sprayed over the underlayment's surfaces to allow it to permeate through this compacted cement-soil mixture layer. When the permeated water comes in contact with the CBC grains, the acid-base reaction of cement is initiated, thereby binding the soil particles into a cohesive mass, which is responsible for developing a compressive strength of at least 40 psi.

In our work to validate the process technology described above, a 4.7 % moisture-containing soil was mixed directly with the CBC, and then this mixture, the backfill underlayement material, was filled in the cylindrical mold (3-in.-diam. x 6-in.-long) until it reached the cylinder's surface. Next, to make a highly compacted underlayment, a 4.4 lb tamping tool was applied to the top surface of the mixture of the cylinder mold. Tamping continued until there was no depression of the underlayment. Its sinking depth under a burden was ~ 1.8 in. Then, 0.4 lb water was poured into the space (3-in.-diam. x 1.8-in.-height) created by depressing the underlayment. The volume fraction of the compacted underlayment to water was 2.7 to 1.0. The compacted underlayment allowed water to percolate its layers easily. Most of the water had permeated in an hour after pouring.

Three mixing formulations, with wet soil/CBC ratios of 90/10, 80/20, and 70/30 by weight, were employed in this experiment. Figure 15 shows the changes in compressive strength of these specimens as a function of curing times up to 12 days at room temperature. The results were very promising; namely, the specimens made with the 80/20 and 70/30 ratios provided a compressive strength of > 40 psi, that is required for use as the backfill underlayment materials.

4.5. Lightweight CBC Concrete

To formulate a very lightweight CBC concrete, we incorporated the commercial ceramic micospheres called Extendospheres (EX, PQ Corporation) having a density of 0.67 g/cc, instead of using sand and aggregate, into the dry CBC. The designed formulations of lightweight CBC slurries are shown in Table 17. Table 18 gives the results of dry bulk density and compressive strength for 3-day-aged lightweight cement specimens. The dry bulk density of the CBC specimens depends mainly on the content of EX microspheres. Correspondingly, the density of neat CBC pastes dramatically fell to 0.96 g/cc from 1.87 g/cc by incorporating a 34.6 wt% microspheres into the CBC slurry. As expected, the compressive strength of the specimens declined with a decrease in their density. Also, the data revealed that the ceramic hollow microspheres are responsible for strengthening the lightweight CBC concrete specimens. Even though the specimens had a very low density of 0.96 g/cc, they developed a compressive strength of 37 psi. However, with a density of < 0.7 g/cc, the strength of 3-day-aged specimens was too weak to be measured.

4.6. Standard Dry Packaging of Capping CBC Composite and Full-scale Field Demonstration

To prepare the dry packed CBC composite mixture consisting of the five ingredients, BA, CAC, type I, NaP, sand aggregate, and coarse aggregate, an ~ 500 lb raw BA was transferred from the KeySpan's Northport Power Pant to BNL. Prior to pulverizing the bulky BA fragments using a portable crushing machine, BNL's Environmental Services Department assessed the rate of air pollution due to fine particles containing some heavy metals emitted during the entire operational period under the 0% emission policy. They informed us that the crushing machine must be modified to permit its operation, which was carried out in a laboratory hood. Thus, our

efforts were diverted to modifying and redesigning this machine to comply with the BNL regulation. Finally, modified crushing machine (Figure 16) did not allow any pollutants to be emitted. All the raw BA was crushed into an average particle size of 200 mesh. The dimensions of the test pit were 2-ft.-wide, 8-ft.- length, and 6-in.- depth. The formulation of composite slurry used in this field test was shown in Table 19. With this formulation, the following amounts of each of the ingredients were required to fill up this pit; a 394 lb BA, 207 lb CAC, 49 lb Type I cement, 65 lb NaP, 35 lb ASC, 8 lb glass fiber, 71 lb coarse aggregate, 106 lb sand, and 160 lb water.

On November 15th, a full-scale demonstration test was carried out to validate the technical feasibility of using the BA-based CBC composite material for rapid/permanent road restoration at KeySpan Energy's site in Brentwood at an atmospheric temperature of 35°F. This field test was performed to ascertain that the results of the in-house studies can be duplicated in the field, and also to develop the process technology for placing the composite slurry. Figures 17-20 show the appearance of each ingredient used in preparing the dry CBC composite packages. All the components, except for the ASC, glass fiber, and water, were weighed and blended together in a concrete mixer at BNL (Figures 21,22), and then were bagged into water-proofing paper sacks to make a 78.2 lb dry composite package (Figure 23). BNL provided twelve sacks of composite to fill this pit. The other components; ASP, glass fiber, and water, were added to the dry packed composite in the field.

In the field, the composite slurry was prepared and placed in accordance with the procedures described below:

A. Preparation of Composite Slurry

To ensure thorough mixing of the three major components, dry CBC composite, water, and glass fiber, we adopted the following mixing sequence. First, 40 lb water was poured into a rotary shear concrete mixer, and the mixer was rotated for ~ 10 sec to wet its entire interior surfaces. Second, 2 lb glass fiber was added to the continuously rotating wet mixer, and followed by adding a total of 223 lb dry composite removed from the three paper sacks (Figure 24).

Finally, 8.7 lb ASC dispersion was blended with the fiber-incorporated composite slurry, and then mixed for approximately 5 min (Figure 25).

B. Placement of the Composite Slurry

The slurry was discharged from the mixer into a pail, and subsequently poured into the test pit (Figure 26). The slurry had an adequate consistency to possess a self-leveling characteristic (Figure 27). This process of preparing and placing the composite slurry was repeated another three times, until 1094 lb of the composite slurry had been placed in the pit.

C. Surface Finishing and Curing of Placed Slurry

To make a smooth surface texture, the surface of the placed slurry was finished by troweling, and it was left to cure. About 90 min after its placement, the composite surface developed a sufficient strength to be stepped upon (Figure 28).

In monitoring the development of CBC composite being placed in the pit, the composite slurry that was used in this demonstration was poured into 3-in.-diam. x 6-in.-length cylindrical molds. Afterward, they were left in an atmospheric environment at 35°F. The changes in compressive strength of the specimens as a function of time up to 14 days (336 hours) were reported (Figure 29). One hour after placement, the specimens had developed an excellent strength of 860 psi. Since an initial compressive strength of ~ 500 psi allows vehicular traffic to resume over the patching concrete, we believe that this developed shortly after placement might be enough to sustain the concrete patch without any damage after traffic was resumed. As expected, its strength tends to increase with an extended curing time. The 5600 psi determined from the 14-day-cured specimens was more than six times higher than that of the 1-hour-cured specimens. Also, the resulting curve revealed that the compressive strength of the specimens promptly develops in the first 2 days of curing time; beyond that, it gradually increases with an elapsed time.

5. Conclusion

In an attempt to recycle boiler ash (BA) waste of which ~ 270 tons is generated annually at the KeySpan's power plants into a potential end-use product, a BA-based chemically bonded cement (CBC) was formulated for use as a binder for rapid-setting patch repair material in all seasons. The optimized formulation of dry CBC consisted of 55 wt% pulverized BA, 29 wt% Secar #51 calcium aluminate cement (CAC), 7 wt% Type I portland cement (TypeI), and 9 wt% sodium polyphosphate (NaP). When this neat CBC was mixed with water and icy over the temperature range of 0° to 40°C, the cement pastes set within 30 min and developed the compressive strength of at least 200 psi in the first two hour 's curing period. Extending the curing time to 28 days provided a compressive strength of ~ 4500 and ~ 3200 psi at 40° and 0°C, respectively. By contrast, no strength was attained with commercial Type I cement pastes even after 5 hours at 25°C. Thus, we are convinced that the formulated CBC can be used as a binder of both for the capping patch, which extends ~ 6 in. in depth from the top of the patch's surfaces , and for the backfill underlayment with ~ 30 in. thickness beneath the top capping layer. The capping layer must have a compressive strength of > 4000 psi, whereas the backfill underlayment needs a low compressive strength of only ~ 40 psi because of the subsequent requirement for its excavation by hand.

In developing a strong, tough, durable capping material system, four additives, silica coarse aggregate (CA), silica sand aggregate (SA), chopped glass fiber (size, 8-μm-diam. x 6 mm long), and acrylic-styrene copolymer (ASC) emulsion, were incorporated into the CBC binder. The designed composite system consisting of 65.3 wt% CBC, 6.5 wt% CA, 9.7 wt% SA, 0.7 wt% glass fiber, 3.2 wt% ASC and 14.6 wt% water, not only fully satisfies its material criteria, but also provides excellent ductile-related properties. For instance, 24-hr-cured composite specimens at 25°C developed bending strength of > 350 pis and tensile strength of > 240 psi. The composites also showed an outstanding adherence to dry, wet, and icy surfaces of old cement concrete. Although there are no quantitative data on the degree of its adherence to asphalt surfaces, we visually observed that some asphalt clings to the composite's surfaces. The ASC in the composite system played an important role in sequestering the vanadium (V) metal present in the raw BA and in densifying the composite structure, thereby lowering its

permeability to water and porosity. Among the other advantageous characteristics of the composite were 1) its excellent freezing-thawing durability, 2) its low linear dry shrinkage, and 3) its good bonding to the surfaces of epoxy-coated steel reinforcement bars, compared with that of the conventional portland cement concrete.

Consequently, on November 15, 2000, a full-scale demonstration of the capping composite was carried out at the KeySpan Energy's site in Brentwood to ensure that the results of in-house work were reproducible and to evaluate the technical feasibility of using the composite for rapid/permanent road restoration. The dimensions of a test pit used for the demonstration were 2- ft.-wide, 8-ft.-length, and 6-in.-deep and the atmospheric temperature at the test site was 35°F. The preparation of composite slurry and its placement in the pit was accomplished in the following sequence:

1) 40 lb water was poured into a rotary shear concrete mixer,
2) Mixer was rotated for ~ 10 sec to wet its entire interior surface,
3) 2 lb glass fiber was put into the continuously rotating wet mixer, followed by adding 223 lb dry CBC composite,
4) 8.7 lb ASC emulsion was blended with the fiber-incorporated composite slurry, and then mixed for approximately 5 min,
5) Slurry was discharged from the mixer into a pail, and subsequently poured into the test pit,
6) This process of preparing and placing the composite slurry was repeated another three times, so that altogether 1094 lb of the composite slurry was placed in the pit.
7) Surface of the placed slurry was troweled to create a smooth texture, and the composite was left to cure.

A very successful demonstration revealed that, about 90 min after its placement, the composite surfaces developed sufficient strength to be stepped upon, and the required compressive strength of > 4000 psi was attained after a curing time of ~ 24 hours.

In the soil-containing CBC backfill underlayment system, specimens made with the CBC/ wet soil (7.3 wt% moisture) ratios of 20/80 and 30/70 by weight developed a compressive strength of ~ 40 psi, meeting the material criterion. In using the excavated soil, one concern was its contamination by NaCl, which arises from rock salt used to de-ice roadways. Soil highly

contaminated with NaCl acted to retard the curing rate of CBC. However, specimens containing 2.0 wt% NaCl-contaminated soil met material criterion after 6 days curing time.

We developed the following technical sequence for placing the backfill underlayment:

1) Excavated soil containing some moisture was mixed directly with an appropriate amount of dry packed CBC in a conventional concrete mixer or with hand mixing tools,
2) The well-mixed backfill material was placed in the pit, and then its surfaces were tamped to create a densified underlayment structure,
3) A sufficient amount of water was sprayed over the underlayment's surfaces, allowing it to permeate through this compacted CBC-soil mixture layer.

When the permeated water comes in contact with the CBC, an acid-base reaction is initiated, thereby binding the soil into a cohesive mass which is responsible for developing a compressive strength of ~ 40 psi.

However, two major questions that must be asked still remain. First, would this technology being developed in the laboratory be feasible in the field? Second, does the placed CBC backfill material congeal satisfactorily and have good compatibility with the capping layer made with the CBC composite and conventional asphaltic concrete?

References

[1] T. Sugama and K. Yager, "Chemically Bonded Cements from Boiler Ash and Sludge Wastes", Phase I Report, August 1998.

[2] T. Sugama and K. Yager, "Chemically Bonded Cement from Boiler Ash and Sludge Wastes", Phase II Report, August 1999.

Table 1. Elemental Composition of Boiler Ash.

Test/Parameter	Result	Units	Analysis Method
Arsenic (As) **	176	mg/Kg dry wt.	EPA 206.2
Barium (Ba) **	721	mg/Kg dry wt.	EPA 208.1
Cadmium (Cd) **	<0.20	mg/Kg dry wt.	EPA 213.1
Calcium	42900	mg/Kg dry wt.	SW 846; 6010B
Chromium (Cr) **	22.5	mg/Kg dry wt.	EPA 218.2
Copper (Cu) **	1610	mg/Kg dry wt.	EPA 220.1
Iron (Fe) **	12000	mg/Kg dry wt.	EPA 236.1
Lead (Pb) **	264	mg/Kg dry wt.	EPA 239.1
Loss on ignition	0.005	% by dry wt	Lab Method
Magnesium (Mg)	35700	mg/Kg dry wt.	SW 846; 6010B
Manganese (Mn) **	336	mg/Kg dry wt.	EPA 243.1
Mercury (Hg) **	<0.25	mg/Kg dry wt.	SW 846; 7471A
Moisture	<0.5	% by wt.	Lab Method
Nickel (Ni) **	11600	mg/Kg dry wt.	EPA 249.1
Selenium (Se) **	12	mg/Kg dry wt.	EPA 270.2
Vanadium (V) **	86700	mg/Kg dry wt.	EPA 286.1

Table 2. Formulations of Neat BA-based CBC Specimens.

Specimen No.	Formulation, wt%				
	BA	CAC	Type I	NaP	Water
70	42.6	27.8	0.0	7.0	22.6
71	42.6	22.2	5.6	7.0	22.6
72	42.6	16.7	11.1	7.0	22.6
73	42.6	11.1	16.7	7.0	22.6
74	42.6	5.6	22.2	7.0	22.6

Table 3. Compressive Strength of BA-based CBC Specimens After Curing for 24 Hours at 0°, 10°, 25°, and 40°C.

Specimen No.	Compressive Strength, psi			
	0°C	10°C	25°C	40°C
70	1680	*	*	*
71	1520	2330	2680	2910
72	1470	2300	2480	2400
73	1300	2000	2150	2080
74	950	1850	1790	1800

* Quick setting

Table 4. Changes in Compressive Strength of 25°C-24-hour-cured Specimens as a Function of the Amount of Aggregate.

Specimen No.	CBC, wt%	CA*, wt%	SA**, wt%	Water, wt%	Compressive strength, psi
76	26.6	31.0	31.0	11.4	481
77	35.3	26.6	26.6	11.5	875
78	44.1	22.1	22.1	11.7	1458
79	52.3	17.4	17.4	12.9	2010
80	60.2	12.9	12.9	14.0	2394
81	68.1	8.5	8.5	14.9	3172
82	77.4	0.0	0.0	22.6	2780

In Tables 4 to 12, the following abbreviations are used:
*CA: coarse aggregate (size, 9.5 to 2.4 mm)
**SA: sand aggregate (size, 1.2 to 0.15 mm)

Table 5. Effect of CA/SA Ratio on Compressive Strength of 25°C-24-hour-cured Specimens Made at a Constant Amount of 52.3 wt% CBC.

Specimen No.	CBC, wt%	CA, wt%	SA, wt%	Water, wt%	Compressive strength, psi
83	52.3	20.9	13.9	12.9	2000
84	52.3	13.9	20.9	12.9	2018
85	52.3	10.5	24.3	12.9	1868
86	52.3	3.5	31.3	12.9	1779

Table 6. Effect of CA/FA Ratio on Compressive Strength of 25°C-24-hour-cured Specimens Made at a Constant Amount of 60.2 wt% CBC.

Specimen No.	CBC, wt%	CA, wt%	SA, wt%	Water, wt%	Compressive strength, psi
88	60.2	15.5	10.3	14.0	2319
89	60.2	10.3	15.5	14.0	2442
90	60.2	7.7	18.1	14.0	2021
91	60.2	2.6	23.2	14.0	1834

Table 7. Effect of CA/SA Ratio on Compressive Strength of 25°C-24-hour-cured Specimens Made at a Constant Amount of 68.1 wt% CBC.

Specimen No.	CBC, wt%	CA, wt%	SA, wt%	Water, wt%	Compressive strength, psi
93	68.1	10.2	6.8	14.9	2980
94	68.1	6.8	10.2	14.9	3200
95	68.1	5.1	11.9	14.9	2820
96	68.1	1.7	15.3	14.9	2613

Table 8. Recommended Formulation of BA-based CBC Concrete.

Formulation, wt%			
BA cement	**CA**	**SA**	**Water**
68.1	6.8	10.2	14.9

Table 9. Formulation of ASC-modified CBC Slurries.

Specimen No.	CBC, wt%	Water, wt%	ASC additive, wt%	ASC/CBC ratio, %
92	77.4	22.6	0	0
93	72.0	24.4	3.6	5
94	67.4	25.9	6.7	10
95	63.2	27.3	9.5	15

Table 10. Vanadium leachability of ASC-modified CBC Specimens.

ASC/CBC ratio, %	Leachability, mg/l
0	271.0
5	4.3
10	6.2
15	3.1

Table 11. Formulations of ASC-modified CBC Concrete Specimens.

Specimen No.	CBC, wt%	CA, wt%	SA, wt%	Water, wt%	ASC solution, wt%	ASC/CBC ratio, %
97	68.1	6.8	10.2	14.9	0	0
98	66.4	6.6	10	13.7	3.3	5
99	64.9	6.5	9.7	12.4	6.5	10
100	63.5	6.4	9.5	11.1	9.5	15

Table 12. Optimized Formulation of Glass Fiber-reinforced CBC Composite.

CBC, wt%	CA, wt%	SA, wt%	ASC, wt%	Glass fiber, wt%	Water, wt%
65.3	6.5	9.7	3.2	0.7	14.6

Table 13. Bond Strength at the Joints between the Cement Concrete Adherend and CBC Composite or Type I Cement Concrete Adhesives for 7-day-aged Specimens.

Adhesive	Surface of old concrete adherend	Curing temperature, °C	Bond strength, psi	Adhesion failure mode
Composite	Dry	25	26.8	Cohesive failure in aherend
Composite	Wet	25	27.0	Cohesive failure in aherend
Type 1	Dry	25	8.2	Adhesive failure at interfaces
Type 1	Wet	25	9.0	Adhesive failure at interfaces
Composite	Dry	0	18.0	Mix mode of cohesive and adhesive failures
Composite	Icy	0	18.9	Mix mode of cohesive and adhesive failures
Type 1	Dry	0	2.9	Adhesive failure at interfaces
Type 1	Icy	0	*	Adhesive failure at interfaces

* Too weak to be measured.

Table 14. Some Physical Properties of CBC Systems.

Cement system	**Density, g/cc**	**Porosity, %**	**Water permeability, millidarcys**
Ordinary portland cement (OPC)	2.27	38.42	0.92
CBC	2.84	35.68	0.79
ASC-modified CBC	2.88	30.52	0.58
Glass fiber-reinforced CBC composite containing ASC	2.28	33.72	0.59

Table 15. Formulations of Soil Cement Specimens.

Specimen No.	CBC/soil ratio	CBC, wt%	Soil, wt%	ASC, wt%	Water, wt%
1	10/90	8.1	73.2	0.4	18.3
2	20/80	16.5	66.1	0.8	16.5
3	30/70	24.7	57.6	1.2	16.5
4	40/60	32.8	49.2	1.6	16.4

Table 16. Compressive Strength of Soil Cement Specimens after Curing for 24 hours at 25°C.

CBC/soil ratio	Compressive strength, psi
10/90	8
20/80	28
30/70	52
40/60	165

Table 17. Formulations of Lightweight CBC Concrete Slurries.

Specimen No.	CBC, wt%	EX microsphere, wt%	Water, wt%
L-1	81.1	0.0	18.9
L-2	59.3	19.8	20.9
L-3	47.6	28.5	23.9
L-4	34.6	34.6	30.8
L-5	23.8	39.7	36.5
L-6	18.2	54.5	27.3

Table 18. Dry Density and Compressive Strength of the 3-day-aged Lightweight CBC Concrete Specimens.

Specimen No.	Dry density, g/cc	Compressive strength, psi
L-1	1.87	2100
L-2	1.33	613
L-3	1.15	158
L-4	0.96	37
L-5	0.78	4
L-6	0.70	*

* Too weak to be measured.

Table 19. Formulation of BA-based CBC Composite Used in a Full-scale Field Demonstration.

Ingredient of CBC, wt%				**Other ingredients, wt%**				
BA	CAC	Type I	NaP	CA	SA	Glass fiber	ASC	Water
36.0	18.9	4.6	5.9	6.5	9.7	0.7	3.2	14.6

Figure 1. Boiler ash waste generated from KeySpan power pant.

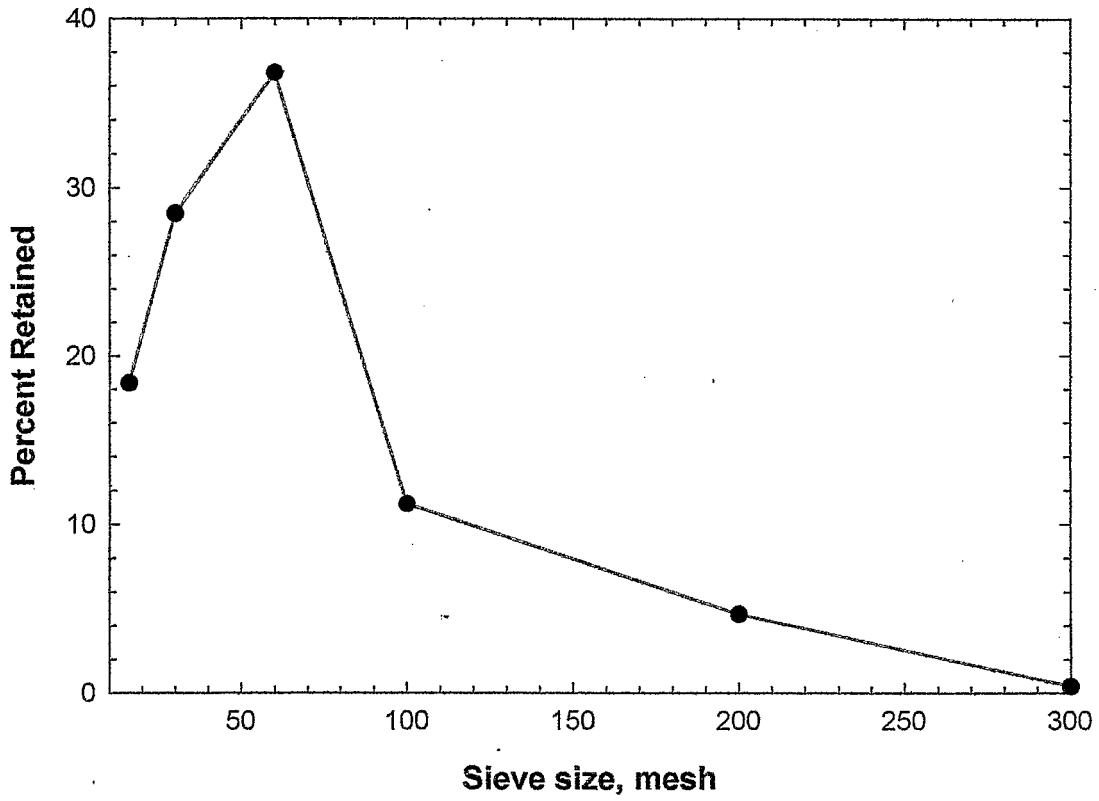


Figure 2. Sieve size analysis of crushed BA powders.

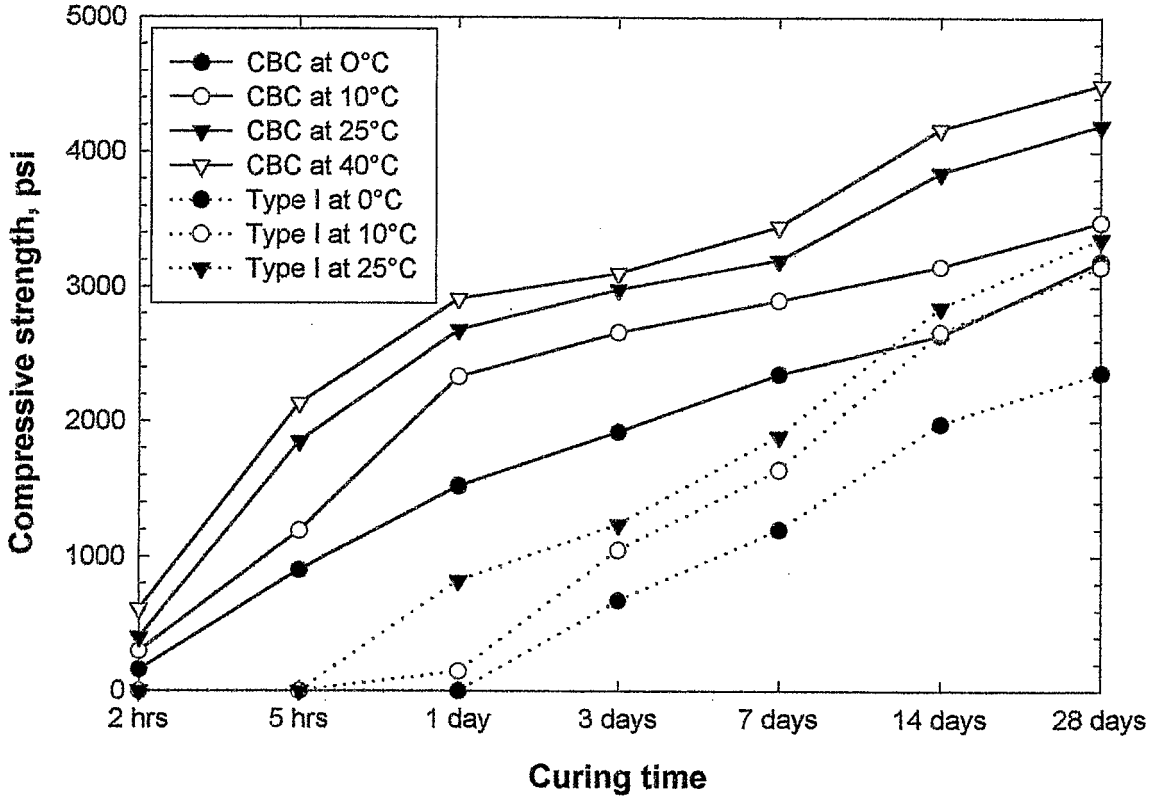


Figure 3. Comparison of the changes in compressive strength of CBC and commercial Type 1 cement specimens as a function of curing time at temperatures of 0°, 10°, 25°, and 40°C.

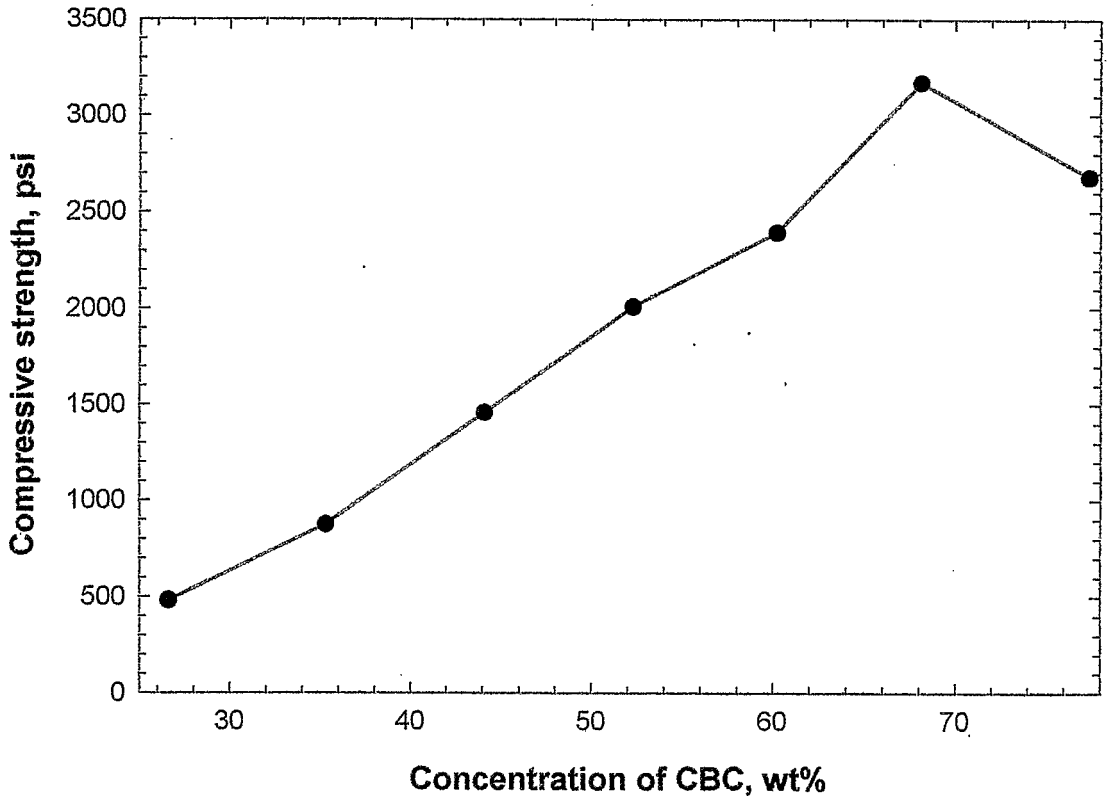


Figure 4. Changes in compressive strength of 25°C-24-hour-cured concrete specimens as a function of CBC content.

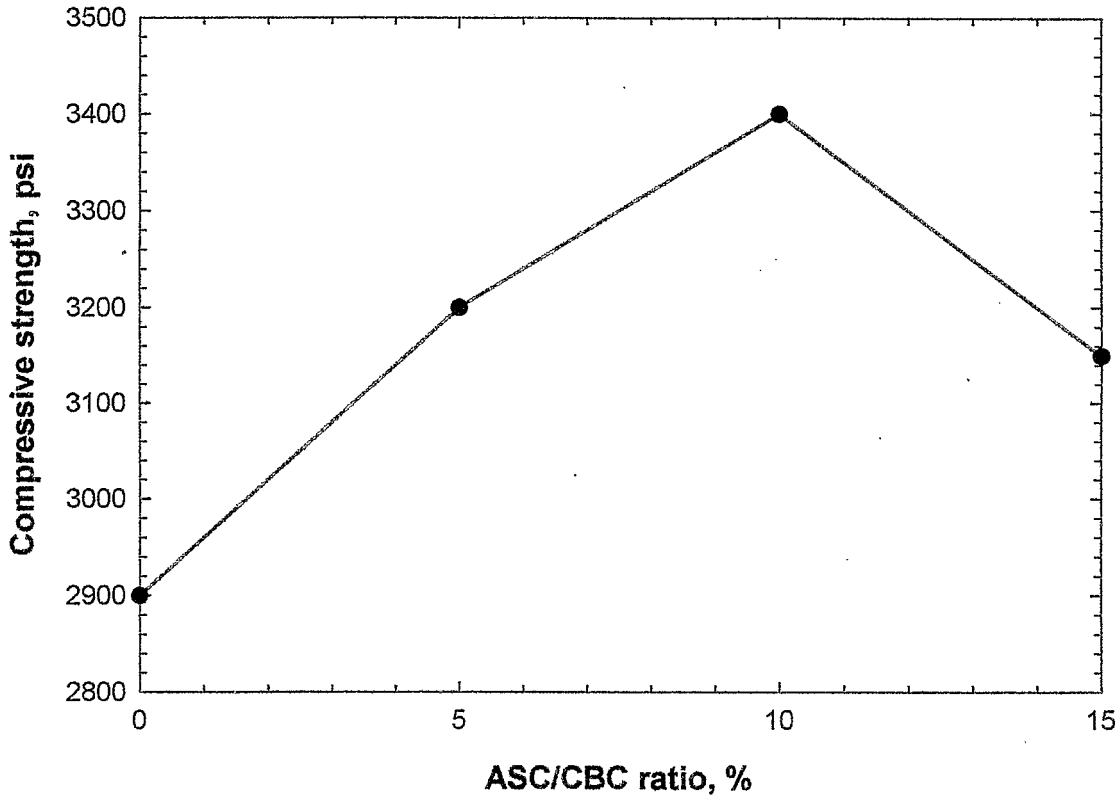


Figure 5. Changes in compressive strength of the ASC-modified CBC specimens at 25°C-24-hour-curing age as a function of ASC/CBC ratio.

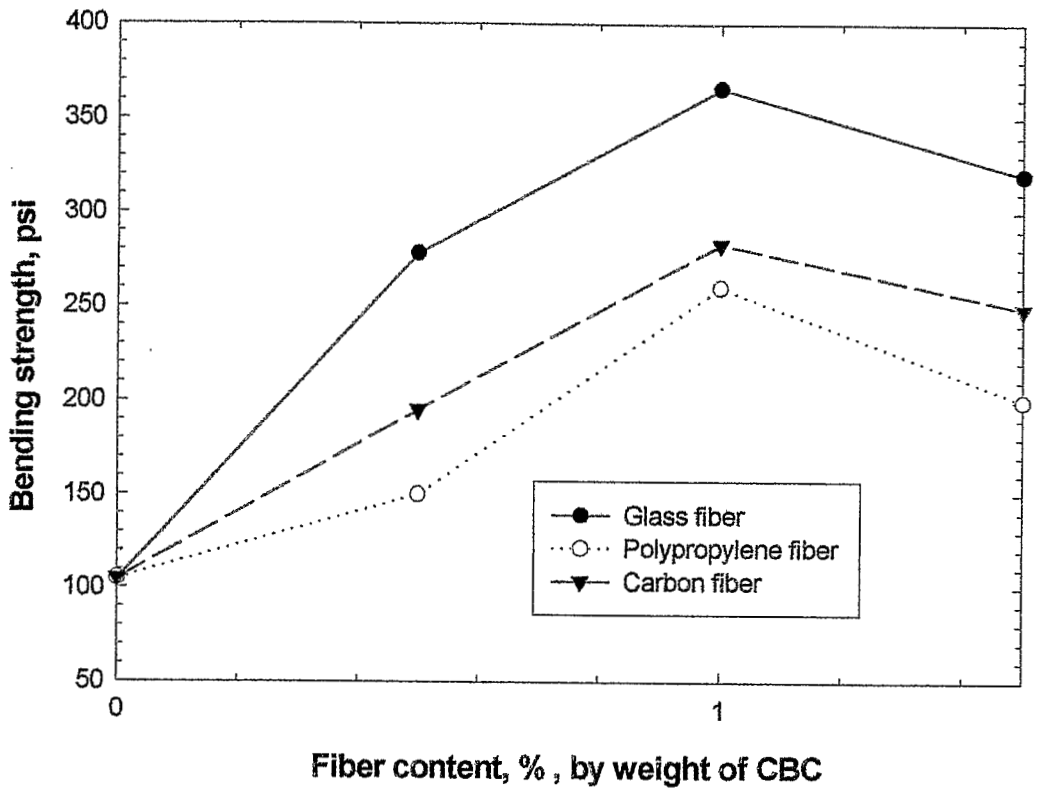


Figure 6. Bending strengths of CBC composites reinforced with various fibrous materials after 24 hours at 25°C.

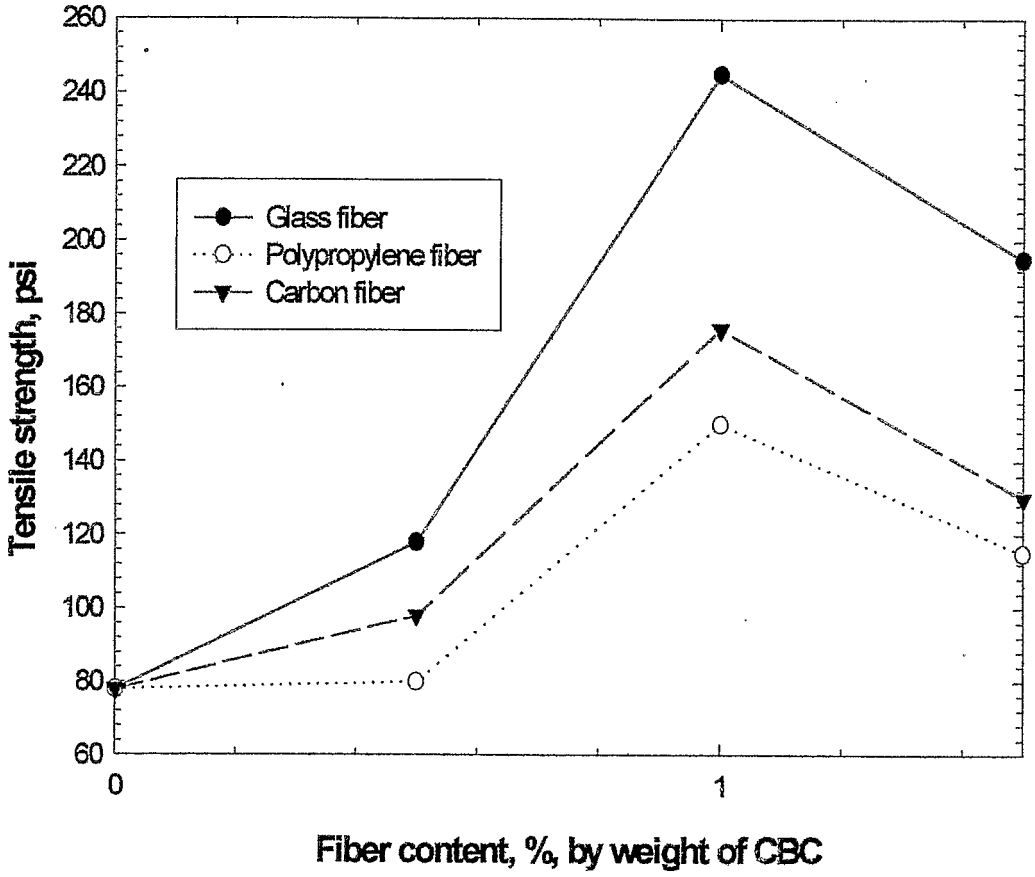


Figure 7. Tensile strength of CBC composites reinforced with various fibrous materials after 24 hours curing at 25°C.

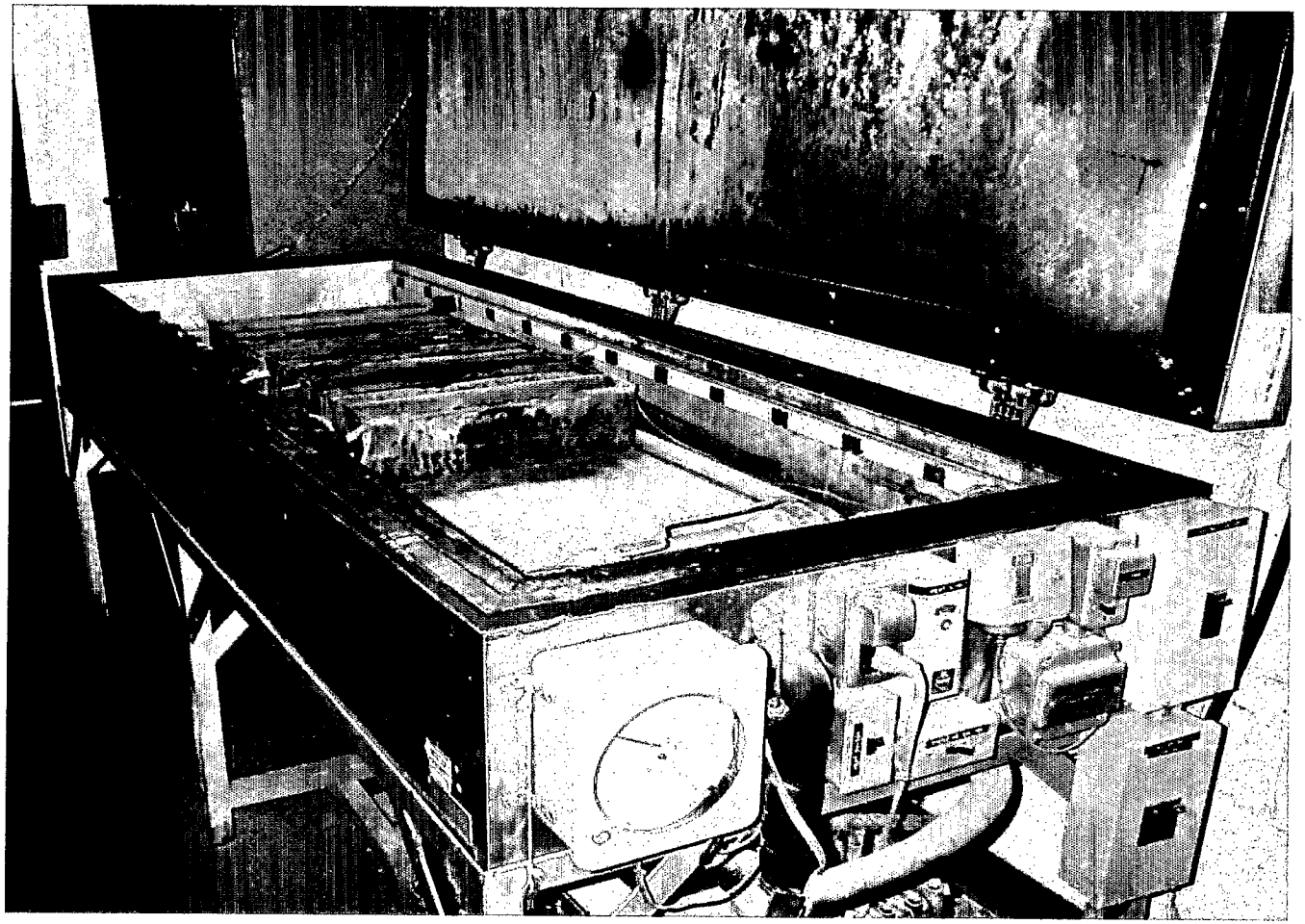


Figure 8. The rapid freezing and thawing cycle apparatus.

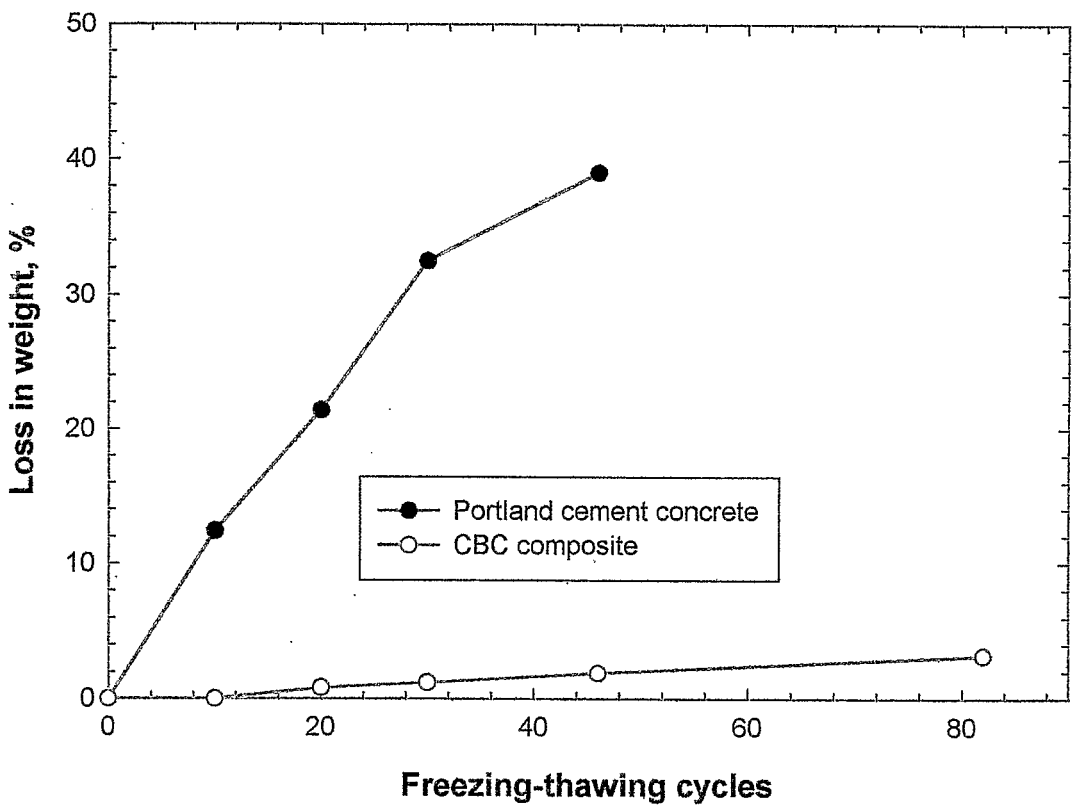


Figure 9. Loss in weight of conventional portland cement concrete and CBC composite specimens as a function of freezing-thawing cycles.

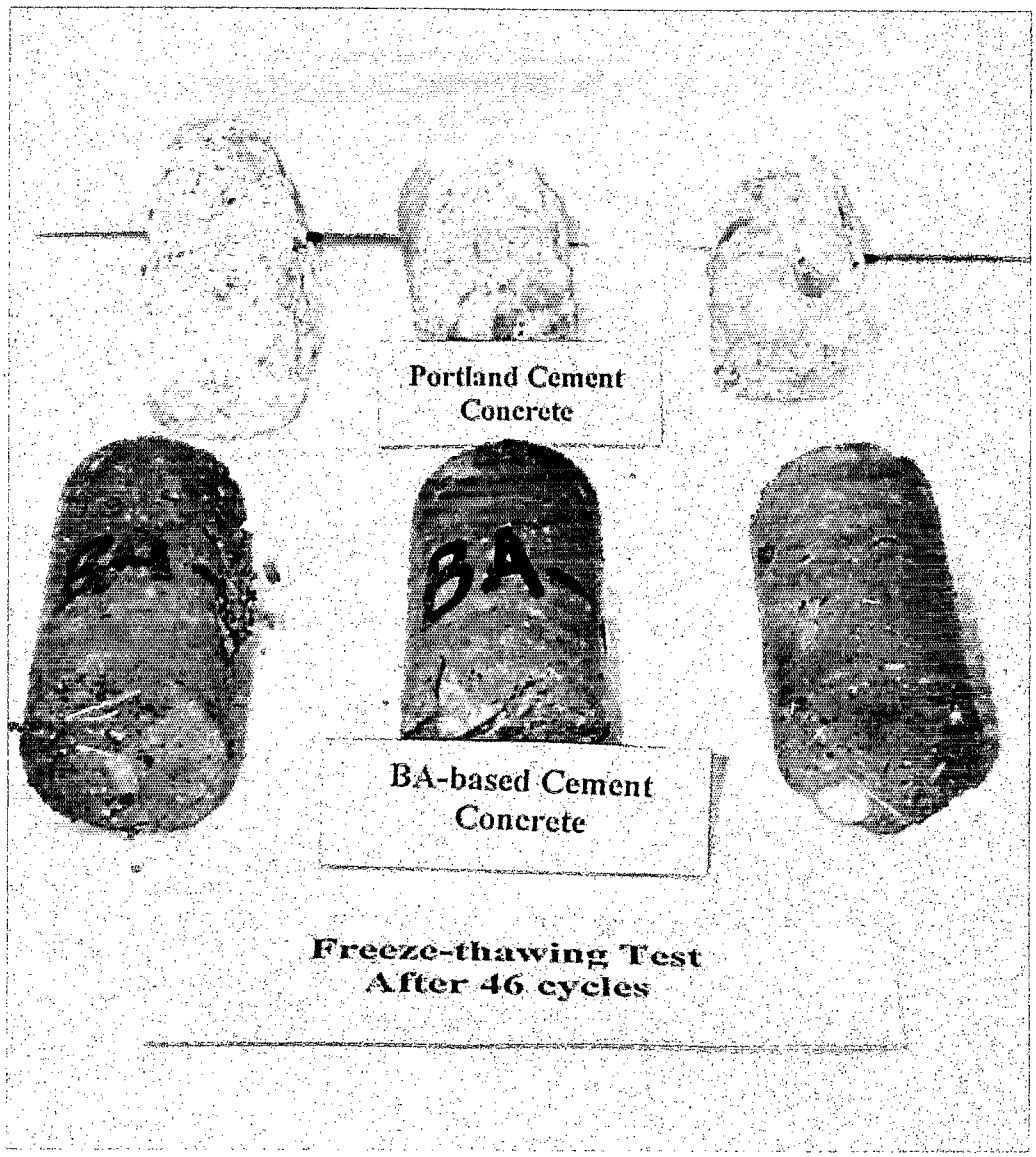


Figure 10. Appearance of CBC composite specimens and conventional portland cement concrete specimens after 46 cycles in freezing and thawing chamber.

Figure 11. Linear dry shrinkage measurement apparatus.

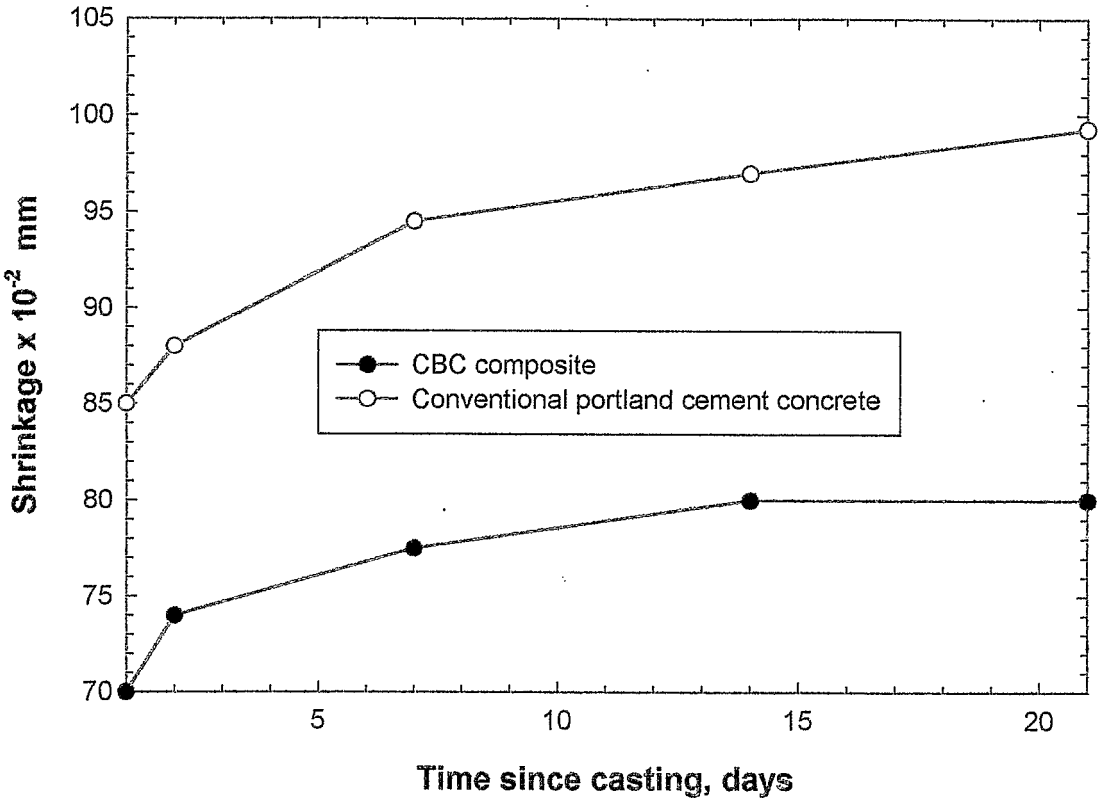


Figure 12. Shrinkage of CBC composites and conventional portland cement concrete specimens as a function of time after casting.

Figure 13. Steel bars removed from CBC composite and conventional portland cement concrete after immersion for three months in 90°C brine.

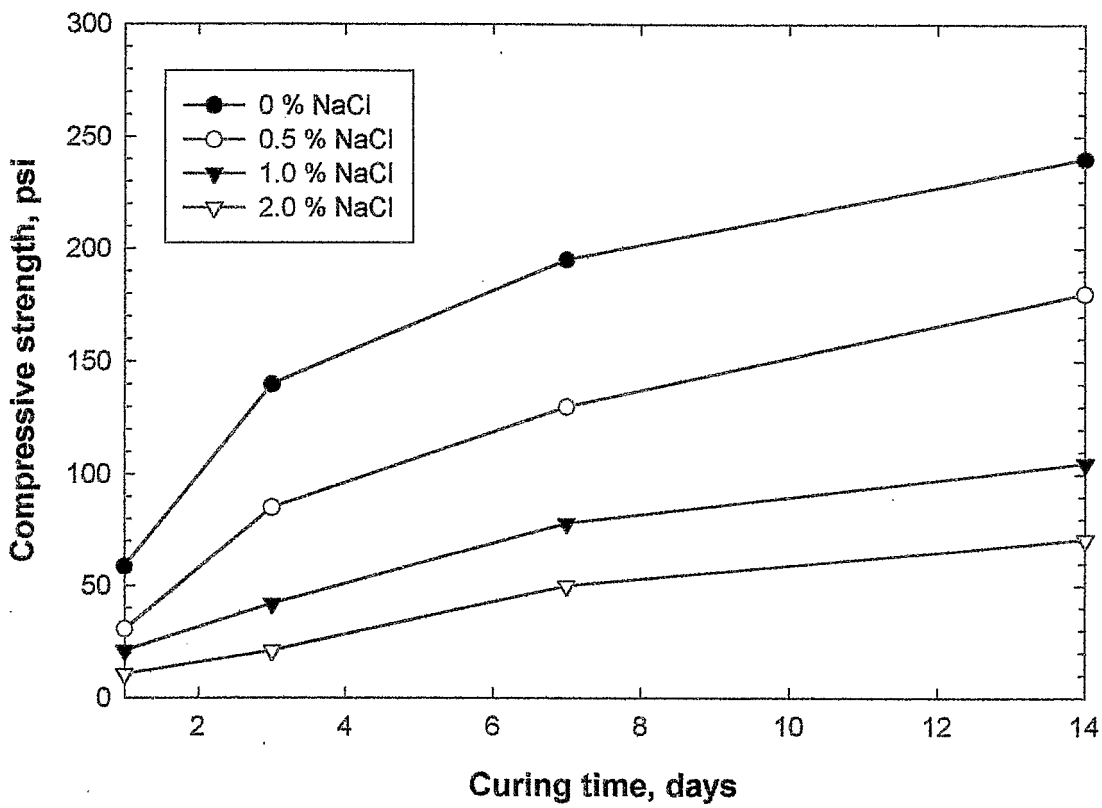


Figure 14. Changes in compressive strength of NaCl-contaminated cementitious backfill specimens made at 30/70 CBC/soil ratio as a function of curing time.

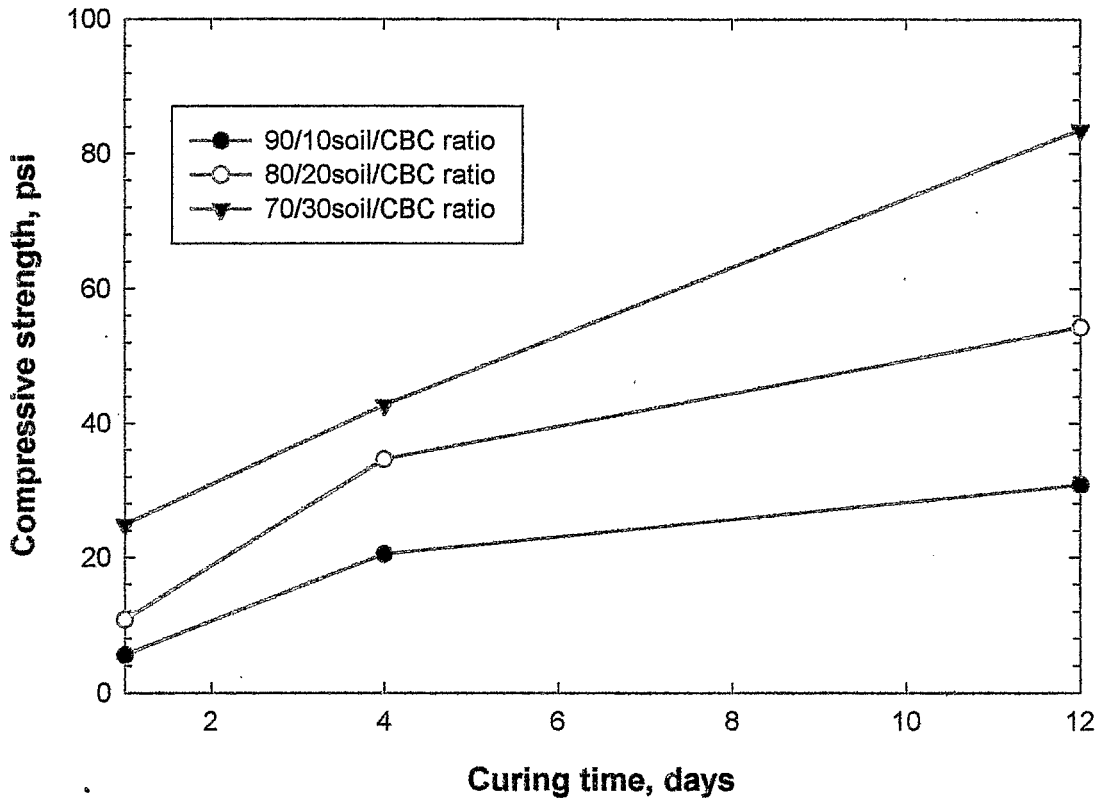


Figure 15. Changes in compressive strength of backfill underlayments as a function of curing time at room temperature.

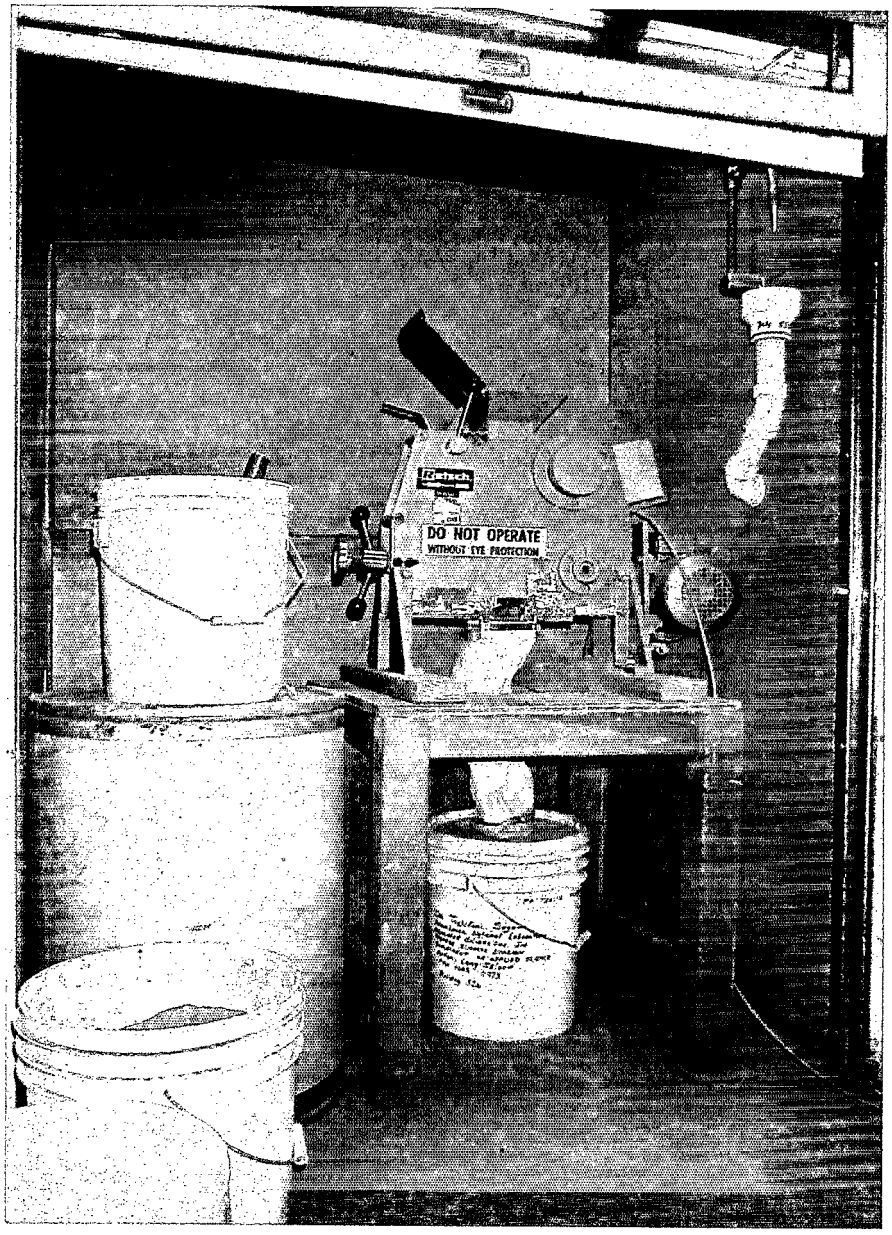


Figure 16. Crusher system redesigned to meet the 0 % emission policy at BNL.

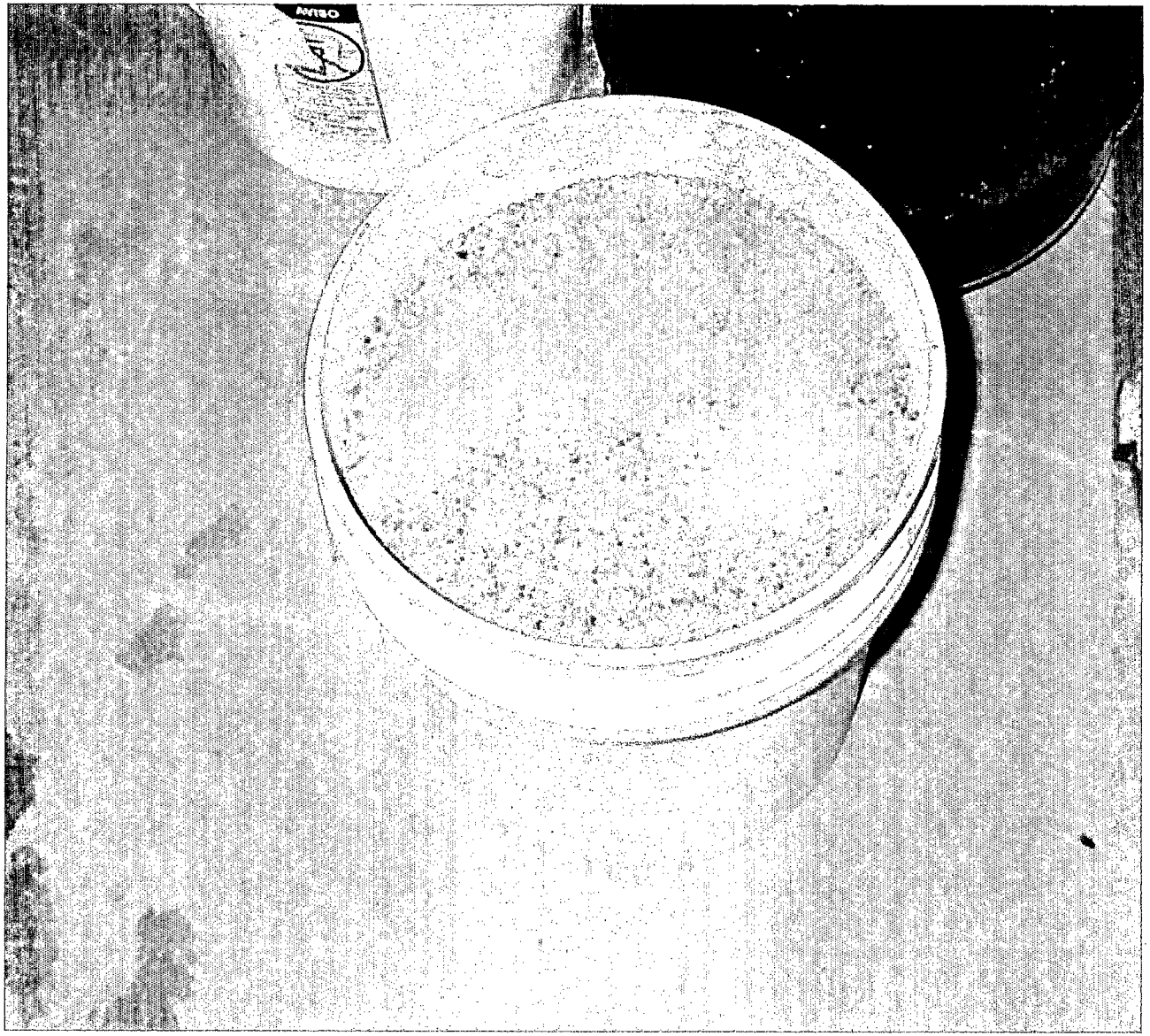


Figure 17. Crushed boiler ash (BA).

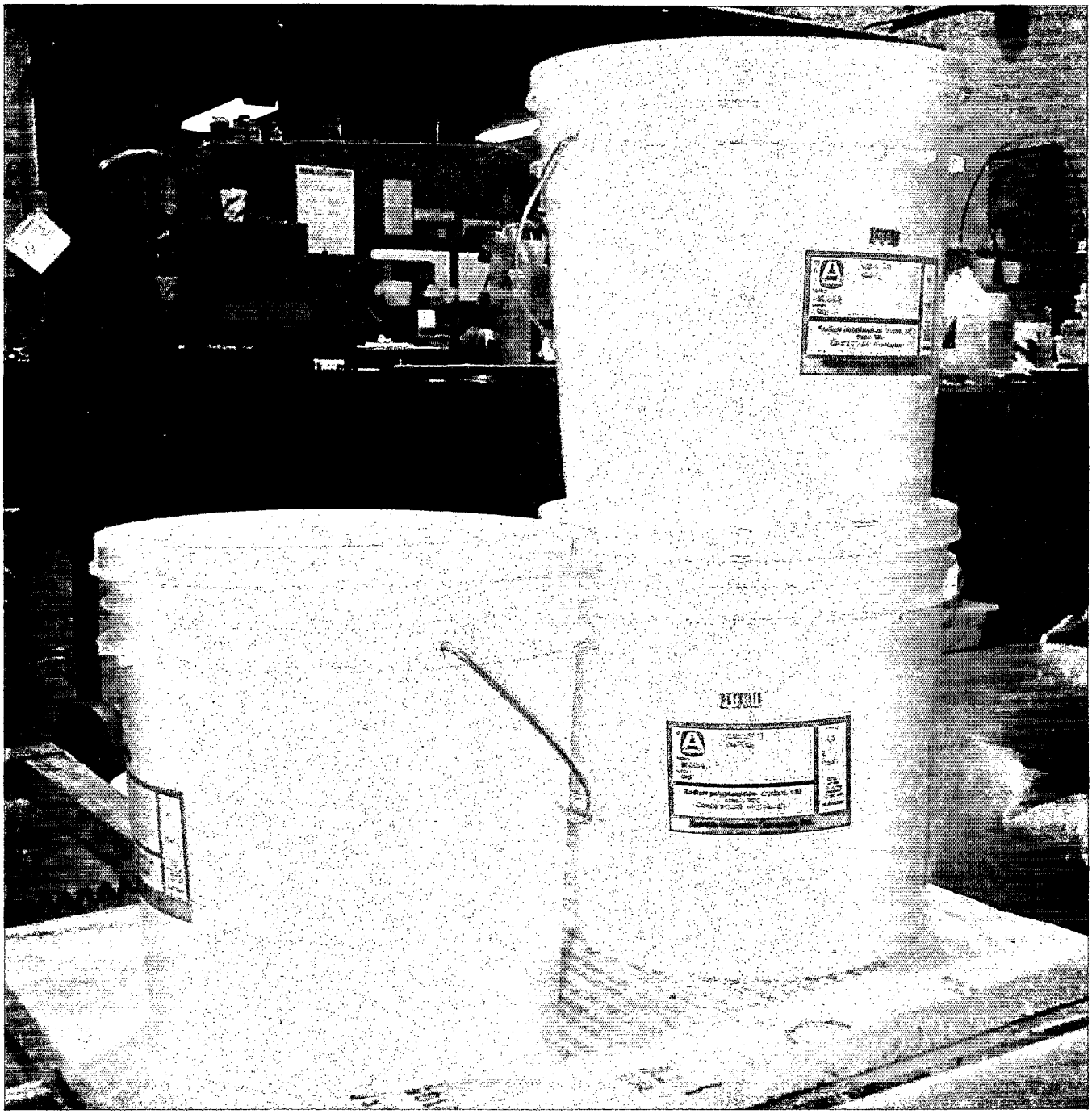


Figure 18. Sodium polyphosphate granular in 5 kg plastic containers.

Figure 19. Additives: # 51 calcium aluminate cement (Right); and type 1 portlant cement (Left).

Figure 20. Coarse silica aggregate.

Figure 21. Weight measurement for all ingredients.

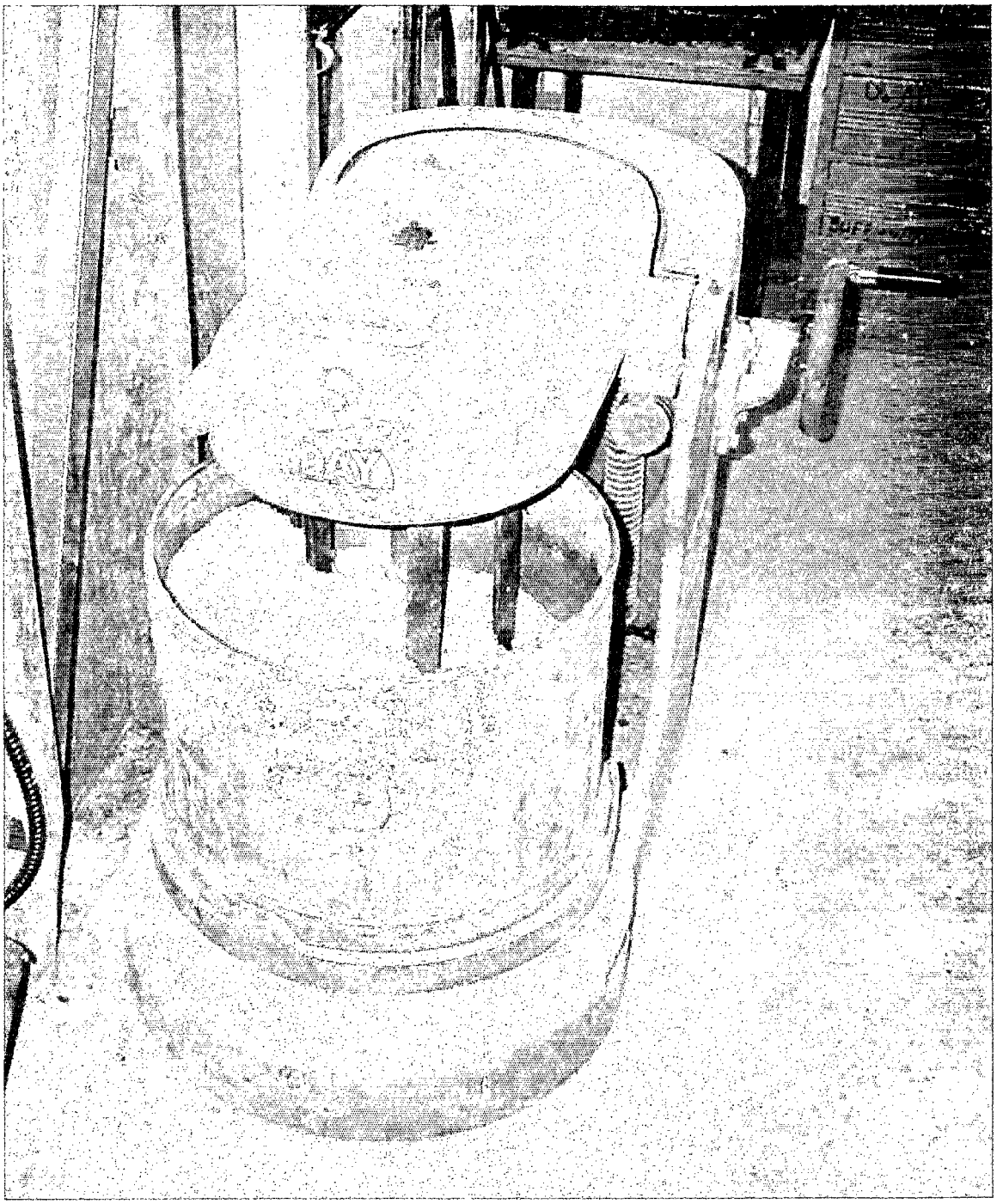


Figure 22. Preparation of dry cement composite mixture in concrete blender.

Figure 23. Dry cement composite packages containing BA, CAC, type 1 cement, NaP, sand and coarse aggregate.

Figure 24. Incorporation of dry cement composite into the mixer containing water and glass fibers.

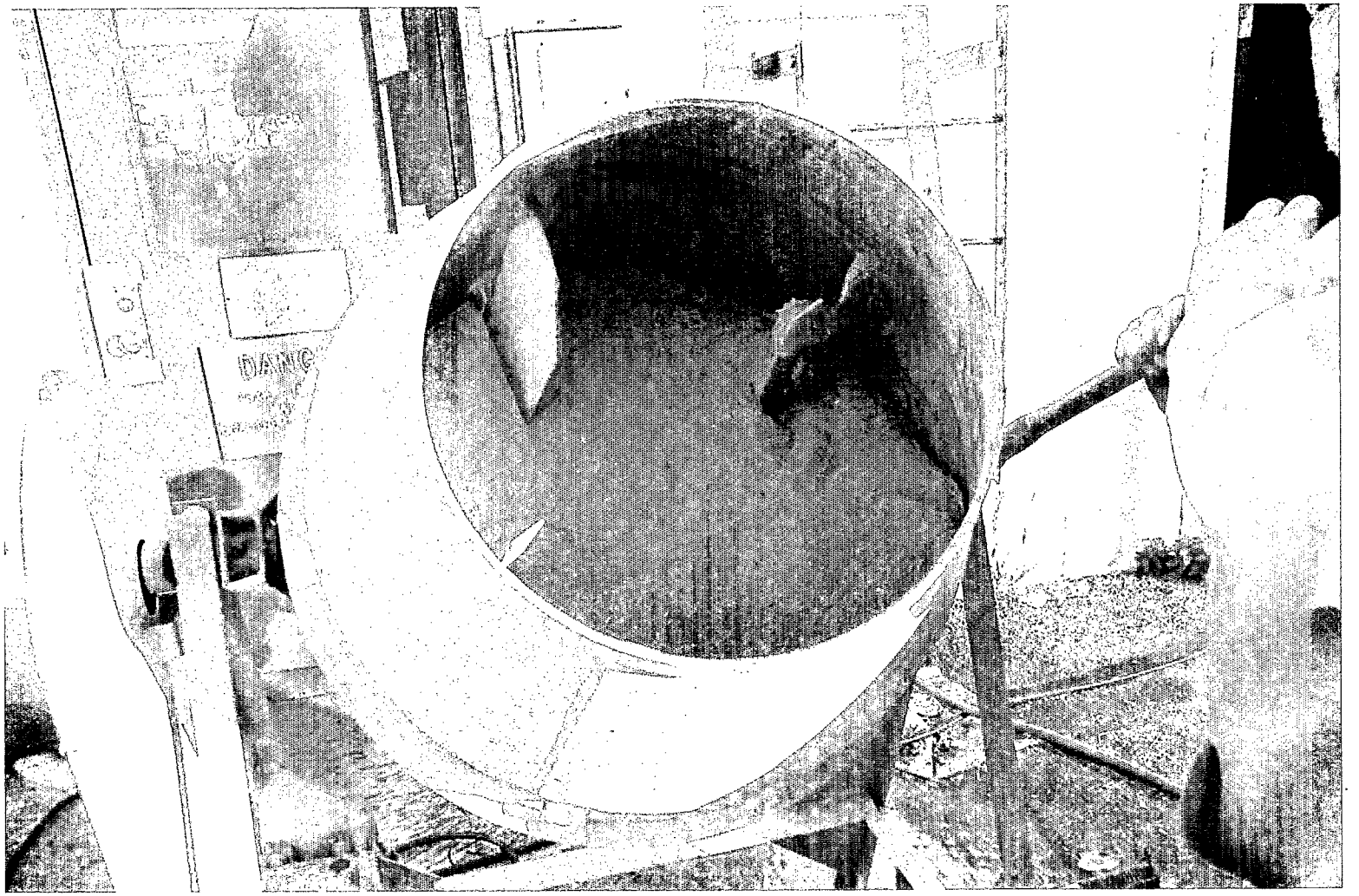


Figure 25. Cement composite slurry after ~ 5 min mixing.

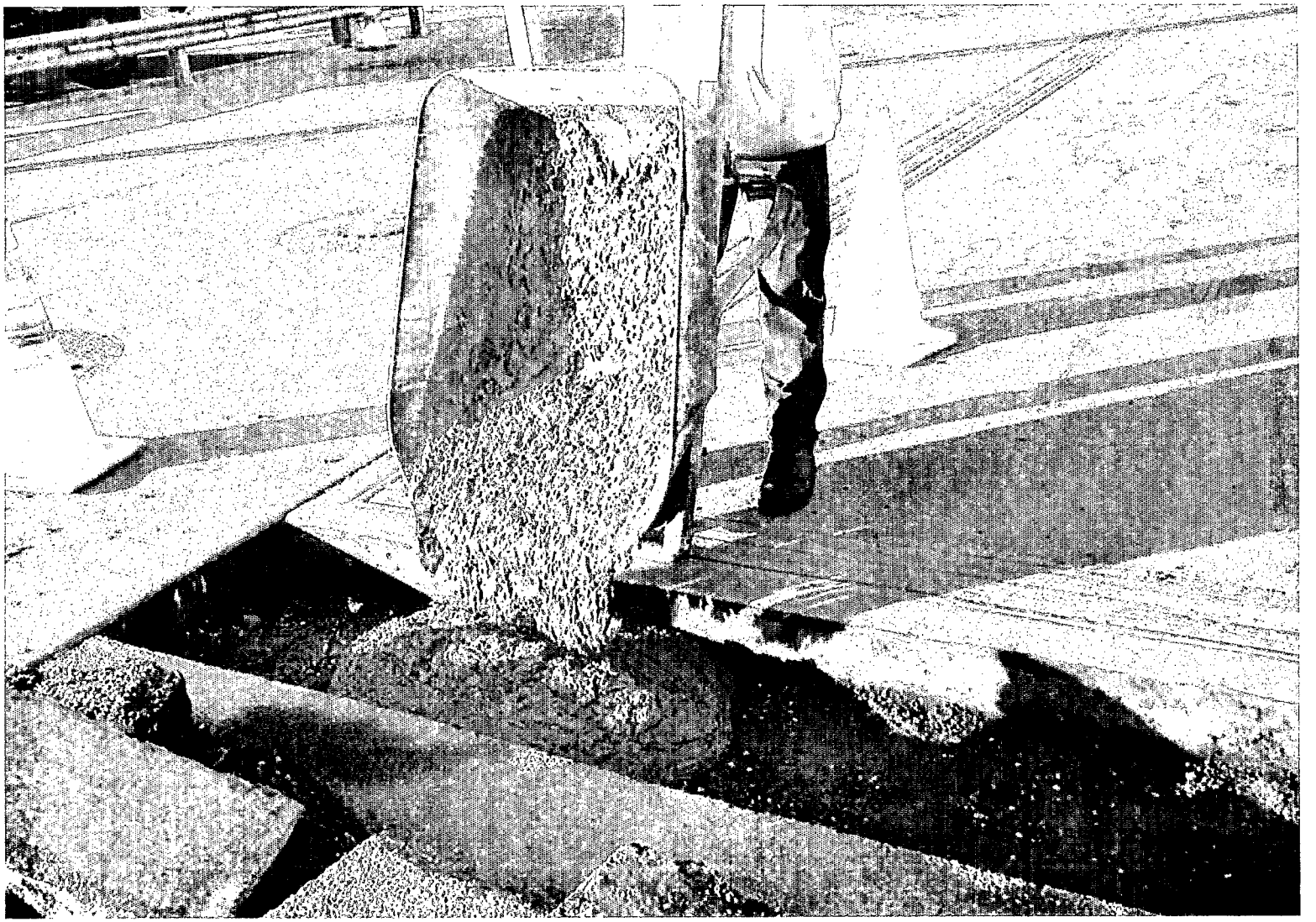


Figure 26. Pouring composite slurry into the pit.

Figure 27. Self-leveling characteristic of slurry.

Figure 28. Cured composite surfaces at about 90 min after its placement.

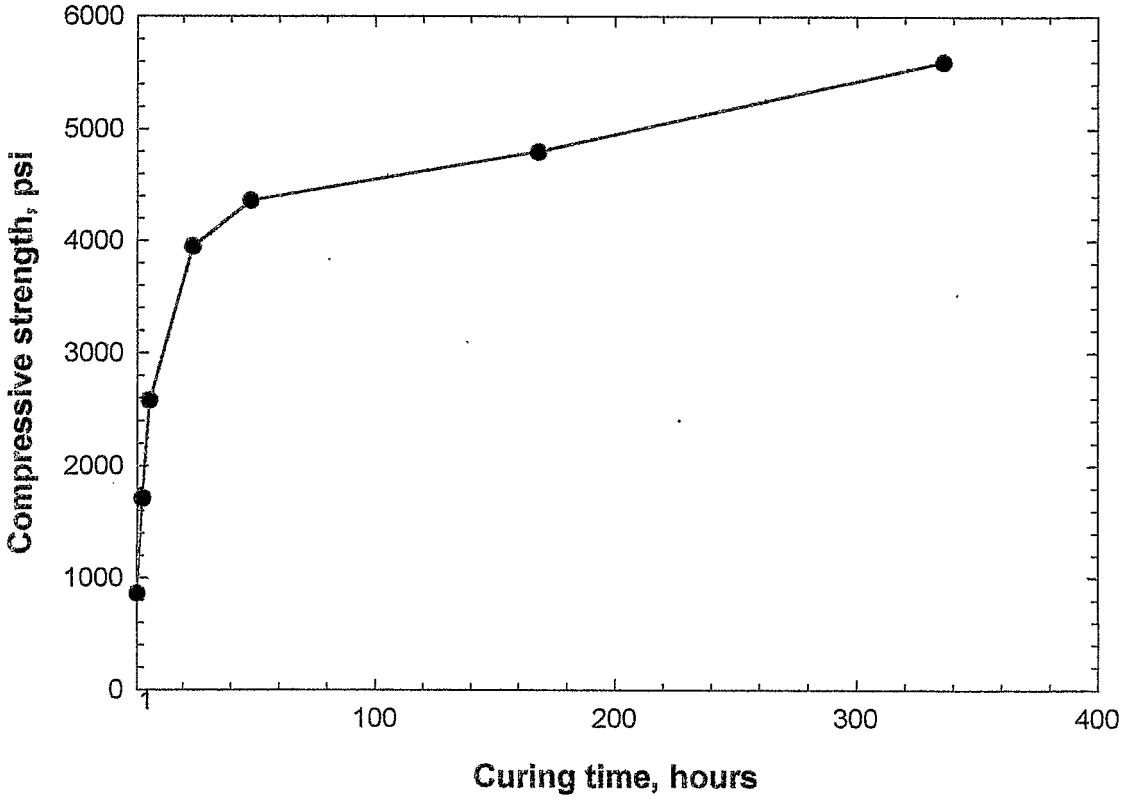


Figure 29. Changes in compressive strength of CBA composite specimens as a function of curing time after placement.

Appendix: Program Expenditure

The total completion cost of this program for the period of August 1999 through July 2001 was $150,000. A month by month graphical representation of this program's expenditure is present in Figure 30.

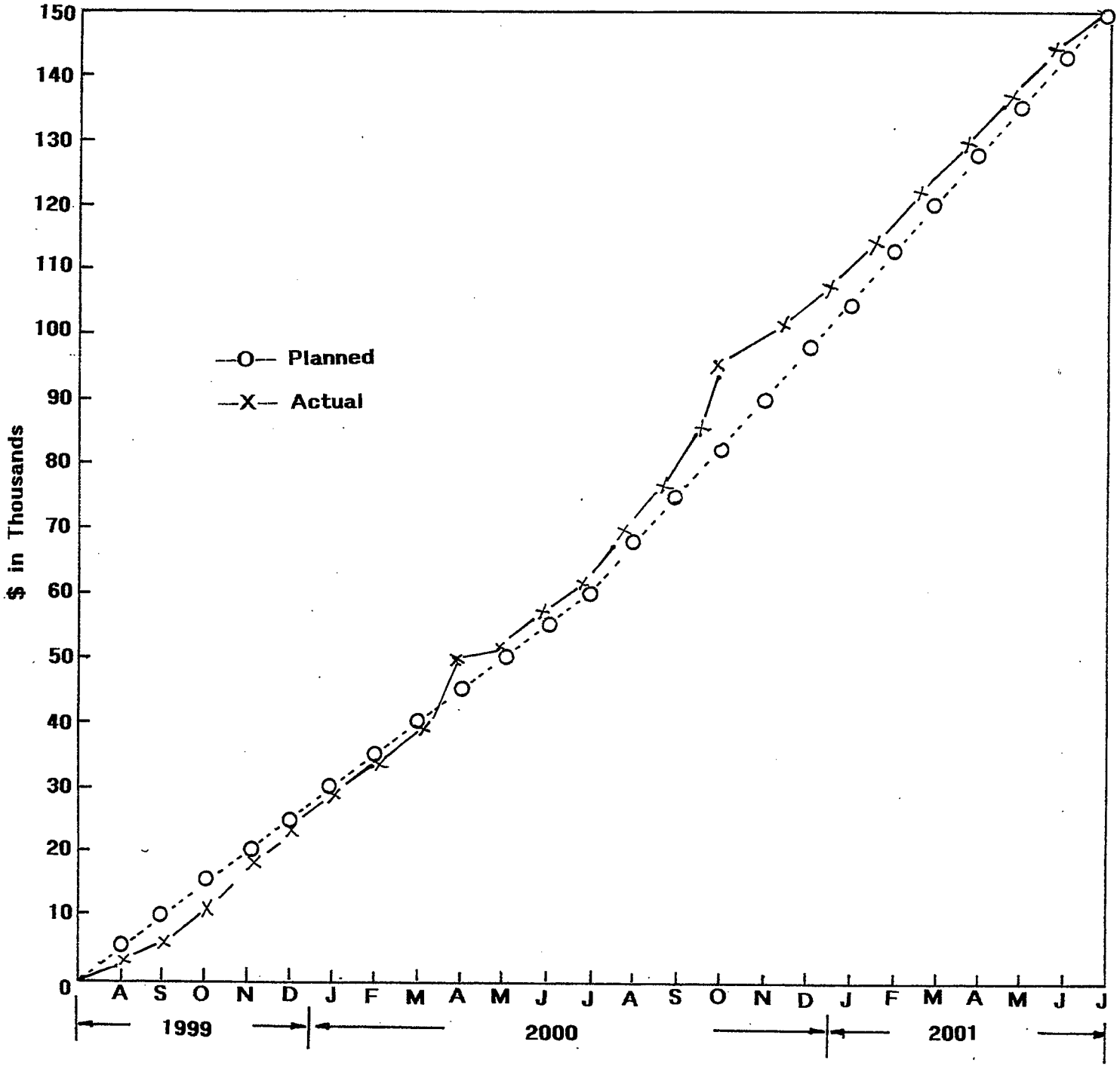


Figure 30. Rate of Spending for 1999, 2000, and 2001