A STUDY OF THE FEASIBILITY OF BINDING UP INDUSTRIAL WASTE WATERS IN A POZZOLANIC CEMENT FOR USE AS A POSSIBLE METHOD OF WASTE TREATMENT

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ABSTRACT

A treatment method of general applicability to aqueous wastes and of especial interest for complex, aqueous based, industrial waste liquids and sludges has been studied. A series of hydraulic cement mixes have been utilized to bind up the waste waters in a solid, insoluble form. The method has been applied to three waste waters: a spent steel pickling liquor containing ferrous sulfate and sulfuric acid, and two aqueous wastes from a petrochemical plant, each containing chlorinated hydrocarbons, phenolics and sludge material. Tap water was used as a control.

The cement mixes studied were 1:3 and 1:9 portland cement - fly ash, and 1:3 and 1:9 hydrated lime - fly ash. A 100 per cent fly ash mix, not a hydraulic cement by itself, was studied for comparison purposes. Pastes of dry, normal, and fluid consistencies (with flow values of roughly 50, 100 and 150

respectively) were prepared from each mix. The compressive strength of the portland cement - fly ash pastes were determined after 7 or 14 days, 28 days, 3 months and 5 months curing time. The strength of the fly ash and the hydrated lime - fly ash pastes were determined at 28 days, 3 months and 5 months. At these times the leaching characteristics of the waste substance from the hardened paste was determined by distilled water circulation.

A less complete study of this treatment procedure relative to three waste sludges was also performed.

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1. INTRODUCTION

Cementitious materials have been used for approximately thirty years to bind up radioactive wastes in a bulk, insoluble form. Generally, the waste material has been bound up or contained in a dense concrete. Depending on the activity of the waste and its solubility in ground water, this concrete mass would be buried in the ground or else contained in some impervious material such as dense rock or metal.(1)

A logical progression from this procedure would be to use a cement to bind up non-radioactive wastes if this were shown to be technically and economically feasible. Sewage can be adequately treated, generally by the action of bacteria in various processes such as activated sludges, percolating filters or land treatment.(2) Industrial wastes, on the other hand, are often difficult and/or relatively expensive to treat. This is mainly due to the wide variety of wastes which occur, some of which are relatively innocuous while others may be very corrosive or poisonous.

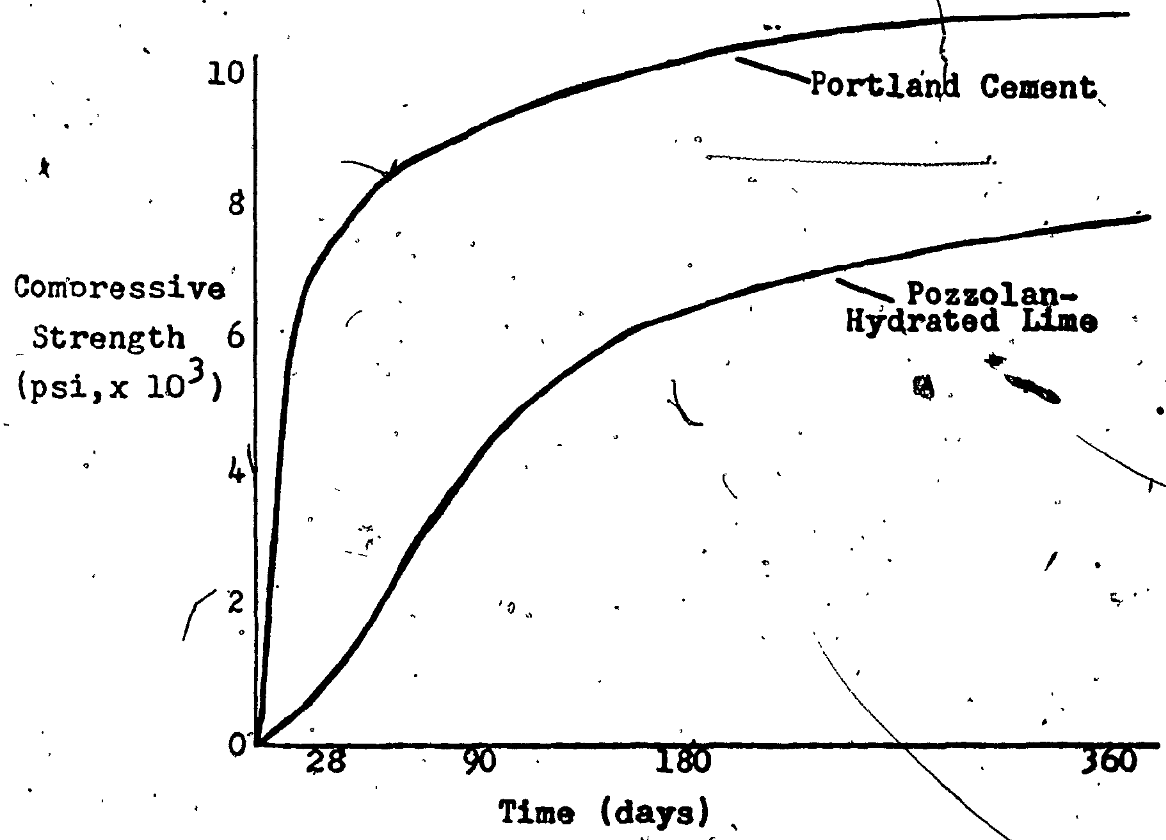
A high proportion of industrial wastes are water-carried, and would thereby lend themselves to combination with a hydraulic cement which requires water for the setting process to occur. Portland cement is a hydraulic cement and has the qualities of quick setting, early development of high strength, low permeability to water and easy availability in bulk quantities. However it is relatively expensive. In addition, the quick setting and high early strength characteristics which are so desirable in construction work could be an impediment when dealing with large volumes of the cement-waste water mix.

Pozzolans are an alternative to portland cement. These materials will combine with calcium hydroxide in the presence of water to yield a cementitious product. They set at a significantly slower rate than portland cement. The setting characteristics of the two cements are given in Figure 1.

Fly ash, the fine, incombustible ash from the combustion of coal in power stations, is the most commonly-used pozzolan in North America. It has fairly widespread availability and is produced in great quantities (over 24 million tons in North America in 1965). Of this, only 10 per cent was constructively utilized, the rest being disposed of in some fashion.(3) Being a waste product it is a very low-cost material. In addition, the possibility of using one waste to treat another one is naturally attractive. Since portland

Figure 1

Strength-Time Relationships of a Portland Cement Paste and a Pozzolan-Hydrated Lime Paste



cement, upon setting, liberates calcium hydroxide as a result of the hydration of the cementitious compounds present, fly ash could be combined with either portland cement or with hydrated lime (calcium hydroxide) to form the cementing mix.

1.1 Pozzolanic Materials.

Pozzolans can be defined as materials which, although they do not possess cementing properties in themselves, contain constituents which will combine with calcium hydroxide at ordinary temperatures in the presence of water to form stable, insoluble compounds possessing cementing properties.(4) The pozzolans can be divided into two groups, natural and artificial. Natural pozzolans are mostly materials of volcanic origin, but certain diatomaceous earths may also be included. Artificial pozzolans are mainly products of heat treatment (of the order of 500°C) of clays, shales and certain silicious rocks, and fly ash. Pozzolans in general contain a high percentage of amorphous material in which the content of silica plus alumina is at least 60 per cent.(5)

Pozzolans have been used in mortars since the time of the ancient Greeks and Romans and are still used extensively in Europe in mortars and concrete. They are not in common use in North America since portland cement is easily available and is a much superior construction material. However, when used in combination with portland cement in concrete pozzolans can offer certain advantages. Some of these are increased resistance to certain aggressive waters such as acid ground waters, sulfate waters and sea water, lowered heat evolution, higher impermeability in lean mixes, and inhibition of expansion due to reaction between the alkalis present in the cement and certain alkali-sensitive aggregate.(6)

As mentioned previously, fly ash is the most commonly-used pozzolan in North America due to its low cost and widespread availability. Its properties as a pozzolan were first investigated by Davis and co-workers in 1937.(7) The composition and properties of fly ash depend both on the type of coal burnt and the efficiency of the combustion process. Thus the utility of the material obtained from different power stations can vary widely.

The ash is a very finely-divided material with a specific surface in the range of 2000 - 5000 cm^2/g as determined by the air permeability method. This is the same degree of fineness as portland cement.

Its major component is glass, with quartz, mullite, hematite and magnetite as the more important crystalline components. The glass consists of silica and alumina with some iron oxide, lime, alkalis, and magnesia. Combustible material is always present, but in well burnt materials it is below 10 percent and often below 3 percent.(8) An analysis of what could be considered as a typical fly ash is given in Table 1.(9)

The glass is the active material, as in the case of other pozzolans. The value of a fly ash as a pozzolan therefore depends on the glass content, as well as the fineness and composition. There is, however, no close correlation between these parameters and their contribution to strength development. This is another reason why they are rarely used as cement in combination with only hydrated lime. Significant strength, for example 75 percent of the ultimate strength, is not developed before 3-6 months ageing, and this strength can not be predicted beforehand.

The nature of the reaction between pozzolans and calcium hydroxide is not yet well understood, but it appears to consist mainly of combination of the $Ca(OH)_2$ with the silica and alumina of the glass. The reaction products vary somewhat depending on the

Table 1

Analysis of an Ontario Hydro Fly Ash

Component	Percent by weight
Silicon dioxide	44.2
Iron oxide	23.0
Aluminum oxide	19.2
Titanium oxide	0.82
Calcium oxide	1.89
Magnesium oxide	0.89
Alkalis	2.53
Sulphur trioxide	1.05
Loss on ignition	4.62
	98.2

pozzolan and the temperature. At 20°C with burnt kaolin and calcium hydroxide the main products are gehlenite hydrate $2CaO.Al_2O_3.SiO_2\cdot aq$,* a hydrated calcium silicate $3CaO.2SiO_2\cdot aq$ and hydrated tetracalcium aluminate $4CaO.Al_2O_3\cdot aq$.(10) The products from the reaction between fly ash and calcium hydroxide are mainly a hydrated calcium silicate of the general composition $CaO.SiO_2\cdot aq$ and hydrated tetracalcium aluminate.(11) X-ray diffraction data from pozzolan-portland cement pastes indicate the presence of a calcium silicate hydrate of the tobermorite type. Also present are ettringite: $3CaO.Al_2O_3.3CaSO_4.32H_2O$ and hydrated tetracalcium aluminate.

1.2 Portland Cement

Portland cement may be defined as a product obtained by intimately mixing together calcium-containing and clay-containing, or other silica-, alumina-, and iron oxide-bearing materials, burning

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*This notation is used only to show the constituent oxides which make up these compounds. It is not meant to indicate that these oxides have separate existence within these compounds.

them at a clinkering temperature, and grinding the resulting clinker. A typical analysis is given in Table 2 on the next page.(13)

The clinkering temperature is in the range 1300 to 1450°C. The resultant cementitious compounds which are formed are tricalcium silicate: $3CaO.SiO_2$, β-dicalcium silicate, tricalcium aluminate: $3CaO.Al_2O_3$, and a ferrite phase of average composition: $4CaO.Al_2O_3.Fe_2O_3$.(14) From the analysis given in Table 2, the distribution of these compounds in the cement would be calculated to be:

$3CaO.SiO_2$	42 percent
$2CaO.SiO_2$	34 percent
$3CaO.Al_2O_3$	6.7 percent
$4CaO.Al_2O_3.Fe_2O_3$	9.5 percent
	92 percent

These values are obtained by the Bogue calculation, which gives good agreement with the average of analyses by classical methods, x-ray crystallography, and gravimetric or differential thermal analysis.(15)

Portland cement sets by the hydration of these compounds. The two calcium silicates constitute about 75 percent by weight of portland cement and make the major contribution to the strength of hardened cement. Of the two, tricalcium silicate has the dominant effect,

Table 2

Typical Analysis of Ordinary Portland Cement

Component	Percent by weight
CaO	64.1
SiO_2	22.9
Al_2O_3	4.5
Fe_2O_3	3.1
MgO	0.79
TiO_2	0.24
Na_2O	0.54
K_2O	0.64
SO_3	2.37
Loss by difference	0.8
	100.0

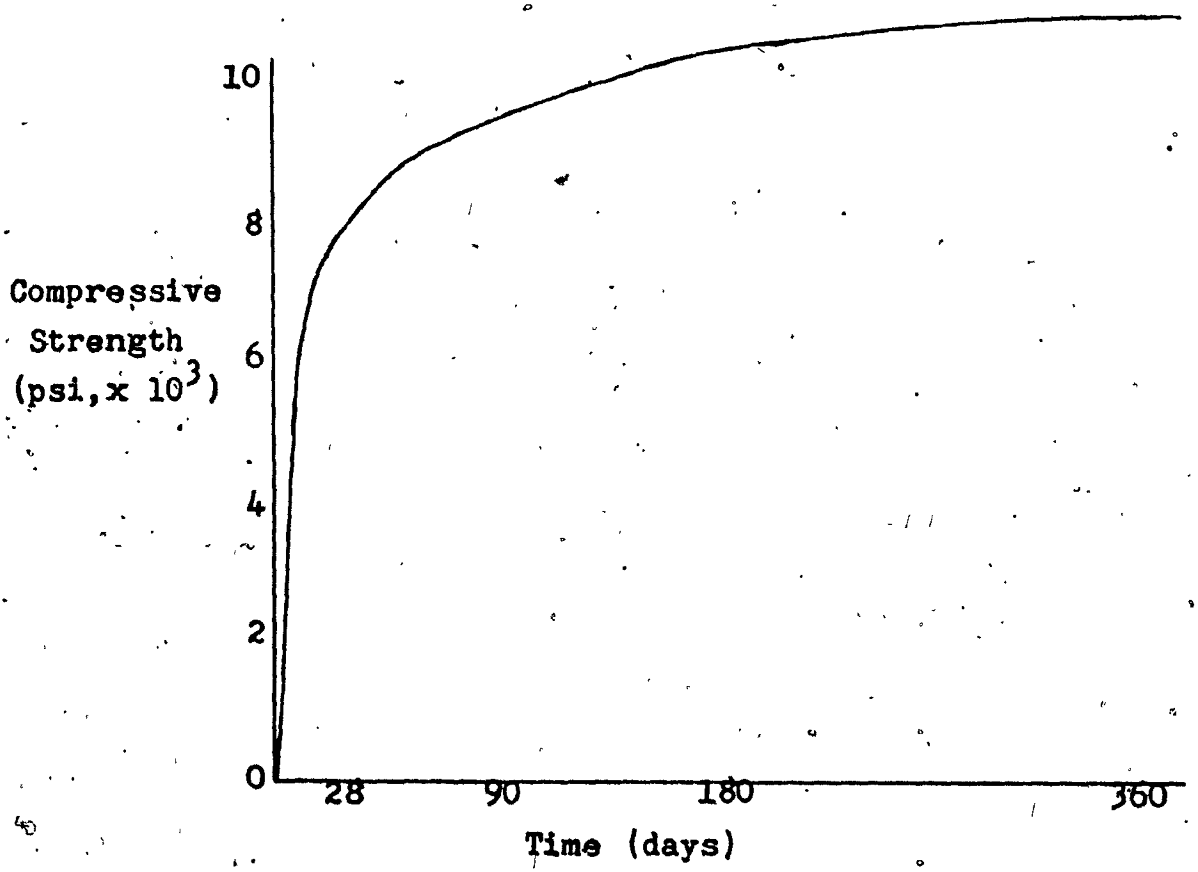
contributing almost all of the strength in the first month. β-Dicalcium silicate, hydrating more slowly, begins to make a significant contribution after that period. Both compounds produce similar calcium silicate hydrates approximating the composition $3CaO.SiO_2 \cdot 3H_2O$. Because of its similarity to the natural mineral tobermorite, and because of its gel-like properties, this product is called tobermorite gel. This tobermorite gel provides the main cementing action of portland cement.(16)

Due to the rapid hydration of the tricalcium silicate, neat portland cement paste quickly develops high strength, of the order of 5000-6000 psi within 3 days. Final strengths in excess of 10,000 psi are attainable for pastes of normal consistency, that is ones with a water-to-cement ratio (w/c) of 0.3 to 0.4. The strength-time relationship of such a paste is shown in Figure 2.(17)

During a short period, beginning with the gauging of the cement with water and during the time of mechanical stirring or kneading, relatively rapid chemical reactions occur consisting mainly of the hydration of the tricalcium aluminate and tricalcium silicate, but especially of the former. Within five minutes the

Figure 2

Strength-Time Relationship of a Portland Cement Paste of Normal Consistency



reaction rate subsides to a low level. This is due to the insoluble product from the reaction between the tricalcium aluminate hydrate and the added retarder gypsum ($CaSO_4 \cdot 2H_2O$) which coats the cement grains and inhibits hydration. There is subsequently a dormant period of between 40 to 120 minutes during which the paste normally remains plastic. At this time, the paste behaves like a porous, permeable solid with a coefficient of permeability of the order of 10^{-4} cm/sec. (18)

At the end of the dormant period, a second period sets in, lasting about 3 hours. During this period the paste loses its plasticity and passes through arbitrarily-defined degrees of firmness known as initial set and final set. These roughly correspond to compressive strength values of 50 psi and 800 psi respectively. The final set is usually reached about 6 hours from the time of gauging.

After final set, hydration continues at a diminishing rate until all the cement is consumed or until one or more of the conditions necessary to the reaction is lacking. In practice it is usually the latter, although there are detectable increases in strength due to hydration up to two years or more from the time of initial gauging. The hydration products in the hardened paste comprise a poorly-crystallized, porous tobermorite gel in which are imbedded several more or less well crystallized hydrates and unhydrated cement particles.

The water in the hardened paste, when saturated is considered to exist in three states: (1) chemically combined, (2) physically adsorbed on gel surfaces, and (3) in spaces outside the range of surface forces. However, it is not possible to determine the percentage in each state. As the cement hydrates the capillary channels present in the fresh paste are rapidly reduced in volume and length and soon become discontinuous. As a result the coefficient of permeability in a mature, hardened paste (moist cured 28 days) is reduced to a value of the order of 10^{-12} cm/sec. (19) This is a value comparable with that of many dense natural rocks. Even so, it has been proven that all the evaporable water (lost by heating to 105-110°C) is mobile under an external hydraulic gradient.(20) The evaporable water includes that in state (3) as well as a portion of the water in states (1) and (2).

1.3 Combination of Waste Water with Fly Ash or Portland Cement: Literature Survey

There have been a limited number of previous investigations involving fly ash or portland cement in combination with, or as a treatment method for, industrial waste water. Fly ash has been used as an adsorbent or flocculent material, similar in action to activated charcoal, due to its high surface area. This work has been concentrated in Eastern Europe and has been concerned with treating dilute aqueous wastes containing organic material such as phenolic compounds.(21) A recent U.S. patent describes the use of fly ash in combination with gypsum, or other materials containing calcium and soluble sulfate, to bind up industrial chemical waste sludges.(22) The mix hardens after a period of days or weeks by the formation of calcium sulfo-aluminate hydrates. The resulting solid is said to be useful for landfill or as a general-purpose filling material.

While there is a wealth of information concerning the effect of impure waters, especially sulfate waters, on set cement or concrete, only a few publications have described the use of impure waters as the mixing water for cement or concrete.(23), (24) Luckily one of these latter works was a thorough and extensive study of the topic. This investigation was undertaken by Abrams and published in 1924.(25) He determined the effects of a wide variety of naturally-occurring impure waters and certain industrial waste waters on the strength, setting time, and soundness of concrete. All of the waters studied (68 in all) were acceptable in terms of their setting time and soundness. Most gave acceptable strength results, reducing the average compressive strength by less than 15 percent. The unacceptable waters were a strongly acid water, a lime-water soak from a tannery, refuse from a paint factory, a highly-carbonated mineral water, and waters containing more than 5 percent common salt. However, even with these highly-contaminated waters, he found that an increase in the quantity of the mixing water in the control samples prepared with pure water, for example from a w/c of 0.68 to 0.82, caused a greater reduction in compressive strength than the use of the impure water at a w/c of 0.68.

1.4 Purpose and Direction

In view of this favourable information concerning concrete and impure mixing waters it appeared likely that it would be feasible to bind up industrial waste water with a hydraulic cement, strength requirements not being critical. Certain impurities would have to be avoided since they are known to severely inhibit or prevent the setting of portland cement. These are sugar, borax, and some polyhydric alcohols, such as glycerol.(26) Salts of copper, lead, and zinc are reported to have similar retarding effects, although possibily not as severe.(27)

It was decided to use cement mixes of portland cement/fly ash and hydrated lime/fly ash, with fly ash being the major component. These would give a low-cost mix with a range of strength development rates, the former being expected to yield a faster set and better early strength development. The waste waters which were treated by this method were a spent pickling liquor from a steel treatment bath, containing ferrous sulfate and sulfuric acid, and two aqueous wastes containing phenolic compounds, obtained from a petrochemical plant.

2. EXPERIMENTAL APPROACH

2.1 Materials

The portland cement and hydrated lime were obtained commercially. The portland cement was manufactured by the Independent Cement Company under the name Portland Cement. The hydrated lime was a product of Domtar Chemicals Limited with the trade name Limo: Masons Hydrated Lime. The fly ash was obtained from the Lakeview Generating Station of Ontario Hydro. The first fly ash shipment was sent directly from Ontario Hydro and contained 0.5 percent moisture. The second quantity received came via Goodfellow Enterprises as part of an earlier shipment to them. It had been wetted down for ease of handling and storage, and contained 25 percent moisture.

The spent steel pickling liquor was shipped from Stelco, in Hamilton, in a 45 gallon drum. As received, the drum contained 120 pounds precipitated green salts, mainly ferrous sulfate, and 480 pounds (40 gallons) of a dark green liquid. Before use as a mixing water for the cements, the pickling liquor was diluted 1:1 by weight with tap water. To get the proper proportions, the salts, the supernatant liquid, and tap water were mixed in the ratio 1:4:5. The

1:1 diluted solution was analyzed and found to contain 16 percent iron sulfate (more than 95 percent as ferrous sulfate), and 3 percent sulfuric acid, plus traces of carbon.

The two phenolic waste waters were obtained from a Dow Chemical petrochemical plant in Sarnia. Both were complex mixtures, broken down roughly into the following general components:

Phenolic waste water (I)
70 percent: aqueous layer, strongly basic
7 percent: black organic layer, containing chlorinated hydrocarbons
23 percent: sludge at 17 percent solids

Phenolic waste water (II)
64 percent: aqueous layer, basic
28 percent; black organic layer containing chlorinated hydrocarbons
8 percent: sludge at 23 percent solids

The sludge was intermixed with the dense organic layer. Both waters contained 10 ppm phenols, calculated as phenol.

Except as noted for the pickling liquor, all materials were used as-received.

2.2 Preparation and Curing of the Cement Pastes

The mixes of hydrated lime plus fly ash, and portland cement plus fly ash, were blended in a covered, one gallon polyethylene bucket on a 1/4 horsepower U.S. Stoneware rolling mill operating at 260 rpm. The required quantities of these dry components and the gauging water were weighed on a Mettler P-3 top-loading balance of 3000 gram capacity. The blended cement and the gauging water were mixed to form the cement paste according to the ASTM standard C305-65.(23) The batch sizes ranged from 8 to 12 kilograms.

The flow of the paste was determined according to the ASTM standard C109-73, part 9, except that the flow table was dropped through a height of 1/2 inch 10 times in 6 seconds.(28) The flow of a cement paste is an empirical measure of its fluidity or consistency. It is the percentage increase in the base diameter of a truncated cone, formed from the paste, after it has been subjected to the specified jarring action.

After completion of the flow test, the paste used in the test was returned to the mixing bowl and the entire batch was remixed at medium speed for 15 seconds. Molding of the specimens was started within 2 1/2 minutes of the completion of the initial mixing. The samples were molded in single-use, paraffin-coated cardboard cylinders with a metal base. The molds were 3 inches in diameter and 6 inches in height.

The molds were filled in three, approximately equal, layers. Each layer was rodded 25 times, uniformly over the cross-section of the mold, with a tamping rod having a base diameter of 1 inch and weighing about 1/2 pound. The purpose of the rodding is to obtain a uniformly compacted specimen. After molding, the paste was cut off to a plane surface, flush with the top of the mold, by drawing the straight edge of a trowel across the top of the mold.

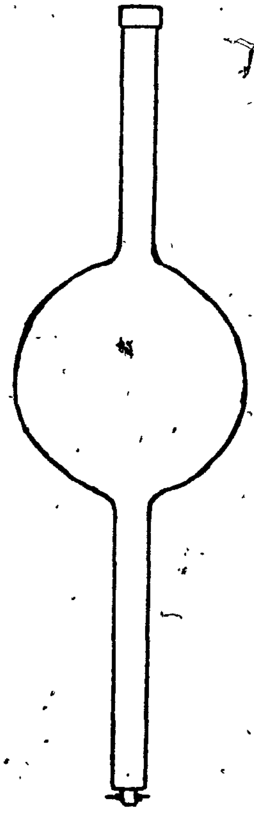
The molded specimens were stored on level shelves in a moist room kept at 23±2°C, and at greater than 90 percent relative humidity, all in accordance with ASTM standard C 511-63.(30) After the cements had set, the molds were removed and discarded. The samples were kept in the moist room until the time of compressive strength testing.

2.3 Setting Time of the Cement Pastes

Setting time determinations were performed on the samples every day until the cement had set. The measurement procedure was a modification of the test for initial set of hydraulic cement by Gillmore needles, ASTM standard C 266-71.(31) The test was performed on the molded cylinders. The setting time, in days, was taken as the time when the specimen was able to bear, without appreciable indentation, the weight of the initial Gillmore needle. This needle weighs 1/4 pound and the tip has a diameter of 1/12 inch. Its shape is indicated in Figure 3. From its weight, and the surface area of its tip, the pressure exerted by the initial Gillmore needle can be calculated to be approximately 40 psi.

Figure 3

Initial Gillmore Needle



1/12 in.

2.4 Compressive Strength Measurement

Prior to obtaining the compressive strength of the hardened specimens, the ends of the cylinders were capped to provide a smooth, level, reproducible surface to be in contact with the bearing plates of the compression testing machine. The cylinders were capped with a commercially available mixture of sulfur and granular material. This mixture was poured hot (130-145°C) into an oiled, circular metal mold. The diameter of the mold was 3 inches at the base, 3 1/2 inches at the top, and it had a depth of 1/4 inch. The ends of the cylinder were wiped dry, and then one end was lowered into the mold, being kept perpendicular to the base of the mold by guiding support rods. The capping compound was allowed to cool, the cylinder was removed from the mold, and then the other end was capped in the same way. The caps were allowed to harden for at least two hours before the specimens were tested for compressive strength. Except while being capped, the specimens were kept in a moist room.

The compressive strength was measured using a Tinius Olsen univeral testing machine of 120,000 pounds capacity, with three ranges: 0-3,000, 0-30,000, and 0-120,000 pounds. The range used for a particular cylinder was chosen to give the highest percentage of full-scale deflection without going off-scale. The cylinders were tested in a moist state, but with the capped ends clean and dry.

To test the specimens, the cylinders were placed in the center of the base block and the movable upper face was slowly brought to bear on the top of the cylinder. Once uniform contact had been achieved, the load was applied to the cylinder at a rate that would cause the failure point of the cement to be reached in not less than 20 seconds and not more than 80 seconds. Three cylinders were tested for each mix and curing period, the average of these compressive strength values being reported as the compressive strength. Occasionally samples were broken in handling, especially while being capped. If two specimens remained, the average from these two was utilized. Otherwise, more samples had to be prepared for that particular mix and curing period. This was generally only a problem with the weaker specimens.

2.5 Leaching Tests

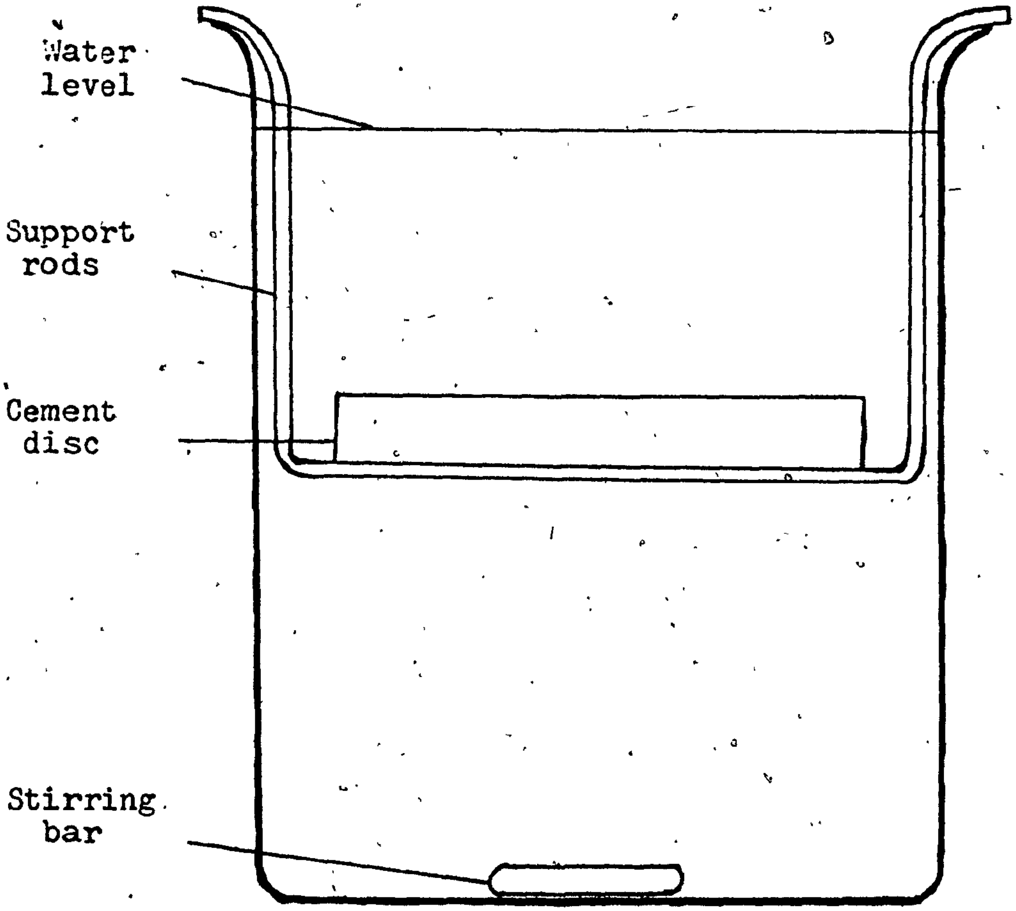
The leaching tests were carried out on discs cut from the cylinders after the compressive strength determination, one disc for each particular mix and curing period. The discs were approximately 1/2 inch thick with a diameter of 3 inches. Their weight ranged between 90 and 120 grams.

The leaching apparatus was simple in construction. It is shown in Figure 4. The cement disc was supported on two glass rods in the middle of a one litre beaker, containing 800 ml of distilled water. Circulation of the water was accomplished by means of a magnetic stirrer. The leaching was continued for a period of 48 hours. Suitable aliquots were withdrawn at the required times, generally after 4, 8, 24, 32 and 48 hours leaching. Any water lost by evaporation was replaced 5-10 minutes before taking the leach sample.

The leach for the cement samples made from the 1:1 pickling liquor was analyzed for iron. The iron concentration in a 10 ml aliquot was determined by atomic absorption spectroscopy. Initially, a Perkin Elmer Atomic Absorption Spectrophotometer,

Figure 4

Leaching Apparatus



Model 290, with a Model 303-0589 multiple element lamp, was used. The instrumental parameters are listed below:

Air pressure	30 psi
Air flow	13.80-14.00
Acetylene pressure	8 psi
Acetylene flow	14.00
Lamp current	8 ma
Dial setting	143-144

The analyses on the samples from the leaching tests performed after three months curing were obtained using a Perkin Elmer Atomic Absorption Spectrophotometer, Model 503, with a Model 303-6037 Fe lamp. The instrumental parameters were as follows:

Air pressure	30 psi
Air flow	55
Acetylene pressure	8 psi
Acetylene flow	32
Lamp current	30 ma
Dial setting	248

The leach materials from the cement samples prepared using the phenolic waste water were analyzed colorimetrically for total phenols, based on phenol as the standard. The entire 800 ml was necessary for the analytical method due to the required sensitivity of less than 20 ppb. As a result, the leaching apparatus was refilled after each sample was taken.

The analytical procedure was based on the Aminoantipyrine Method for Halogenated Phenols, from Standard Methods for the Examination of Water and Waste Waters, published by the American Public Health Association.(32) It involved a petroleum ether extraction of the phenols from an acidified aqueous sample, followed by an alkaline aqueous extraction of the phenols from the petroleum ether, and colour development with 4-aminoantipyrine and potassium ferricyanide at pH 7.9 ± 0.1. The absorbance measurements at 500 nm were obtained, against a reagent blank, using a Spectronic 20 spectrophotometer, with a one inch path length.

2.6 Accelerated Curing Tests

At the beginning we wished to utilize an accelerated curing procedure for the hydrated lime-fly ash cements in order to obtain, within a reasonable period of time, an approximation of the ultimate strength of these cements. This was desirable because of their slow rate of strength development.

There are a number of accelerated curing techniques which have been used, three alone being described in various pertinent ASTM standards.(33,34,35) They involve curing the cement at elevated temperatures for periods of between 2 to 7 days. The strength development rate of pozzolans is markedly enhanced at higher temperatures.

The accelerated curing method adopted involved curing the cement in a hot water bath, set at 54 ± 2°C, for 7 days. The pastes were molded into cubes, two inches on a side, according to ASTM standard C 109-73, section 10.(36) The filled molds were covered with a glass plate and stored in the moist room. Two hours after molding, the covered molds were placed in the hot water bath. After 48 hours in the bath, the cubes were removed from the molds and immediately returned to the bath. The cubes were kept in the bath for 5 more days. Four hours before the compression strength test, the specimens were removed from the bath and placed in the moist room. The cubes did not have to be capped since the surfaces which had been in contact with the mold were smooth and plane. The compression tests were performed as described previously (Section 2.4).

The method of accelerated curing was discontinued after several weeks for a number of reasons. The cubes expanded in the molds and, as a result, they were often broken while being removed from the molds. Due to the expansion, the areas of the surfaces of the cube faces were difficult to determine. In addition, it was decided that these tests, while applicable to pozzolans gauged with tap water, would probably give irregular ~~and~~ misleading results when industrial waste waters and sludges, containing high, variable concentrations of a number of foreign substances, were used as the gauging waters. The results which were obtained up to that point are included for completeness.

3. RESULTS AND DISCUSSION

3.1 Compressive Strength and Time of Set

3.1.1 Tap water

As outlined previously, the various cement mixes of interest were gauged with tap water to establish the limits of strength obtainable from these mixes. As expected, the mixes containing portland cement set faster and had higher initial strength development. This is due to the much greater initial rate of hydration of portland cement as compared to that of the hydrated lime-pozzolan reaction. The difference became less significant after three months moist curing, by which time the lime-pozzolan reaction was yielding appreciable strength. The mixes consisting entirely of fly ash, while they were considered to have set within 2 to 14 days, depending on the water to cement ratio, did not develop any significant strength. The setting in the case of these cements is believed due to physical forces between the finely-divided, water-dispersed fly ash particles, resulting in a firm gel-type of structure, in contrast to the chemical bonds of hydration present in the pozzolanic cements.

The results of these preliminary investigations with tap water are detailed in Tables 3 and 4. The cements containing portland cement had all set within one day of the initial mixing. The others required from 1 to 14 days to set. The compressive strength developed after the specified periods of moist curing ranged from 20 psi (1:9 hydrated lime:fly ash, w/c = 0.6, 28 days) to 3700 psi (1:3 portland cement:fly ash, w/c = 0.3, 150 days). As pointed out in Section 1.3, the water-to-cement ratio has a substantial effect on the strength development. For example, sample 9 (1:9 portland cement:fly ash, w/c = 0.5) took 5 months to develop a strength similar to that which sample 8, the same mix, with a water-to-cement ratio of 0.4, showed after 1 month. In the case of the hydrated lime/fly ash mixes, the water-to-cement ratio also had a significant effect on the setting time.

3.1.2 1:1 Pickling liquor

The steel pickling liquor diluted 1:1 with tap water had a strongly adverse effect upon both the setting rate of the cements and the strength they developed. This was not surprising considering

Table 3

Initial Parameters and Setting Times of Cement Pastes Gauged with Tap Water

Sample	Mix[a]	w/c	Flow[b]	Time of set (days)
1	1:3 PC:FA	0.30	50	1
2	"	0.40	90	1
3	"	0.50	120	1
4	1:9 PC:FA	0.30	15	1
5	"	0.40	90	1
6	"	0.50	~150	1
7	1:3 HL:FA	0.40	55	1
8	"	0.50	90	4
9	"	0.60	125	8
10	"	0.70	>150	12
11	1:9 HL:FA	0.40	80	2
12	"	0.50	115	7
13	"	0.60	~150	10
14	FA	0.30	30	2
15	"	0.40	110	7
16	"	0.50	>150	14

[a] HL=hydrated lime, PC=portland cement, FA=fly ash

[b] The measurable flow range is 0-150

Table 4

Compressive Strength of Cements Gauged with Tap Water

Sample	Compressive strength (psi) after specified periods of moist curing			
	7 days	28 days	90 days	150 days
1	1600 ± 100*	3100 ± 160	3500 ± 160	3700 ± 160
2	660 ± 65	1700 ± 210	2200 ± 200	2500 ± 120
3	440 ± 7	1000 ± 100	1500 ± 210	1900 ± 100
4	520 ± 55	560 ± 80	800 ± 150	860 ± 150
5	250 ± 10	410 ± 35	580 ± 40	660 ± 40
6	130 ± 25	260 ± 20	320 ± 25	400 ± 15
7	-	330 ± 55	1500 ± 170	2200 ± 100
8	-	160 ± 15	1300 ± 160	1600 ± 160
9	-	50 ± 10	190 ± 15	490 ± 55
10	-	20 ± 7	140 ± 40	270 ± 50
11	-	70 ± 4	200 ± 45	260 ± 40
12	-	20 ± 5	60 ± 25	80 ± 10
13	-	10	30 ± 7	40 ± 15
14	-	20 ± 5	20 ± 5	30 ± 10
15	-	10	10	10
16	-	0	-	-

* Standard deviation

the acidity of the water (3 percent H_2SO_4) and the high solids content (19 percent). Nearly twice as much of this mixing water, compared with tap water, was required to obtain the desired paste flow. In addition, the temperature of the paste rose from 23°C to 45-50°C during the mixing.

From the results in Table 6, it appears that the cementing potential of the 1:9 mixes were effectively neutralized by this mixing water. These pastes did not develop significant strength. The 1:3 mixes, containing greater quantities of cementitious materials, did develop strength but only after one month or more of curing.

Some of the cylinders cracked while curing. This may have been due to poor compaction of the samples, or due to the expansive effects of the formation of gypsum, by the reaction of $Ca(OH)_2$ with the sulfate ions present in the mixing water.

3.1.3 Phenolic waters

The phenolic waste waters did not adversely affect the setting time and strength development of the cements relative to tap water. In fact, including the 25 percent water contained in the fly ash used for these tests in the determination

Table 5

Initial Parameters and Setting Times of Cements Gauged with 1:1 Steel Pickling Liquor

Sample	Mix	w/c	Flow	Time of Set (days)
1	1:3 PC:FA	0.50	45	3
2	"	0.70	75	5
3	"	0.90	100	8
4	1:9 PC:FA	0.50	45	3
5	"	0.70	110	5
6	"	0.90	>150	7
7	1:3 HL:FA	1.0	70	10
8	"	1.4	95	10
9	"	1.8	120	21
10	1:9 HL:FA	1.0	75	did not set
11	"	1.2	110	
12	"	1.4	130	
13	FA	0.40	70	
14	"	0.50	100	
15	"	0.60	~150	

Table 6

Compressive Strength of Cements Gauged with 1:1 Steel Pickling Liquor

Sample	Compressive strength (psi) after specified periods of moist curing			
	14 days	28 days	90 days	150 da[illegible]
1	50 ± 5*	660 ± 15	1500 ± 100	1900 ± 60
2	50 ± 10	220 ± 30	500 ± 50	480 ± 25
3	20 ± 5	samples cracked		
4	10			
5	10	10	20 ± 5	20 ± 5
6	10	10	10	10
7	-	120 ± 7	240 ± 55	280 ± 25
8	-	30 ± 7	60 ± 20	50 ± 10
9	-	0	-	-

Samples 10 to 15, inclusive, did not set

* Standard deviation

of the water-to-cement ratio, yielding the values in brackets in Tables 7 and 9, the results in Tables 7, 8, 9, and 10 indicate a reduction in the setting time and an increase in the strength relative to the use of tap water.

This anomaly may be due to a combination of different factors. The water in the fly ash, while increasing the effective water-to-cement ratio, also causes an increase in the percentage of portland cement or hydrated lime in the dry mix. The value in the nominal 1:3 mixes is increased from 25 to 31 percent, and in the 1:9 mixes from 10 to 13 percent. If the organic and sludge material are inert towards the cementing substances, the effective water-to-cement ratio would be reduced. Finally it is known that the setting of portland cement is accelerated in the presence of strong bases.(37) A similar effect may occur in the hydrated lime/fly ash reaction. It appears that some acceleration has taken place, since the 1:9 mixes prepared with phenolic waste water (I) of pH 13 have attained their ultimate strength by the time of the first test of compressive strength.

Table 7

Initial Parameters and Setting Times of Cements Gauged with Phenolic Water (I)

Sample	Mix	w/c[a]	Flow	Time of Set (days)
1	1:3 PC:FA	0.30(0.60)	75	1
2	"	0.40(0.73)	110	1
3	"	0.50(0.85)	140	1
4	1:9 PC:FA	0.30(0.68)	70	1
5	"	0.40(0.81)	90	1
6	"	0.50(0.94)	130	1
7	1:3 HL:FA	0.40(0.73)	65	1
8	"	0.50(0.85)	85	1
9	"	0.60(0.98)	120	2
10	1:9 HL:FA	0.40(0.81)	60	2
11	"	0.50(0.94)	90	3
12	"	0.60(1.1)	120	3
13	FA	0.20(0.60)	20	2
14	"	0.30(0.73)	105	4

a: Values in brackets include the 25 percent water in the fly ash in the determination of the w/c.

Table 8

Compressive Strength of Cements Gauged with Phenolic Water (I)

Sample	Compressive strength (psi) after specified periods of moist curing			
	7 days	28 days	90 days	150 days
1	850 ± 70*	1300 ± 70	1500 ± 100	1500 ± 10
2	610 ± 65	930 ± 15	1000 ± 40	1100 ± 70
3	440 ± 20	610 ± 20	640 ± 35	700 ± 15
4	350 ± 10	460 ± 20	460 ± 50	540 ± 85
5	300 ± 10	370 ± 15	360 ± 30	410 ± 20
6	140 ± 5	150 ± 5	120 ± 5	110 ± 15
7	-	510 ± 70	830 ± 45	500 ± 95
8	-	350 ± 45	530 ± 110	620 ± 20
9	-	210 ± 20	360 ± 35	480 ± 60
10	-	400 ± 55	380 ± 35	480 ± 25
11	-	250 ± 35	270 ± 20	240 ± 20
12	-	190 ± 10	190 ± 20	180 ± 10
13	-	20 ± 5	20 ± 5	20 ± 5
14	-	0	-	-

* Standard deviation

Table 9

Initial Parameters and Setting Times of Cements Gauged with Phenolic Water (II)

Sample	Mix	w/c [a]	Flow	Time of Set (days)
1	1:3 PC:FA	0.20(0.48)	35	1
2	"	0.30(0.60)	75	1
3	"	0.40(0.73)	130	1
4	1:9 PC:FA	0.20(0.55)	20	1
5	"	0.30(0.68)	90	1
6	"	0.40(0.81)	140	1
7	1:3 HL:FA	0.40(0.73)	85	4
8	"	0.50(0.85)	100	7
9	"	0.60(0.98)	120	9
10	1:9 HL:FA	0.30(0.68)	70	2
11	"	0.40(0.81)	100	4
12	"	0.50(0.94)	140	7
13	FA	0.20(0.60)	40	6
14	"	0.30(0.73)	95	did not set

[a]: Values in brackets include the 25 percent water in the fly ash in the determination of the w/c.

Table 10

Compressive Strength of Cements Gauged with Phenolic Water (II)

Sample	Compressive strength (psi) after specified periods of moist curing			
	7 days	28 days	90 days	150 days
1	1100 ± 20*	2300 ± 100	3000 ± 270	3100 ± 70
2	820 ± 20	1500 ± 100	2600 ± 70	2600 ± 100
3	430 ± 10	970 ± 20	1700 ± 220	1700 ± 20
4	520 ± 90	1000 ± 180	1600 ± 70	1600 ± 20
5	130 ± 5	220 ± 15	260 ± 15	290 ± 15
6	80 ± 2	130 ± 20	140 ± 15	160 ± 7
7	-	240 ± 10	750 ± 100	950 ± 35
8	-	150 ± 5	620 ± 25	930 ± 7
9	-	100 ± 3	550 ± 25	750 ± 40
10	-	370 ± 20	540 ± 90	600 ± 50
11	-	250 ± 5	410 ± 60	460 ± 7
12	-	120 ± 15	250 ± 30	260 ± 15
13	-	10	10	10
14	-	10	10	10

* Standard deviation.

3.2 Leaching Tests

The leaching tests indicated that leaching of the waste materials, either iron or phenols, from the cement should be minimal. The amount of iron found in the leach was less than 1 ppm, even after 48 hours continuous leaching. This was the case at the three test periods: 14 days, 28 days, and 90 days, as shown in Table 11. This result is not difficult to explain; the cement paste is alkaline, yielding an alkaline leach, conditions under which uncomplexed iron is insoluble.

The leaching results for the two phenolic waste waters, given in Tables 12 and 13, cannot be explained as simply. The cement discs used in the tests initially contained between 200 and 400 μg phenols. These values are based on an average disc weight of 100 gm, a concentration of 10 ppm phenols in the waste water, and a range of water to cement ratios from 0.20 to 0.60. Therefore the maximum possible concentration of phenols in the leach samples would be between 250 and 500 ppb. However, phenols were not detected in the samples, the sensitivity of the analytical test being 10 ppb.

Table 11

Results of Leaching Tests on Cements Gauged with 1:1 Steel Pickling Liquor

Sample	Age at time of test	Iron concentration[a] (ppm) after specified number of hours of continuous leaching				
		4	8	24	32	48
	14 days					
1[b]		< 1	<1	< 1	<1	<1
2		< 1	<1	<1	<1	<1
	28 days					
1[c]		-	<1	< 1	-	<1
2		-	<1	< 1	-	< 1
5		< 1	<1	< 1	<1	< 1
7		< 1	<1	< 1	<1	< 1
8		< 1	<1	< 1	<1	< 1
	90 days					
1[c]				0.05		0.22
2				< 0.05		0.05
5				0.09		-
7				< 0.05		0.18
8				0.18		0.10

a: The results at 14 days and 28 days were obtained using the Perkin Elmer Model 290 Atomic Absorption Spectrophotometer, those at 90 days with the Model 503.

b: Samples 3,4,5, and 6 were broken apart by the addition of the leaching water.

c: Samples 3 and 4 had cracked. Sample 6 was broken by the addition of the leaching water.

Table 12

Results of Leaching Tests on Cements Gauged with Phenolic Waste Water (I)

Sample	Age at time of test	Concentration of phenols (ppb) after specified number of hours of continuous leaching				
		4	8	24	32	48
	7 days					
2		< 10	< 10	< 10	< 10	< 10
4		< 10	< 10	< 10	< 10	< 10
6		< 10	< 10	< 10	< 10	< 10
	28 days					
2		< 10	< 10	< 10	-	< 10
4		< 10	< 10	< 10	-	< 10
6		< 10	< 10	< 10	-	< 10
8		< 10	< 10	< 10	< 10	< 10
10		< 10	< 10	< 10	< 10	< 10
12		< 10	< 10	< 10	< 10	< 10
	90 days					
2				< 10		< 10
4				< 10		< 10
6				< 10		< 10
8				< 10		< 10
10				< 10		< 10
12				< 10		< 10

Table 13

Results of Leaching Tests on Cements Gauged with Phenolic Waste Water (II)

Sample	Age at time of test	Concentration of phenols (ppb) after specified number of hours of continuous leaching				
		4	8	24	32	48
	7 days					
2		< 10	< 10	< 10	< 10	< 10
4		< 10	< 10	< 10	< 10	< 10
6		< 10	< 10	< 10	< 10	< 10
	28 days					
2		< 10	< 10	< 10	-	< 10
4		< 10	< 10	< 10	-	< 10
6		< 10	< 10	< 10	-	< 10
8		< 10	< 10	< 10	< 10	< 10
10		< 10	< 10	< 10	< 10	< 10
12		< 10	< 10	< 10	< 10	< 10
	90 days					
2				< 10		< 10
4				< 10		< 10
6				< 10		< 10
8				< 10		< 10
10				< 10		< 10
12				< 10		< 10

There may be a number of reasons for these results. The very low permeability of the cement causes the leaching to be concentrated on the surface of the disc, reducing the quantity of phenols accessible to the leaching water. The phenols would probably be tightly adsorbed on the surface of the fly ash particles. (The use of fly ash as an adsorbent was mentioned in Section 1.3.) In addition, phenols are easily oxidized in an alkaline medium, such as is present in these cements.(38)

3.3 Accelerated Curing Tests

The results of the accelerated tests described in Section 2.6 are given in Table 14. The significant points which can be taken from these results are that high strengths should be attainable from hydrated lime/fly ash cements (the results in Table 4 are in agreement with this conclusion), and that the fly ash used in the project would meet the ASTM specification C 595,(39) although the ASTM accelerated curing test is slightly different from the one used in this investigation.

Table 14

Results of Accelerated Curing Tests on Hydrated Lime/Fly Ash Cements

Mix		Compressive Strength (psi)		
	w/c:	0.4	0.5	0.6
1:2 HL:FA		880	1000	900
1:3 HL:FA		1000	860	-
1:4 HL:FA		890	540	460

3.4 Discussion

The results of this investigation indicate that binding up industrial waste waters in a pozzolanic cement would be a feasible method of waste water treatment. The three waste waters studied, while they cannot be considered as representative of the many, varied kinds of waste water which occur, do give an indication of the type of aqueous wastes which could be treated by this procedure.

Consideration of the findings of Abrams in combination with the results of this study indicates that the acidity and the total solids, or the total nonaqueous portion, of the waste waters are the two main deleterious factors relative to the setting time and strength development for these cements. The acid acts by neutralizing an equivalent quantity of cement. High solids cause more mixing water to be added to obtain a certain consistency, increasing the percentage of inert or noncementitious materials in the cement paste.

Relevant data from Abrams' study concerning the five types of impure waters which he found unacceptable for use as mixing water for concrete are given in Tables 15 and 16.(40) The worst case was a 20 percent salt solution which reduced the strength of the concrete 30 to 40 percent, depending on the age of the concrete at the time of the test. A diluted steel pickling liquor, sample 117, similar to the 1:1 pickling liquor used in this investigation, but of 20 percent its strength, was one of these five waters. It had a total solids content of 4 percent and an acidity of approximately one half percent. It caused a reduction in strength of the concrete of only 10 to 15 percent, and just several hours increase in the setting time. Therefore it appears probable that a concentrated, highly acidic waste water such as the 1:1 pickling liquor could be diluted with a neutral or basic waste water to result in a water much less severe in its effects upon these cements.

The levels of iron and phenols in the leach samples from the cements containing these substances were below the values of 17 ppm and 20 ppb, respectively, set for their maximum desirable concentration in the effluent from chemical plants according to the Ontario Objectives for ~~Water~~ Quality Control.(41)

Table 15

Composition of Certain of the Impure Waters Studied by Abrams

Sample	Concentration of the impurities (ppm)						
	Total solids	Fe	Ca &Mg	Na &K	Cl	SO_4	Organic & S
11	223,100	-	60	87,800	135,200	15	-
12	2,140	-	130	670	100	270	-
115	6,220	-	990	-	2,910	210	640
116	10,180	30	250	-	130	5,430	440
117	36,100	9100	-	-	160	23,000	-

a: 11- a synthetic salt solution
12- a carbonated mineral water
115- a tannery lime-water soak
116- refuse from a paint factory
117- a spent steel plating bath diluted to
20 percent its initial concentration

Table 16

Compressive Strength of 1:4 Concretes[a] of Normal Consistency

Sample	w/c	Compressive strength[b] (psi) after specified period of moist curing			
		7 days	28 days	3 months	1 year
	0.88				
control		1640	3080	4360	5450
11		1130 (70)	1870 (61)	2660 (61)	3210 (59)
12		1600 (100)	2360 (72)	3590 (83)	4650 (85)
	0.75				
control		2130	3680	5280	6000
115		1870 (88)	3130 (85)	4120 (78)	4900 (82)
116		1740 (82)	3210 (87)	4200 (80)	5210 (87)
117		1840 (86)	3250 (88)	4630 (88)	5340 (89)

a: 1 part cement to 4 parts aggregate by volume

b: Values in brackets are the percentage of the control strengths.

The combination of low permeability of the cements, adsorbent action of the fly ash, and basicity of the cement, should keep the leaching of many of the waste substances which might be bound up in this manner, to a minimum. However, certain metals, such as zinc, which are soluble in alkaline solutions, could present a problem, as shown by the results for the zinc filter sludge given in Appendix A. In addition, depending on where the resulting solid product is placed, either above ground or below, by being buried or used as land fill, other tests might be required to measure the effects of hydraulic pressure which would occur in the water table, or leaching which might occur while the cement was setting and during the first few days thereafter. These conditions were not investigated.

Nonetheless, long term studies at Chalk River concerning the movement of radioactive ions through the soil have shown that this movement is relatively slow, averaging 10 meters per year.(42) These substances came from a storage pit containing uncombined, low-level radioactive aqueous wastes. The rate of movement was found to depend on the properties of the soil and the nature of the waste, as well as on the rate of movement of the ground water.

Therefore, while there are many contributing factors which would have to be considered for each waste material and disposal site, it appears that leaching of the waste, even if it occurs to an appreciable extent, in many cases would not significantly affect the surrounding environment. In some of the other, more sensitive cases, the treatment procedure might be modified in order to obtain an acceptable final product.

4. CONCLUSIONS

The method of fixation of industrial waters and sludges in a pozzolanic cement has been shown, on a laboratory scale, to be a feasible method of treating complex, highly contaminated aqueous wastes. Depending on the water-to-cement ratio employed and the composition of the cement mix, the cement can develop final compressive strength values from 100 to over 3500 psi. The cements which yield appreciable strength (100 psi or more) set within 14 days of the initial mixing, the ones containing portland cement within 5 days.

Highly-acidic wastes of high total-solids content appear to be the worst in their effect on the setting time and strength development of the cements. Waste substances which are insoluble in, or decomposed by, alkaline media, and those which can be tightly-adsorbed on fly ash, should not present a problem relative to the leaching action of rain or ground water. Generally it would be expected that higher strength cements would have lower permeability to water and thus reduced loss by leaching due to water.

Appendix "A"

A Less Complete Investigation of the Treatment Procedure Applied to Three Waste Sludges

In addition to the study of the treatment procedure relative to the three waste waters described in this thesis, a less complete investigation of the method applied to three waste sludges was undertaken as well. These sludges were a brine treatment sludge, a lime-iron sludge, and a zinc chloride filter sludge.

The brine treatment sludge was approximately 80 percent solids, with calcium sulfate the major component. Magnesium and ferric hydroxides, sodium chloride, and graphite were present in lesser amounts, along with elemental mercury at a concentration of 120 ppm.

The lime-iron sludge contained 20 percent solids, iron and calcium hydroxides as the major components, with minor quantities of various chlorides and sulfides. 0.8 percent Hg was present in the form of sulfides and/or oxides.

The zinc chloride filter sludge, at 75 percent solids, consisted of iron and zinc hydroxides, zinc oxychlorides, and ammonium chloride. The zinc content was 3.7 percent.

The cement pastes were prepared as described previously, and limited compressive strength tests and leaching tests were performed. The leaching apparatus was somewhat different in design from that utilized in the main part of the research. The leaching water was pumped continuously, from an 18 litre reservoir, over the cement disc which was supported in a large funnel. The water then drained through the funnel and returned to the reservoir. The leach samples were analyzed commercially by Eco-Research Laboratories Limited of Pointe Claire, Quebec.

Due to the very high solids content of the sludges, high water to cement ratios, or more appropriately, sludge to cement ratios, were required. These ranged from 1.5 to 3.0. As a result, the cements set only very slowly and, in most cases, did not develop very high strengths. This is shown in the Tables 17, 18, and 19. However, it is significant that at least one of the mixes used for each of the sludges developed strengths

Table 17

Compressive Strength and Setting Time of Cements Prepared with Brine Treatment Sludge

	Mix[a]	w/c	Time of set (days)	Compressive strength (psi) after specified period of moist curing		
				7 days	28 days	90 days
1.	1:3 PC:FA	2.0	2	120	sample cracked	
2.	"	3.0	5	70	240	-
3.	1:3 PC:FA + 0.02% Na_2S	2.0	2	140	-	1200
4.	1:9 PC:FA	1.5	4	20	-	cracked
5.	"	2.0	5	20	-	430
6.	"	2.5	7	10	sample cracked	
7.	1:3 HL:FA	3.0	did not set			
8.	FA	3.0	did not set			

a: PC = portland cement
HL = hydrated lime
FA = fly ash

b: The Na_2S was added to combine with the free mercury to prevent leaching of the mercury.

Table 18

Compressive Strength and Setting Time of Cements Prepared with Lime-Iron Sludge

	Mix	w/c	Time of set (days)	Compressive strength (psi) after specified period of moist curing		
				7 days	28 days	90 days
1.	1:3 PC:FA[a]	1.5	2	150	320	290
2.	"	2.0	5	40	-	-
3.	1:3 HL:FA	1.5	5	-	20	40
4.	"	2.0	9	-	20	120
5.	FA	2.5	did not set			

a: PC = portland cement
HL = hydrated lime
FA = fly ash

Table 19

Compressive Strength and Setting Time of Cements Prepared with Zinc Chloride Filter Sludge

	Mix	w/c	Time of set (days)	Compressive strength (psi) after specified period of moist curing		
				7 days	28 days	90 days
1.	1:3 PC:FA[a]	2.0	5	40	-	620
2.	"	2.5	8	-	35	60
3.	1:3 HL:FA	2.5	12	-	-	50
4.	"	3.0	16	-	-	50
5.	FA	2.0	did not set			

a: PC = portland cement
HL = hydrated lime
FA = fly ash

of 200 psi or greater since the usual, and most practicable, method of disposal of these types of sludges is by solidification of the waste in some manner.

The results of the leaching tests given in Table 20 indicate that mercury was not leached from the cements, the detection limit being 5 ppb. However, there was extensive leaching of zinc from the cement containing the zinc chloride filter sludge. The level of zinc in the leach was 120 ppm after 12 hours leaching. The zinc compounds are evidently only loosely bound up in this weak (50-60 psi) cement and are easily removed by the alkaline leaching water. A chemical additive, which forms an insoluble compound with zinc, might be one solution to this particular leaching problem.

Table 20

Results of the Leaching Tests on the Cements[a] Containing the Waste Sludges

Sludge used in the cement	Element analyzed in the leach	Concentration of the element in the leach after specified number of hours continuous leaching		
		0	1	12
Brine treatment sludge	Hg (ppb)	<5	< 5	< 5
Lime-iron sludge	Hg (ppb)	<5	< 5	< 5
Zinc chloride filter sludge	Zn (ppm)	<0.1	38	120

[a] The leaching tests were carried out on the cements with w/c = 2.0 after 14 days moist curing.

Appendix "B"

Composition and breaking force readings for the cements gauged with tap water

1. Composition

The cement mixes were prepared by weight. The uncertainty in the measurements was approximately 25 grams. This was mainly due to minor losses in transferring the materials. The cement pastes were prepared in two batches, of approximately equal size, totalling the weights listed in Table 21.

2. Breaking force readings

The breaking force readings as obtained, in pounds force applied to the cylinder, are given in Table 22 along with the corresponding compressive strength values determined by dividing the force applied at the breaking point by the cross sectional area of the cylinders, 7.1 square inches.

Table 21

Composition of the Cements Prepared with Tap Water

Component	Component weight (gm)					
Sample:	1	2	3	4	5	6
portland cement	2750	3000	2600	1500	1400	1300
fly ash	8250	9000	7800	13500	12600	11700
water	4400	3600	5200	4500	5600	6500
total	15400	15600	15600	19500	19600	19500

Sample:	7	8	9	10	11	12	13
hydrated lime	2500	2250	2250	2100	900	800	750
fly ash	7500	6750	6750	6300	8100	7200	6750
water	4000	4500	5400	5380	3600	4000	4500
total	14000	13500	14400	13780	12600	12000	12000

Sample:	14	15	16
fly ash	9000	9000	8000
water	2700	3600	4000
total	11700	12600	12000

Table 22

Strength Readings and Corresponding Compressive Strength Values
for the Cements Gauged with Tap Water

	Strength after specified period of moist curing							
	7 days		28 days		90 days		180 days	
	(lbs)	(psi)	(lbs)	(psi)	(lbs)	(psi)	(lbs)	(psi)
1.	12,300	1700	23,900	3200	26,200	3700	29,400	3900
	11,300	1600	20,100	3000	25,000	3500	26,400	3700
	10,700	1500	22,000	3100	23,900	3400	25,500	3600
Average:		1600 ± 100*		3100 ± 100		3500 ± 160		3700 ± 160
2.	5200	730	13,200	1900	16,400	2400	17,300	2400
	4700	650	11,400	1600	15,700	2200	18,600	2600
	4250	600	10,600	1500	14,300	2000	17,100	2400
Average:		660 ± 65		1700 ± 210		2200 ± 200		2500 ± 120
3.	3050	430	7800	1100	12,400	1700	13,100	1800
	3100	440	6300	890	11,400	1600	14,000	2000
	3100	440	7000	990	9200	1300	13,900	1900
Average:		440 ± 7		1000 ± 100		1500 ± 210		1900 ± 100
4.	3800	520	4600	650	4700	660	7100	1000
	3400	470	3500	490	6900	970	6300	890
	4150	580	4000	560	5500	770	4900	690
Average:		520 ± 55		570 ± 80		800 ± 150		860 ± 150

*: Standard deviation

Table 22 continued

Strength after specified period of moist curing

	7 days		28 days		90 days		150 days	
	(lbs)	(psi)	(lbs)	(psi)	(lbs)	(psi)	(lbs)	(psi)
5.	1900	260	3100	440	4400	620	4900	690
	1820	250	2600	370	4000	570	4800	680
	1740	240	2900	410	3800	540	4400	620
Average:		250 ± 10		410 ± 35		580 ± 40		660 ± 40
6.	800	110	1700	240	2500	350	2840	400
	870	120	2000	280	2100	300	2980	420
	1130	160	1850	260	2200	310	2780	390
Average:		130 ± 25		260 ± 20		320 ± 25		400 ± 15
7.			1920	270	10,300	1400	16,300	2300
			2500	350	11,200	1600	14,600	2100
			2700	380	8900	1300	15,600	2200
Average:				330 ± 55		1500 ± 170		2200 ± 100
8.			1040	140	9200	1300	11,300	1600
			1220	170	8100	1100	10,800	1500
			1140	160	9700	1400	12,600	1800
Average:				160 ± 15		1300 ± 160		1600 ± 160
9.			310	45	1300	180	3400	480
			300	40	1400	200	3100	440
			430	60			4000	560
Average:				50 ± 10		190 ± 15		490 ± 55

Table 22 continued

Strength after specified period of moist curing

	28 days		90 days		150 days	
	(lbs)	(psi)	(lbs)	(psi)	(lbs)	(psi)
10.	120	15	1000	140	2360	330
	170	25	700	100	1650	230
		—	1300	180	1920	2[illegible]
Average:		20 ± 7		140 ± 40		2[illegible]0 ± 50
11.	540	75	1700	240	1850	260
	550	75	1450	200	2170	290
	490	70	1050	150	1470	210
Average:		70 ± 4		200 ± 45		260 ± 40
12.	140	20	250	35	630	90
	145	20	410	55	530	75
		—	590	85		—
Average:		20		60 ± 25		80 ± 10
13.	70	10	210	30	220	30
	60	10	300	40	360	50
		—	190	30	180	25
Average:		10		30 ± 7		40 ± 15
14.	150	20	160	20	200	30
	110	15	210	30	240	35
	190	25	140	20	180	25
Average:		20 ± 5		20 ± 7		30 ± 5

Table 22 continued

Strength after specified period of moist curing

	28 days		90 days		150 days	
	(lbs)	(psi)	(lbs)	(psi)	(lbs)	(psi)
15.	70	10	65	10	80	10
	70	10	70	10	60	10
		—	55	10	75	10
Average:		10		10		10
16.	10	0				
	0	0				
	5	0				
Average:		0				

Appendix "C"

Composition and breaking force readings for the cements gauged with 1:1 steel pickling liquor

1. Composition

The cement mixes were prepared as described in Appendix B for the cements gauged with tap water. The relevant data is given in Table 23.

2. Breaking force readings

The breaking force readings and corresponding compressive strength values are given in Table 24.

Table 23

Composition of the Cements Prepared with 1:1 Steel Pickling Liquor

Component	Component weight (gm)					
Sample:	1	2	3	4	5	6
portland cement	2600	2300	2000	1000	900	800
fly ash	7800	6900	6000	9000	8100	7200
water	5200	6400	7200	5000	6300	7200
total	15600	15600	15200	15000	15300	15200

Sample:	7	8	9	10	11	12
hydrated lime	1650	1400	1100	600	500	500
fly ash	4950	4200	3300	5400	4500	4500
water	6600	8340	7920	6000	6000	7000
total	13200	13940	12320	12000	11000	12000

Sample:	13	14	15
fly ash	8500	8000	7500
water	3400	4000	4500
total	11900	12000	12000

Table 24

Strength Readings and Corresponding Compressive Strength Values
for the Cements Gauged with 1:1 Steel Pickling Liquor

	Strength after specified period of moist curing							
	14 days		28 days		90 days		150 days	
	(lbs)	(psi)	(lbs)	(psi)	(lbs)	(psi)	(lbs)	(psi)
1.	330 380	45 55	4600 4600 4800	650 650 680	11,600 10,900 9800	1600 1500 1400	13,900 13,200	2000 1900
Average:		50 ± 5		660 ± 15		1500 ± 100		1900 ± 60
2.	250 420	35 60	1670 1410	240 200	3500 3900 3200	490 550 450	3300 3600 3300	470 510 470
Average:		50 ± 10		220 ± 30		500 ± 50		480 ± 25
3.	170 150	25 20						
Average:		20 ± 5						
4.	60 80	10 10						
Average:		10						

*: Standard deviation

Table 24 continued

Strength after specified period of moist curing

	14 days		28 days		90 days		150 days	
	(lbs)	(psi)	(lbs)	(psi)	(lbs)	(psi)	(lbs)	(psi)
5.	80	10	80	10	170	25	140	20
	70	10	60	10	145	20	175	25
		—	75	10	120	15		—
Average:		[illegible]		10		20 ± 5		25 ± 5
6.	80	10	65	10	65	10	60	10
	75	10	70	10	80	10	85	10
		—	80	10	75	10	70	10
Average:		10		10		10		10
7.			880	120	1300	180	2140	300
			830	120	2070	290	1860	270
			810	110	1710	240	2030	290
Average:				120 ± 7		240 ± 55		280 ± 25
8.			220	30	310	40	320	45
			200	30	400	50	370	50
			280	40	580	80	430	60
Average:				30 ± 7		60 ± 20		50 ± 10
9.			10	0				
			0	0				
Average:				0				

Appendix "D"

Composition and breaking force readings for the cements gauged with phenolic waste water (I)

1. Composition

The cement mixes and corresponding pastes were prepared as described in Appendix B for the cements gauged with tap water. The relevant data is given in Table 25.

2. Breaking force readings

The breaking force readings and corresponding compressive strength values are given in Table 26.

Table 25

Composition of the Cements Prepared with Phenolic Waste Water (I)

Component	Component weight (gm)					
Sample:	1	2	3	4	5	6
portland cement	3000	2400	2400	1100	1000	950
fly ash	9000	7200	7200	9900	9000	8550
water	3600	3840	4800	3300	4000	4750
total	15600	13440	14400	14300	14000	14250

Sample:	7	8	9	10	11	12
hydrated lime	2000	2000	1700	800	700	650
fly ash	6000	6000	5100	7200	6300	5850
water	3200	4000	4080	3200	3500	3900
total	1120	1200	10880	11200	10500	10400

Sample:	13	14
fly ash	9500	9000
water	1900	2700
total	11400	12000

Table 26

Strength Readings and Corresponding Compressive Strength Values for the Cements Gauged with Phenolic Waste Water (I)

	Strength after specified period of moist curing							
	7 days		28 days		90 days		180 days	
	(lbs)	(psi)	(lbs)	(psi)	(lbs)	(psi)	(lbs)	(psi)
1.	5700 6400	800 900	8900 9500 9400	1200 1300 1300	10,800 11,100 9600	1500 1600 1400	11,000 11,000 10,900	1500 1500 1500
Average:	*	850 ± 70		1300 ± 70		1500 ± 100		1500 ± 10
2.	4000 4600	560 650	6500 6700	920 940	7400 7000	1000 990	7100 8000 7900	1000 1100 1100
Average:		610 ± 65		930 ± 15		1000 ± 40		1100 ± 70
3.	3200 3000	450 420	4400 4500 4200	620 630 590	4800 4600 4300	680 650 610	4800 5000 5000	680 700 700
Average:		440 ± 20		610 ± 20		640 ± 35		700 ± 15
4.	2400 2570 2480	340 360 350	3300 3100 3400	460 440 480	3300 3600 2900	460 510 410	4400 3800 3200	620 540 450
Average:		350 ± 10		460 ± 20		460 ± 50		540 ± 85

*: Standard deviation

Table 26 continued

Strength after specified period of moist curing

	7 days (lbs)	7 days (psi)	28 days (lbs)	28 days (psi)	90 days (lbs)	90 days (psi)	150 days (lbs)	150 days (psi)
5.	2130	300	2500	350	2440	340	2950	420
	2090	290	2700	380	2770	390	2730	380
		—	2600	370	2390	340	3000	420
Average:		300 ± 10		370 ± 15		360 ± 30		410 ± 20
6.	990	140	1000	140	840	120	840	120
	1040	150	1100	150	850	120	860	120
	1000	140	1100	150	840	120	650	90
Average:		140 ± 5		150 ± 5		120 ± 5		110 ± 15
7.			3100	440	5500	780	4300	610
			3700	520	6200	870	3000	420
			4100	580	5900	830	3600	490
Average:				510 ± 70		830 ± 45		500 ± 95
8.			2400	340	4500	630	4400	620
			2750	390	3800	540	4700	660
			2150	300	2900	410	4600	650
Average:				350 ± 45		530 ± 110		620 ± 20
9.			1350	190	2800	390	3000	420
			1650	230	2500	350	3400	480
			1500	210	2300	320	3800	540
Average:				210 ± 20		360 ± 35		480 ± 60

Table 26 continued

Strength after specified period of moist curing

	28 days		90 days		150 days	
	(lbs)	(psi)	(lbs)	(psi)	(lbs)	(psi)
10.	3150 2400 3000	440 340 420	3000 2600 2500	390 370 350	3400 3300 3600	480 460 510
Average:		400 ± 55		380 ± 35		480 ± 25
11.	1650 2000 1550	230 240 220	1900 2080 1760	270 290 250	1700 1960 1530	250 260 220
Average:		250 ± 35		270 ± 20		240 ± 20
12.	1400 1250 1400	200 180 200	1220 1510 1320	170 210 190	1350 1180 1230	190 170 170
Average:		190 ± 10		190 ± 20		180 ± 10
13.	170 130 170	25 20 25	170 110 130	25 15 20	180 150 140	25 20 20
Average:		20 ± 5		20 ± 5		20 ± 5
14.	15 5	0 0				
Average:		0				

Appendix "E"

Composition and breaking force readings for the cements gauged with phenolic waste water (II)

1. Composition

The cement mixes and corresponding pastes were prepared as described in Appendix B for the cements gauged with tap water. The relevant data is given in Table 27.

2. Breaking force readings

The breaking force readings and corresponding Compressive strength values are given in Table 28.

Table 27

Composition of the Cements Prepared with Phenolic Waste Water (II)

Component — **Component weight (gm)**

Sample:	1	2	3	4	5	6
portland cement	3000	2800	2600	1200	1100	1000
fly ash	9000	8400	7800	10800	9900	9000
water	2400	3360	4160	2400	3300	4000
total	14400	14560	14560	14400	14300	14000

Sample	7	8	9	10	11	12
hydrated lime	2000	1900	1700	850	800	700
fly ash	6000	5700	5100	7650	7200	6300
water	3200	3800	4080	2550	3200	3500
total	11200	11400	10880	11050	11400	10500

Sample:	13	14
fly ash	9500	11000
water	1900	3300
total	11400	14300

Table 28*

Strength Readings and Corresponding Compressive Strength Values for the Cements Gauged with Phenolic Waste Water (II)

	Strength After specified Period of moist curing							
	7 days		28 days		90 days		150 days	
	(lbs)	(psi)	(lbs)	(psi)	(lbs)	(psi)	(lbs)	(psi)
1.	7600	1100	15,500	2200	20,300	2900	21,800	3100
	7800	1100	17,100	2400	23,200	3300	21,600	3000
			16,300	2300	19,600	2800	22,200	3100
Average:		1100 ± 20		2300 ± 100		3000 ± 270		3100 ± 70
2.	5700	800	11,500	1600	18,000	2500	18,000	2500
	5900	830	10,700	1500	18,200	2600	18,700	2600
	5800	820	9600	1400	18,600	2600	19,100	2700
Average:		820 ± 20		1500 ± 100		2600 ± 70		2600 ± 100
3.	3000	420	7000	990	11,500	1600	12,000	1700
	3100	440	6900	970	13,200	1900	11,800	1700
	3100	440	6800	960			11,700	1700
Average:		430 ± 10		970 ± 20		1700 ± 220		1700 ± 20
4.	3100	430	6100	860	11,400	1600	11,100	1600
	4400	610	7300	1000	10,800	1500	11,400	1600
	3800	540	8200	1200	11,600	1600		
Average:		520 ± 90		1000 ± 180		1600 ± 70		1600 ± 20

*: Standard deviation

Table 28 continued

Strength after specified period of moist curing

	7 days		28 days		90 days		150 days	
	(lbs)	(psi)	(lbs)	(psi)	(lbs)	(psi)	(lbs)	(psi)
5.	940	130	1600	230	1800	250	1900	270
	970	140	1500	210	1770	250	2130	300
	940	130		—	2010	280	2090	290
Average:		130 ± 5		220 ± 15		260 ± 15		290 ± 15
6.	590	80	1000	140	1010	140	1120	160
	560	80	900	110	1160	160	1040	150
		—		—	900	130	1160	160
Average:		80 ± 2		130 ± 20		140 ± 15		160 ± 7
7.			1600	230	6000	850	6600	930
			1800	250	5400	760	7000	990
			1700	240	4600	650	6600	930
Average:				240 ± 10		750 ± 100		950 ± 35
8.			1050	150	4200	590	6600	930
			1100	150	4500	630	6500	920
			1000	140	4500	630	6600	930
Average:				150 ± 5		620 ± 25		930 ± 7
9.			720	100	3900	550	5100	720
			700	100	3800	530	5600	790
			680	100	4100	580	5200	730
Average:				100 ± 3		550 ± 25		750 ± 40

Table 28 continued

Strength after specified period of moist curing

	28 days		90 days		150 days	
	(lbs)	(psi)	(lbs)	(psi)	(lbs)	(psi)
10.	2750	390	4400	620	4700	660
	2650	370	3900	550	4200	590
	2900	410	3100	440	4000	560
Average:		370 ± 20		540 ± 90		600 ± 50
11.	1750	250	2400	340	3300	460
	1800	250	3000	420	3200	450
	1800	250	3300	460	3300	460
Average:		250 ± 5		410 ± 60		460 ± 7
12.	900	130	1940	270	1750	250
	750	100	1640	230	1920	270
	900	130		—		—
Average:		120 ± 15		250 ± 30		260 ± 15
13.	60	10	60	10	75	10
	70	10	55	10	90	15
		—	80	10	60	10
Average:		10		10		10
14.	70	10	80	10	65	10
	45	5	60	10	70	10
	60	10	70	10		—
Average:		10		10		10

Appendix "F"

Data from the leaching tests

1. Iron determinations

Standardization values for the iron determinations made using the Perkin Elmer Model 290 Atomic Absorption Spectrophotometer are listed below:

Fe concentration (ppm)	Reading
0	0
1.0	2.5
2.5	4.5
5.0	7.5
10.0	14.5

All the readings obtained after 14 or 28 days moist curing were 0, 0.5, or 1 and so the iron concentration was reported as less than 1 ppm.

Standardization values for the iron determinations made using the Perkin Elmer Model 503 Atomic Absorption Spectrophotometer are listed below:

Fe concentration (ppm)	Absorbance
1.0	0.021
2.0	0.047
3.0	0.066
4.0	0.092
5.0	0.120

Results of the leaching tests performed at 90 days:

Sample	Absorbance	
	24 hours leaching	48 hours leaching
1	0.001	0.005
2	0.001	0.001
5	0.002	-
7	0.001	0.004
8	0.004	0.002

2. Phenol determinations

Standardization values for the phenol determinations are given below:

Phenols (μg)	Absorbance
10	0.04
30	0.12
50	0.19
70	0.29
100	0.37

In all the phenol determinations the absorbance readings were less than 0.02.

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