



## Properties of Portland cement made from contaminated sediments

Jennifer L. Dalton, Kevin H. Gardner\*, Thomas P. Seager,  
Mindy L. Weimer, Jean C.M. Spear, Bryan J. Magee<sup>1</sup>

*Environmental Research Group, University of New Hampshire, Durham, NH 03824, USA*

Received 12 February 2003; received in revised form 20 September 2003; accepted 31 October 2003

### Abstract

Hundreds of millions of cubic meters of contaminated sediments are dredged from US harbors and waterways annually for maintenance of navigation, environmental remediation, or both. In recent years, inexpensive ocean dumping has been largely eliminated as a disposal alternative causing a crisis in the management of sediment. This paper presents a new beneficial use alternative for contaminated dredged material, which is to use dredged material as a feedstock in the conventional manufacture of Portland cement. The paper demonstrates the efficacy of the process at the bench and pilot scales, and presents a summary of practical and economic considerations. A bench scale manufacture was carried out with feedstock mixtures containing 1–12% dredged material from the New York/New Jersey (NY/NJ) harbor. The clinkers were quantitatively analyzed with X-ray powder diffraction and differences in phase concentrations were observed in the clinker samples manufactured with dredged material (decreased alite and increased belite) suggesting that additional burn time was needed to account for the quartz present in the sediments. The free chloride concentrations in the clinker samples were below ACI limits for cement used with reinforcing steel; however, the chloride in the dredged material remains a manufacturing concern and is expected to increase annual maintenance costs. A pilot scale manufacture was carried out in a batch rotary kiln; X-ray diffraction analysis and ASTM tests for strength, soundness, and setting time suggested that with better optimized burning conditions, dredged material can be successfully incorporated into full scale manufacture.

© 2003 Elsevier B.V. All rights reserved.

*Keywords:* Contaminated sediment; Dredged material; Cement manufacturing; Beneficial use; X-ray diffraction

\* Corresponding author. Tel.: +1-603-862-4334; fax: +1-603-862-3957.

*E-mail address:* kevin.gardner@unh.edu (K.H. Gardner).

<sup>1</sup> Present address: Grace Construction Products, 852 Birchwood Boulevard, Birchwood, Warrington, Cheshire WA3 7QZ, UK.

## 1. Introduction

Passage of the Clean Water Act (CWA) and the Marine Protection, Research and Sanctuaries Act (MPRSA) in the United States has greatly restricted the disposal of contaminated sediment at sea due to risks associated with ecological exposure. These limitations have caused a crisis for the management of dredged material that is too contaminated for ocean disposal (typically one-half to 3/4 of the total volume dredged from Northeast US harbors). Development of cost effective, environmentally sound, and sustainable dredged material management alternatives is a critical issue for continued operations of major ports and harbors, which contribute significantly to the US economy.

For example, between 1976 and 1995, an average of 5,765,000 cubic yards of sediments were removed annually from New York/New Jersey (NY/NJ) harbor (Jones et al., 2001). This was done to increase the harbor's natural depth of approximately 19 ft to nearly 40 ft. Additional material will need to be handled over the next few years as the Port Authority prepares to increase the depth of the region's shipping lanes to 50 ft by the year 2009 (PANYNJ, 2001). This measure is intended to keep the port competitive by allowing the safe passage of a new generation of cargo megaships.

Typical disposal options that have been used for contaminated dredged material include confined disposal facilities (shoreline and offshore) and confined aquatic disposal cells (subaqueous disposal, typically in the harbor). More recently, dredged material has been amended with stabilizing agents such as cement, cement kiln dust, and fly ash, and used as fill material at Brownfield sites and to close an abandoned mine in Pennsylvania. These are important material management options, but no one single approach is likely to solve the region's or nation's on-going predicament: cost effective and, particularly, sustainable approaches are needed for a long-term solution.

The new technologies that are the focus of current research and development converge on the premise of beneficial use, in which the material is transformed into a marketable product and costs recovered by product sales. Success has been demonstrated in using dredged material to manufacture lightweight aggregate, ceramics and glass tiles, bricks, and soil (Amiran and Wilde, 2002; Derman and Schlieper, 1999; Hamer and Karius, 2002; McLaughlin et al., 1999). A construction-grade blended cement has also been produced using a patented thermo-chemical process called Cement Lock™ (Rehmat et al., 2001).

The work reported in this manuscript used contaminated sediments to replace a portion of the raw feedstock materials in conventional Portland cement manufacture. Dredged material contains major fractions of silica, alumina, calcium and iron oxides, all of which are important in Portland cement manufacture. Furthermore, the concept of using recycled materials in Portland cement manufacture is not unique; hazardous wastes are used as kiln fire at 20% of US cement plants, and industrial byproducts such as coal fly ash and petroleum contaminated soils have been used to replace virgin feedstock materials. Consequently, the cement industry is increasingly the focus of studies investigating the potential to exploit key concepts in industrial ecology such as beneficial reuse of waste materials (Van Oss and Padovani, 2002, 2003).

Cement manufacture requires high temperatures, typically 1450 °C with a residence time of 20–30 min at peak temperature. It is expected that organic contaminants will be degraded, and inorganic contaminants (heavy metals) will be stabilized—either locked into the cement

phases or present in the cement kiln dust (a detailed investigation of the fate of contaminants in the process will be published subsequently in a separate paper). This proposed technology is advantageous in that it uses existing facilities and technologies to manage the considerable amount of dredged material produced each year, while reducing the cement manufacturer's demand on raw materials. It is anticipated that this technology can be used in concert with the numerous other available technologies and disposal options described above to manage contaminated dredged material.

This manuscript presents the results of an investigation of the feasibility of using dredged material as an alternative feedstock for Portland cement manufacture. The focus of the work reported here is the production of material on the bench and pilot scales and the characterization of clinker and cement made using the dredged material.

## 2. Background: cement manufacture

Portland cement is a hydraulic binder made from limestone and clay, sand or shale. It was named for its original resemblance to Portland stone, a limestone quarried in the UK. In the year 2001, nearly 82 million tonnes of cement were manufactured in US cement plants, while an additional 22 million tonnes were imported from plants abroad (Portland Cement Association, 2003). Dredged sediments typically have a mineral composition that includes many of the ingredients essential to cement manufacture, including  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{CaO}$ . By adjusting the proportion of all other ingredients, sediments may be blended with virgin materials at mass ratio of 10–12% (depending upon the composition of the sediment and other available raw materials) to obtain the proper mineral composition for Portland cement manufacture. High temperatures are required to convert the combined raw materials to an intermediate product called *clinker*, which must be ground and blended with gypsum to become cement. Even the “final” product is really just one ingredient in the manufacture of construction products. Cement is eventually batched with water and sand to make mortar (which is used between bricks or stone to bind individual masonry units to each other) or, when stone or gravel is added, to make concrete. High compressive strength is obtained from an exothermic chemical reaction between the water and cement that forms entirely new minerals. Thus, concrete does not “dry” in the sense that water escapes from the wet concrete mix; it “cures” in that the water is incorporated into the new molecular structure of the cement paste.

Clinker can be manufactured using either a wet or dry process. With the wet process, the raw materials enter the kiln in a wet slurry form, and in a dry process they enter the kiln in a dry form. Wet process plants (like the Lafarge Corp. plant in Ravena, NY) require more energy than dry process plants (to drive off the additional moisture), and consequently account for less than 20% of the clinker manufactured in the US (USGS, 2001). However, because sediments are removed from aquatic environments, they carry high water contents and may partially reduce the added water requirements at wet process plants. Therefore, wet process plants may be better suited than dry process plants for accepting dredged sediments.

Blended raw materials enter the top of the kiln and travel down as it rotates slowly about its axis at speeds of 1–4 rpm (Taylor, 1997). The feedstock mixture passes through progressively hotter and hotter heating zones. At first the water is driven off (between 500

and 800 °C); then, the chemical bond between calcium and carbonate is broken, evolving carbon dioxide to the atmosphere and leaving CaO in the kiln in a process called *calcination* (at approximately 1000 °C). Eventually the material becomes molten and calcium silicates and other clinker phases are formed. At the bottom end of the kiln, called the burning zone (approximately 1450 °C), the mixture fuses into balls of 0.3 to 2.5 cm diameter clinker (Neville, 1996). Overall residence time in the kiln is a few hours; the Lafarge kiln in Ravenna, NY has a typical residence time of 3 h (Roberts, 2002). From the furnace, the clinker is cooled rapidly with air, and then interground with gypsum in ball mills into the fine powder known as cement. The gypsum is added to control the hydration process and prevent rapid setting.

The mineral phases formed are determined by the raw materials, residence time, and temperatures employed. Four major phases: alite, belite, aluminate, and ferrite, dominate clinker composition (Kohlhaas, 1983; Neville, 1996; Taylor, 1997). Although each performs a different function in the performance of the final product, the most important are alite and belite, which are most abundant in the clinker and make the greatest contribution to compressive strength (Table 1). Minor components in the feedstocks may cause problems in cement manufacture. The most notable of these, in the case of contaminated sediment feedstocks, are the alkali chloride salts, such as sodium chloride and potassium chloride and environmentally important metals such as cadmium, chromium, arsenic, copper, mercury, and lead.

In concrete construction, chloride is anathema. It reduces final strength and may speed corrosion of reinforcing steel. However, in cement manufacture, chloride in raw material feedstocks is somewhat less problematic. When chlorides pass through the kiln, they are ordinarily volatilized at approximately 980 °C, along with alkalis, sulfur, and other elements present in the raw mix. Only a small fraction is typically trapped in the clinker (Bhatty, 1995; Taylor, 1997). As they travel up the kiln with other gases to cooler regions, a portion of the chlorides may precipitate out to form solid or semi-solid salt deposits along the kiln walls. Periodic maintenance can remove the build-up, although production time is lost (Gadayev and Kodess, 1999). The remaining chlorides (as well as alkalis) accumulate in the CKD, which precludes reintroduction of CKD back into the raw feed mix (Taylor, 1997). For plants that use electrostatic precipitators (ESPs) for pollution control, chlorides and alkalis may combine to form a sticky residue that clogs the devices, again requiring additional maintenance (Roger, 2001). High chloride concentrations may also cause early wear on a kiln's brick lining, as well as other manufacturing components, including the emission stacks. However, the tendency of chlorides to scavenge alkali metals from the clinker can be

Table 1  
Properties of major clinker phases

| Mineral phase  | Properties in cement                                       |
|--|--|
| Alite (tricalcium silicate) $3\text{CaO} \times \text{SiO}_2$  | Rapid hydration, high initial and final strength           |
| Belite (dicalcium silicate) $2\text{CaO} \times \text{SiO}_2$  | Slow hydration, good final strength, low heat of hydration |
| Aluminate (tricalcium aluminate)<br>$3\text{CaO} \times \text{Al}_2\text{O}_3$                             | Rapid hydration, high heat of hydration                    |
| Ferrite (tetracalcium aluminoferrite)<br>$4\text{CaO}(\text{Al}_2\text{O}_3 \times \text{Fe}_2\text{O}_3)$ | Slow and moderate hydration, moderate heat of hydration    |

Table 2  
Effects of heavy metals on cement manufacture and properties

| Chemical symbol | Effect on cement manufacture and properties  |
|-----------------|--|
| As              | Typically enters clinker; unlikely to effect cement manufacture  |
| Cd              | Cd concentration in clinker decreases as Cl input to kiln increases<br>High CdO content in clinker will retard hydration; no effect on strength                        |
| Cr              | Reduces viscosity of clinker melt; will get incorporated into clinker phases; accelerates hydration of paste; improves early strength (used for high strength cements) |
| Cu              | Effects vary depending on the form (oxide, salt, or sulfide). Accumulates in CKD   |
| Pb              | Volatile, may exit the kiln as fines and collect in CKD. Can accumulate in clinker without adverse effects if <70 ppm  |
| Hg              | Highly volatile, expected to escape in stack gases. Very little is known about effect on clinker production  |
| Zn              | 80–90% of ZnO will go to clinker (80–90%), with the rest to CKD. Other forms can have varied effects   |

an advantage in producing low alkali cements and reducing undesirable alkali–silica side reactions in concrete.

Metals present in feedstock materials are known to effect clinker phase formation, hydration/setting time, and strength development. Small concentrations of arsenic, cadmium, chromium, copper, lead, mercury, and zinc are typically present in both dredged sediment samples and convention clinkers. Because these elements are typical of those found in trace quantities in virgin raw materials, cement producers have extensive experience with their impact on concrete quality and cement production (see Table 2) (Bhatty, 1995).

Introduction of contaminated sediments containing chloride salts (e.g. from ocean or estuarine waters) or trace metals is likely to result in increased maintenance expenses at the cement manufacturing plant, partially offsetting sediment disposal cost savings. However, the primary purpose of this study is to investigate the impact of dredged material introduction on traditional performance specifications such as compressive strength, setting time, and free chloride content for cement and assess the potential to manufacturer a commercially viable cement product using contaminated dredged material.

### 3. Methods and materials

#### 3.1. Sample collection

Dredged material samples were collected from the New York/New Jersey Harbor in October of 2000. Sampling was conducted along the Harlem River using a standard Ponar sampler. Five gallon buckets of sediment were sampled from three locations in the harbor, all of which were typical depositional environments. The particle size distribution of the dredged material is shown in Fig. 1; the median size was 15  $\mu\text{m}$ . Extensive sampling throughout the NY/NJ harbor has found that dredged sediments have a most probable median size range of 6–20  $\mu\text{m}$ , which includes the median particle size of the dredged material sample analyzed in this work (PANYNJ, 1996). The average water content was 52.5%,

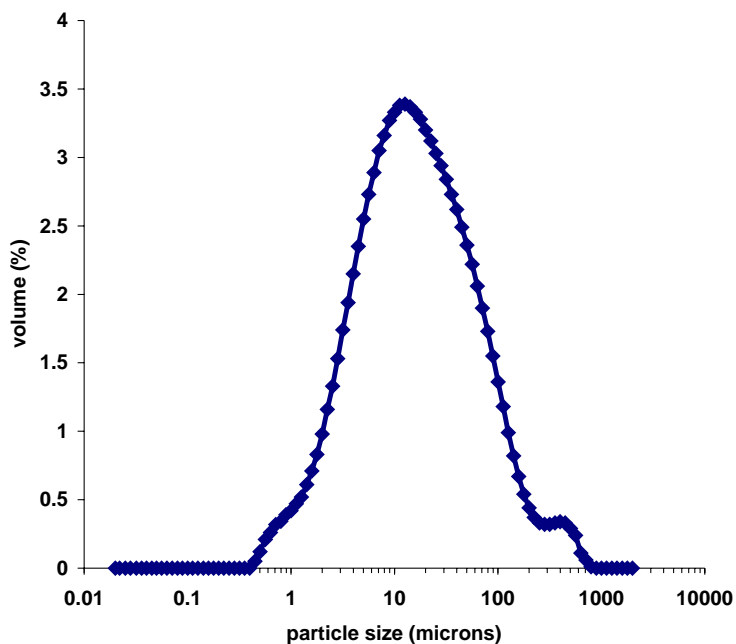


Fig. 1. Particle size distribution measured for dredged material.

within the range of 41.1–64.3% found from dredged material samples taken throughout the NY/NJ harbor (PANYNJ, 1996).

Samples of typical cement production feedstock materials were collected at the Lafarge Building Materials cement plant in Ravena, New York (at the time the plant was owned and operated by Blue Circle Cement). This manufacturing facility uses a blend of six raw feedstock materials, described in Table 3, to prepare their feedstock slurry. Samples of feedstock materials, slurry (the final mixture of feedstock materials entering the kiln), Portland cement clinker, gypsum, and Portland cement were also collected during this trip to the Lafarge cement plant.

Table 3  
Key properties of feedstock materials

| Abbreviated name | Full name                        | Primary mineral(s) supplied   | Source   |
|------------------|----------------------------------|---|--|
| CM               | Coeymans manlius, high lime rock | Calcium ( $\text{CaCO}_3$ )   | Mined from on-site quarry                          |
| Hi mag           | Roundout rock formation          | Calcium ( $\text{CaCO}_3$ ), silica ( $\text{SiO}_2$ )                | Mined from on-site quarry                          |
| Kalk             | Kaulkberg, low lime rock         | Calcium ( $\text{CaCO}_3$ ), silica ( $\text{SiO}_2$ )                | Mined from on-site quarry                          |
| Fly ash          | Coal fly ash                     | Alumina ( $\text{Al}_2\text{O}_3$ ), silica ( $\text{SiO}_2$ )        | Purchased, by-product of coal burning power plants |
| Baux             | Bauxite                          | Alumina ( $\text{Al}_2\text{O}_3$ ), iron ( $\text{Fe}_2\text{O}_3$ ) | Purchased on open market                           |
| Iron             | Iron (mill scale)                | Iron ( $\text{Fe}_2\text{O}_3$ )                                      | Purchased on open market                           |

Table 4  
XRF analysis results for typical feedstock materials (% by mass)

|                                | CM     | Hi Mag | Kalk   | Bauxite | Fly ash | Iron   |
|--------------------------------|--------|--------|--------|---------|---------|--------|
| SiO <sub>2</sub>               | 7.44   | 28.19  | 35.29  | 7.00    | 46.65   | 4.91   |
| Al <sub>2</sub> O <sub>3</sub> | 1.27   | 5.21   | 3.16   | 44.44   | 21.23   | 0.89   |
| Fe <sub>2</sub> O <sub>3</sub> | 0.59   | 3.30   | 1.59   | 19.87   | 6.98    | 86.73  |
| CaO                            | 47.90  | 22.47  | 31.43  | 4.65    | 6.50    | 7.98   |
| MgO                            | 2.47   | 10.69  | 1.34   | 0.34    | 0.88    | 0.38   |
| SO <sub>3</sub>                | 0.74   | 0.18   | 0.49   | 0.54    | 0.48    | 0.08   |
| Na <sub>2</sub> O              | 0.17   | 0.68   | 0.26   | 0.08    | 0.68    | 0.12   |
| K <sub>2</sub> O               | 0.31   | 1.13   | 0.56   | 0.00    | 0.97    | 0.00   |
| TiO <sub>2</sub>               | 0.07   | 0.25   | 0.15   | 1.31    | 0.69    | 0.03   |
| SrO                            | 0.05   | 0.00   | 0.01   | 0.00    | 0.00    | 0.00   |
| P <sub>2</sub> O <sub>5</sub>  | 0.03   | 0.09   | 0.07   | 0.04    | 0.13    | 0.06   |
| MnO                            | 0.00   | 0.07   | 0.01   | 0.03    | 0.00    | 1.78   |
| ZnO                            | 0.00   | 0.00   | 0.00   | 0.00    | 0.00    | 0.00   |
| Cr <sub>2</sub> O <sub>3</sub> | 0.00   | 0.00   | 0.00   | 0.00    | 0.00    | 0.01   |
| F                              | 0.00   | 0.00   | 0.00   | 0.00    | 0.00    | 0.00   |
| Cl                             | 0.02   | 0.03   | 0.01   | 0.02    | 0.02    | 0.03   |
| LOI                            | 38.95  | 27.71  | 25.64  | 21.69   | 14.79   | –3.00  |
| SUM                            | 100.00 | 100.00 | 100.00 | 100.00  | 100.00  | 100.00 |

### 3.2. XRF analysis

The dredged material and feedstock material samples collected were analyzed for major and minor oxide concentrations using X-ray fluorescence (XRF). Samples were prepared in the UNH materials laboratory and then sent to Lafarge's laboratory for XRF analysis on a Bruker 3400SRS XRF unit. Concentrations of the following oxides and elements were analyzed: SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO, MgO, SO<sub>3</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, TiO<sub>2</sub>, SrO, P<sub>2</sub>O<sub>5</sub>, MnO, ZnO, Cr<sub>2</sub>O<sub>3</sub>, F, and Cl. Results of the XRF analysis are shown in Table 4.

### 3.3. Material preparation

The dredged material was dried in an oven at 60 °C. The dried sample was then broken down from clumps to its original particle size with a mortar and pestle and sieved through a 50-mesh (300 μm) sieve. Oversized pieces including shells, and large sand particles were caught on the screen and removed.

The feedstock materials were ground in a crusher to less than 1.5 in. and then in a BICO pulverizer until the material was less than 10 millimeters. The ASTM methods for sampling aggregate (C207 and D75) were applied to collecting samples of feedstock materials for crushing and analysis.

### 3.4. Free chloride content

The free chloride content of the dredged material and clinker samples were measured with a chloride ion selective electrode. Samples were first heated to 550 °C to remove organics

Table 5  
Proportions of feedstock materials in mixtures for bench scale clinker manufacture (% by mass)

| Material | Control | Low DM | Medium DM | High DM |
|----------|---------|--------|-----------|---------|
| CM       | 73.68   | 73.56  | 78.80     | 84.58   |
| Hi mag   | 1.10    | 1.10   | 1.18      | 1.26    |
| Kalk     | 20.16   | 20.34  | 10.83     | 0.33    |
| Fly ash  | 2.00    | 0.00   | 0.00      | 0.00    |
| Baux     | 2.40    | 2.97   | 2.21      | 1.37    |
| DM A     | 0.00    | 1.49   | 6.63      | 12.30   |
| Iron     | 0.66    | 0.54   | 0.36      | 0.16    |

that interfere with the electrode reading. The sample was suspended in deionized water at a 10:1 l/kg liquid to solid ratio.

### 3.5. Bench scale clinker manufacture

The procedures used for manufacturing clinker in the laboratory were based on practices described in the literature (Caponero and Tenorio, 2000; Espinosa and Tenorio, 2000) and correspondence with experts (Glasser, 2001; Kozikowski, 2001; Mischulovich, 2001; Tang, 2001; Tenorio, 2001). Four different batches of cement were manufactured at the bench scale with increasing proportions of dredged material: 0% (control sample), 1.49, 6.63, and 12.3%. Table 5 gives the exact proportions of all feedstock components. Each feedstock mixture was fired in a platinum crucible with a platinum lid to minimize alkali and sulfate escape (Glasser, 2001).

Between 40 and 45 g of feedstock mixture was fired at a time. The furnace program, based on literature data and free lime minimization, consisted of the following: ramp at 20 °C/min to 1000 °C, ramp at 15 °C/min to 1450 °C, and dwell at 1450 °C for 30 min (Caponero and Tenorio, 2000; Dalton, 2002; Espinosa and Tenorio, 2000; Trezza and Scian, 2000). The clinker sample was then cooled to 400 °C in the furnace, removed from the furnace and cooled to room temperature in a desiccator. Although this procedure did not allow for the rapid cooling important to Portland cement manufacture, it was safer to handle the crucible and sample at a lower temperature when the sample had solidified. The clinker sample was broken into small pieces with a mortar and pestle and ground in the ceramic ball mill. Any material that did not pass a 200 µm sieve was further ground with a mortar and pestle.

### 3.6. X-ray diffraction analysis

Ground clinker samples, passing a 50-mesh (300 µm) sieve, were placed in glass sample plates, smoothed over until the samples were spread out evenly, and tapped to achieve random orientation of the crystals. Elemental tungsten, wolfram (W), was added as an internal standard and a  $2\theta$  corrector. A Rigaku-Geigerflex goniometer was used to provide the Cu K $\alpha$  X-ray source (45 kV, 35 mA). Data were collected using Datascan 3.1 (Materials Data Inc. (MDI)). Additional details are available in Dalton (2002).



Table 6  
Proportions of feedstock materials in pilot scale mixture (% by mass)

| Feedstock material | Proportion |
|--------------------|------------|
| CM                 | 87.15      |
| Hi mag             | 3.63       |
| Kalk               | 0.40       |
| Baux               | 1.88       |
| Iron               | 0.29       |
| DM B               | 6.65       |

### 3.7. Pilot scale production

A raw feedstock mixture was prepared and sent to Construction Testing Laboratory (CTL, Skokie, IL) where it was pelletized and fired in a batch rotary kiln. Table 6 presents the proportions of all the raw materials used for the feedstock mixture. Pellets were prepared on a disk pelletizer with a 1 m diameter, rotating at 20 rpm. A moisture content of 31.7% was used to create pellets ranging in size from 0.94 to 1.56 cm (after screening). The pellets were then dried in an oven at 110 °C before firing in the batch rotary kiln. The pelletized feedstock mixture was fired in three separate batches of 5.5–8.2 kg each. The burn conditions, including temperature and time, for each of the batches of feedstock materials fired in the rotary kiln are shown in Fig. 2. After firing was complete, the clinker samples were removed from the kiln, cooled in air, mixed with 6.1% gypsum and ground to a specific surface of 375 m<sup>2</sup>/kg, measured by the Blaine method, to make Portland cement.

ASTM C109, “Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 5 cm cube specimens),” was carried out in the UNH laboratory. ASTM C151, “Standard Test Method for Autoclave Expansion of Portland Cement,” and C191, “Standard Test Method for Time of Setting of Hydraulic Cement by Vicat Needle,” were conducted by CTL.

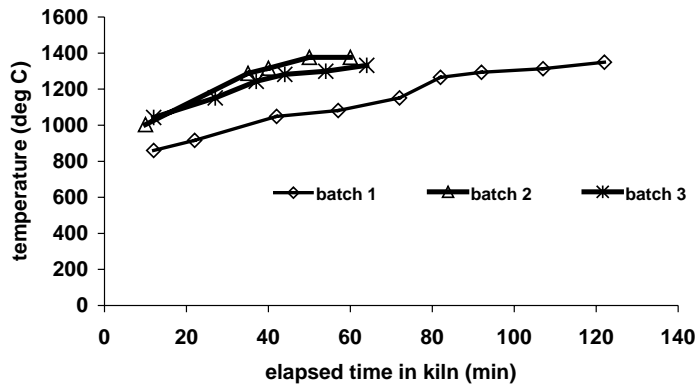


Fig. 2. Pilot scale batch rotary kiln burn conditions.

## 4. Results and discussion

### 4.1. Bench scale manufacture

Six clinker samples were tested for alite ( $3\text{CaO}\times\text{SiO}_2$ ) content using an XRPD semiquantitative RIR method described in Stutzman (1996). Three variables were studied: dredged material content, mixing technique, and firing procedures (full scale rotary kiln or lab scale muffle furnace). The purpose of testing mixing and scale variables was to evaluate the effects of the bench clinkering process employed to make the experimental (containing dredged material) clinkers.

The results for all alite data are shown in Fig. 3. Comparison of control materials fired at full scale with those fired in the lab shows (with 94% confidence) that full scale firing results in greater alite content. This may be attributed to the lack of rapid cooling in the muffle furnace. If cooling occurs too slowly, the alite phase will decompose between 1250 and 1100 °C to form a blended mixture of belite ( $2\text{CaO}\times\text{SiO}_2$ ) and lime ( $\text{CaO}$ ) (Taylor, 1997). In the laboratory, the clinker sample was left in the muffle furnace to cool to 400 °C in order to be able to handle the sample safely. This cooling process took a couple of hours. At a full scale cement plant, the clinker is cooled with an air exchanger upon exiting the rotary kiln to a temperature of at least 1100 °C to minimize decomposition of the alite (Taylor, 1997).

No statistically significant result could be attributed to mixing conditions; consequently, the proportioning and feedstock mixture preparation procedures used in the laboratory were considered representative of those employed at full scale.

Similarly, no significant difference was found between the low dredged material (low DM) clinker samples and the control clinker mixed and fired at the lab scale. However, clinker samples with medium and high dredged material replacement had alite contents significantly different than the control clinker (99% confidence).

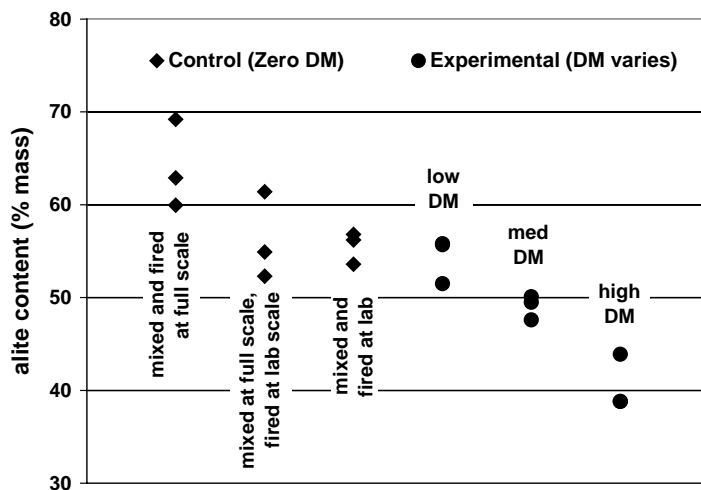


Fig. 3. Alite content in clinker samples.

There are a few possible explanations for the differences in the alite content of the dredged material clinker samples manufactured in the laboratory, the most likely of which is the high concentrations of quartz ( $\text{SiO}_2$ ) in the dredged material. The presence of quartz was noted during a qualitative XRD analysis of the dredged material; this phase had the strongest FOM value of all the minerals detected. Due to their larger size, the presence of quartz crystals in cement manufacture calls for “harder” burning conditions (Taylor, 1997); a higher maximum temperature or longer retention time may be needed to allow for proper reactions to occur. In the final stage of the clinkering process the alite is formed as the lime crystals react with the belite. (Belite is formed in the first stage after  $\text{CaCO}_3$  decomposes and reacts with the  $\text{SiO}_2$ —Taylor, 1997). This final reaction may not have been able to occur completely as the quartz content increased, resulting in lower alite contents as the dredged material content was increased. These conditions could be accounted for in the full scale in order to assure adequate alite contents in the final product.

#### 4.2. Pilot scale experiment

A single mixture containing 6.5% dredged material (dry mass basis—see Table 6) was used in the pilot scale batch experiment. In addition to the major Portland cement clinker phases,  $\text{SiO}_2$  (quartz) was also identified in pilot scale diffractograms. Although XRPD analysis detected quartz in dredged material samples, it was not detected in the full scale cement or the clinker produced at the laboratory bench scale.

The strong presence of belite peaks compared to alite was also observed in the diffractograms from the pilot scale cement. This agrees with the observation made previously for the clinker samples manufactured with dredged material at the bench scale. These results strongly suggest the alite phase may not have fully formed during the final clinkering phase; additional burn time was necessary because of the poor reactivity of the quartz present in the dredged material (Taylor, 1997). This is a particularly cogent hypothesis because the temperature in the pilot scale kiln was less than what was specified and intended for the clinkering: as shown in Fig. 1, the maximum temperature reached in the pilot scale kiln was  $1350^\circ\text{C}$ , less than the intended  $1450^\circ\text{C}$ . Another possible reason for lower alite and higher belite in the pilot scale is that the alite decomposed during cooling into a mixture of belite and lime (Taylor, 1997). Both of these scenarios could also explain the increased intensity of the belite (stronger peaks, better FOM) found in the analysis of the pilot scale cement, as compared to the cement manufactured at the full scale. With improved burn conditions and/or rapid cooling, it is probable that the alite content would increase.

Fig. 4 shows the average and standard deviation of the maximum stress values for set of each mortar cubes made from the pilot scale cement and compares these to the requirements (standard and optional) presented in ASTM C150 for a types I and II Portland cement. The original mixture was proportioned to create a type II/I cement which must meet the higher type I strength requirements (at 3 and 7 days: 28 days strength is the same as type II). The type II strength requirements are shown as a reference.

The mortar cubes made with pilot scale cement had an average maximum stress slightly less than that specified in ASTM C150 at days 3 and 7 (there is no requirement for day 1, it is just recorded) for types I and II cements. By day 28 the dredged material mortar cubes had surpassed the optional strength requirement in ASTM C150 for types I and II

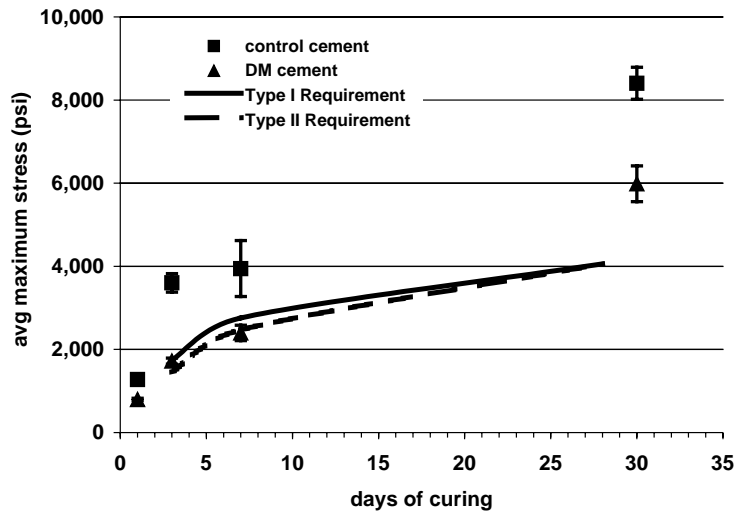


Fig. 4. Average and standard deviation of the maximum compressive stress values for mortar cubes compared to ASTM C150 requirements.

cements. The cement mortar cubes from the pilot scale manufacture did not perform as well as the full scale cement. Without a control cement manufactured under the same pilot scale conditions, it is difficult to resolve why the pilot scale cement was not as strong. Results from the qualitative XRPD analysis of the cement showed the belite peaks to be stronger and the alite peaks to be weaker than the full scale cement. Since the alite and belite are associated with good initial and final strength development, respectively (Kohlhaas, 1983), this difference could explain the weaker than required strength values measured at 3 and 7 days, and the acceptable strength value at 28 days.

A change in length of 0.08% was measured in the hydrated cement specimen under the autoclave conditions specified in ASTM C151. This is well below the 0.80% maximum expansion value in ASTM C150. The initial setting time was found to be 126 min, within the range specified in ASTM C150 of 45–375 min. The final setting time was calculated to be just over 4 h (241 min). Setting time is highly dependent on the presence of gypsum, which was not optimized for the pilot scale clinker; too little gypsum can cause rapid set which can lead to poor strength gain of the cement, and too much will cause a delay in initial setting time (and strength gain). The major clinker phase content can also influence setting time. The alite and aluminate phases are responsible for rapid hydration, while the belite and ferrite phases contribute to slow and/or moderate hydration (Kohlhaas, 1983).

The free chloride contents measured in the clinker samples manufactured in the laboratory are shown in Table 7. It was found that there was little difference between chloride contents of all clinkers, with perhaps an unexpected slight decrease in chloride concentration with increasing dredged material substitution. The free chloride contents measured in the clinker samples are all below the water soluble chloride limit in Portland cements to be used in reinforced concrete (0.15%), as well as the limit for prestressed concrete (0.06%). The

Table 7  
Free chloride content measured in bench scale clinker samples (% by mass)

| Clinker sample | Free Cl <sup>-</sup> |
|----------------|----------------------|
| Control        | 0.018                |
| Low DM         | 0.016                |
| Medium DM      | 0.014                |
| High DM        | 0.013                |

results show that the high chloride content in the dredged material should not affect the quality of the final product.

#### 4.3. Practical considerations

The results presented in this paper suggest a likely practical replacement of 3–6% of the total feedstock material (dry mass basis), considering factors of chloride scaling and SiO<sub>2</sub> burning. Using a hypothetical annual feed of 3.2 million tonnes per year (the annual feed rate of the Lafarge plant cooperating in this study), this material replacement amounts to 96,000–192,000 tonnes per year (dry mass basis). With a typical in-place water content of sediments of 127%, and assuming a bulk density of in-place sediment of 1300 kg/m<sup>3</sup>, this corresponds to a use of 166,700–333,300 m<sup>3</sup> (218,000–436,000 yd<sup>3</sup>) of dredged material per annum at this single cement production facility.

The fraction of raw materials that can be replaced is also a function of the bulk sediment chemistry and the major elemental content of the feedstocks used by the cement facility. At the Lafarge plant collaborating on this work, a 6% feedstock replacement would reduce the required amounts of fly ash, bauxite and iron by 100, 8 and 45%, respectively. A theoretical maximum was found to be 14% dredged material, which would completely replace the bauxite and fly ash feedstocks.

There are numerous additional factors that need to be considered to assess the cost and feasibility of this approach for a particular dredging operation and cement manufacturing plant. Some of the significant costs that need to be considered include the following:

- Transportation to the cement manufacturer.
- Debris removal and disposal.
- Sediment dewatering (if needed).
- Material transfer and storage on site.
- Kiln modifications for introduction of sediments at the hot end of the kiln.
- Incremental operating costs for kiln cleaning.

To balance these costs, there are two revenue streams for the cement manufacturer: raw material savings and tipping fees. Tipping fees will of course depend on the dredged material market, however, with few cost-competitive alternatives currently available, tipping fees can reasonably be expected to be US\$ 45 m<sup>-3</sup> (US\$ 35 yd<sup>-3</sup>), which is a target cost that has been set by the Port Authority of NY/NJ (this figure excludes dredging and transportation costs) (Jones et al., 2001).

## 5. Conclusions

The research reported in this manuscript demonstrates the potential of using contaminated fine-grained dredged material as a feedstock replacement in conventional Portland cement manufacture. It was shown that kiln operational conditions may have to be adjusted depending upon the quartz content of the sediments. High chloride content of the dredged material was demonstrated to not increase the chloride content of the final product, although it remains a practical manufacturing consideration. The potential of this technology to contribute significantly to the sustainable management of dredged material was demonstrated by virtue of the annual volume of material consumable and the apparent technical feasibility of the approach.

## Acknowledgements

Support for this research was provided by the NOAA-UNH Cooperative Institute for Coastal and Estuarine Environmental Technology (CICEET) located at the University of New Hampshire, NOAA grant number NA03NOS4190195. The authors would like to acknowledge the support of Lafarge Cement in Ravena, NY, and particularly the assistance of Lorraine Roberts, Ron Peck, and Jack Dwyer. The authors would also like to acknowledge the expert advice of Ann Thayer, Jennifer Kimball, and Thornton Batty of Dragon Cement in Thomaston, Maine regarding the cement manufacturing process. The assistance of the New York State Department of Environmental Conservation in collecting sediment samples is also gratefully acknowledged.

## References

- Amiran MC, Wilde CL. Sediment decontamination: evolution and practical application of BioGenesis washing technology. In: Pelli M, Porta A, Hinchee RE, editors. Proceedings of the 1st International Conference on Remediation of Contaminated Sediments, 10–12 October 2001, Venice, Italy. Battelle Press, Columbus, OH; 2002. p. 271–81.
- Bhatty JI. Role of minor elements in cement manufacture and use. Research and Development Bulletin RD109T. Skokie, IL: Portland Cement Association; 1995.
- Caponero J, Tenorio JAS. Laboratory testing of the use of phosphate-coating sludge in cement clinker. *Resour Conserv Recycl* 2000;29(3):169–79.
- Dalton JL. Evaluation of dredged material as an alternative feedstock material in portland cement manufacture at bench scale and pilot scale. Durham, NH: MS Thesis, University of New Hampshire; 2002.
- Derman JD, Schlieper HA. Decontamination and beneficial reuse of dredged material using existing infrastructure for the manufacture of lightweight aggregate. Presented at 19th Western Dredging Association Annual Meeting, Louisville, KY; 1999.
- Espinosa DCR, Tenorio JAS. Laboratory study of galvanic sludge's influence on the clinkerization process. *Resour Conserv Recycl* 2000;31(1):71–82.
- Gadayev A, Kodess B. By-product materials in cement clinker manufacturing. *Cem Concr Res* 1999;29:187–91.
- Glasser FP. UK: Aberdeen University, personal communication with University of New Hampshire; 2001.
- Hamer K, Karius V. Brick production with dredged harbour sediments: an industrial scale experiment. *Waste Manage* 2002;22(5):521–30.
- Jones KW, Feng H, Stern EA, Lodge J, Clesceri NL. Dredged material decontamination demonstration for the port of New York/New Jersey. *J Hazard Mater* 2001;85:127–43.

- Kohlhaas B. Cement engineers' handbook. Wiesbaden: Bauverlag; 1983 [van Amerongen C, trans.].
- Kozikowski R. Skokie, IL: Construction Testing Laboratories, personal communication with University of New Hampshire; 2001.
- McLaughlin DF, Dighe SV, Keairns DL, Ulerich NH. Decontamination and beneficial reuse of dredged estuarine sediment: the westinghouse plasma vitrification process. Presented at 19th Western Dredging Association Annual Meeting, Louisville, KY; 1999.
- Mischulovich A. Principal process engineer, personal communication with University of New Hampshire. Skokie, IL: CTL; 2001.
- Neville AM. Properties of concrete—fourth and final edition. UK: Longman Group Limited; 1996.
- Port Authority of NY/NJ (PANYNJ). Summary report: maintenance dredged material properties: NY/NJ Harbor Region; 1996.
- Port Authority of NY/NJ (PANYNJ) Press Center. Port Authority Board approves proposal to deliver 50-foot channels in NY–NJ Port by 2009. PR No. 103-01; 2001.
- Portland Cement Association Industry overview: economics of the U.S. Cement Industry. Portland: Portland Cement Association; 2003. [http://www.portcement.org/econ/econ\\_overview.asp](http://www.portcement.org/econ/econ_overview.asp).
- Rehmat A, Van Remmen T, Mensinger MC. Utilization of a thermochemical process for destroying hazardous chemicals in sediment from harbor dredging operations. In: Proceeding of the International Conference on Incineration and Thermal Treatment Technologies, 14–18 May 2001, Philadelphia, PA. College Park, MD: University of Maryland; 2001. p. 421–5.
- Roberts L. Environmental engineer. Lafarge Building Materials Inc., personal communication with University of New Hampshire; February 2001–March 2002.
- Roger A. UK: Blue Circle Cement, personal communication with University of New Hampshire; June 2001.
- Stutzman PE. Guide for the X-ray powder diffraction analysis of portland cement and clinker, NISTIR 5755. National Institute of Standards and Technology; 1996.
- Tang F. Principal scientist. Skokie, IL: CTL, personal communication with University of New Hampshire; 2001.
- Taylor HFW. Cement chemistry. 2nd ed. London: Thomas Telford Publishing; 1997.
- Tenorio J. Department of Metallurgical and Materials Engineering, University of Sao Paulo, Brazil, personal communication with University of New Hampshire; 2001.
- Trezza MA, Scian AN. Burning wastes as an industrial resource: their effect on Portland cement clinker. *Cem Concr Res* 2000;30(1):137–44.
- USGS. Minerals yearbook 2001: cement. Available on-line from the United States Geological Survey at <http://minerals.usgs.gov/minerals/pubs/commodity/cement/cememyb01.pdf>.
- Van Oss HG, Padovani AC. Cement manufacture and the environment. Part 1: Chemistry and technology. *J Ind Ecol* 2002;6(1):89–105.
- Van Oss HG, Padovani AC. Cement manufacture and the environment. Part 2: Environmental challenges and opportunities. *J Ind Ecol* 2003;7(1):93–126.