The calcination emissions factor is 0.53 (van Oss and Padovani 2003). Using the chemical properties shown in Table 3.2-1, the factor can be calculated as follows:

- If the typical CaO content of clinker is between 65 – 67 percent,
- Then, the amount required to produce 1 ton clinker with 67 percent CaO would be = 0.67 / 0.56 = 1.2, and the amount of CO_2 released per ton of clinker would be = 1.2 x 0.44 = 0.53.

Therefore, for every tonne of clinker produced 0.53 tonnes of CO_2 are released from limestone decomposition, as shown in the derivation above. Since limestone is an integral part of cement production, the cement industry has focused their efforts to reduce CO_2 emissions related to the thermal energy used to make clinker. Therefore, to reduce CO_2 emissions associated with concrete construction, the structural engineer should focus on minimizing the portland cement portion of cementitious materials in the mix design.

Global impact and demand — Worldwide, cement manufacturing accounts for about 7 percent of CO_2 emissions (IPCC 2005). The difference between the United States and worldwide emission percentages can largely be attributed to the greater overall energy use in the United States and its associated CO_2 emissions. Cement is a globally traded commodity and global warming is a global phenomenon, therefore it is logical to consider emissions on a worldwide basis.

To meet a demand greater than domestic supply, the United States imports cement from as far away as China. In 2003, the trade deficit for portland cement between the United States and all international partners was more than $873 million ($58 million was with China). For 2006, these numbers are significantly higher at more than $1.725 billion for world trade and $472 million for trade with China. It is worth noting that currently the second largest cement trading partner with which the United States runs a deficit is Canada (2003:$272 million; 2006 $270 million), which in some cases could be supplying cement in the United States from a location closer than the domestic supply. The increase in imported cement is alarming, and especially alarming is the growth in cement imported from China (U.S. Department of Commerce 2008).

Between 1995 and 2006 global cement production increased 80 percent from 1,390 to 2,500 Mtonnes/yr (U.S. Geological Survey 2008). Nearly half of global production is in China. Unit-based emissions vary from 0.73 to 0.99 kg of CO_2 per kg of cement, with an average of 0.90. While unit-based emissions have decreased somewhat, demand for cement has increased considerably. As a result there has been a significant net increase in CO_2 emissions by the cement industry. Demand is projected to continue to increase; even if best available practices are used to further reduce the unit-based emissions average, by the year 2050 the cement industry will contribute 9 percent of global CO_2 emissions with 70 percent of this coming from calcination (Taylor et al. 2006).

Energy performance indicator — The U.S. Environmental Protection Agency (EPA), as part of the Energy Star Industrial Focus Program, uses an Energy Performance Indicator (EPI) to rate the energy efficiency of cement manufacturers.

The EPI scores the energy efficiency of a single cement plant and allows the plant to compare its performance to that of the whole domestic industry. The tool is intended to help cement plant operators identify opportunities to improve energy efficiency, reduce greenhouse gas emissions, conserve conventional energy supplies, and reduce production costs. The tool scores a plant from 1 to 100. A score of 75 or higher deems the plant as energy efficient. Although a voluntary program, nearly half of domestic cement companies are participating in the Energy Star Industrial Focus program. Owners and engineers can encourage further industry participation by specifying cement from companies participating in this program.

Recycled materials as fuel — Cement production is mostly dependent on thermal energy, on average only 15 percent of the energy used is electrical (accounting for 10 percent of total emissions), so switching over to clean electricity sources like wind and solar will not go very far in reducing the overall energy related emissions. To supply the thermal energy required for burning clinker, mostly fossil fuels such as pulverized coal, oil and natural gas are used. Worldwide, the cement industry is increasingly using industrial wastes such as spent oils, old tires and other energy-rich alternative fuels to help meet their needs. Today, many plants meet 20 percent of their energy requirements with alternative fuels, and some have achieved 70 percent. On average, burning of waste materials currently satisfy 10 percent of the thermal energy needs of cement kilns.

These waste fuels include scrap tires, carpet, used waste oil, solvents, sludge from the petroleum industry, plastics, and agricultural wastes such as almond shells. Common wastes such as spent solvents, printing inks, paint residues, and cleaning fluids often are designated as hazardous because they are flammable; however they have high fuel value. These and other high-energy wastes, such as used motor oil and scrap tires, cannot be safely disposed in landfills. However, they can be burned to destruction as fuel in a cement kiln. Recovering their energy value in cement manufacturing helps reduce the use of fossil fuels for cement production; however, the impact on air quality has to be carefully evaluated.

The EPA has performed studies of the waste combustion technologies used in the cement industry and has also examined and revisited their impact on the environment. The EPA has previously concluded that using hazardous waste as a fuel in regulated, properly operated cement kilns poses no greater risk to human health and the environment than cement kilns that do not recover energy from waste. However, a recent EPA draft report indicates an eight-fold increase in dioxin releases compared to non-hazardous burning plants (National Center for Environmental Assessment 2003). To further complicate the issue, in some ways cement kilns are a good fit with waste fuels because the inherent alkaline scrubber effect of the system captures emissions such as hydrochloric and hydroflouric acids (Sintef and Cement Sustainability Initiative 2006). There is a large body of literature, much of it by the EPA, which discusses toxic emissions from waste combustion in cement kilns. The reader is encouraged to review this literature for more information on the subject.

Solid waste — Cement kiln dust (CKD) is created during the third stage of manufacturing when clinker is formed. Electrostatic and bag filters capture the dust for recycling. It is standard practice for CKD to be recycled at the plant back into the cement kiln as raw material. Recycling this byproduct reduces somewhat the amount of virgin limestone and other raw materials required. In the United States more than 75 percent of cement kiln dust is recycled at the plant. Other uses for CKD include agricultural soil benefaction and soil stabilization.

Engineering solutions

Each of concrete's three principal constituents — cement, aggregate, and water — can be specified to improve concrete's sustainability. Limiting the quantity of cement in a mix to that required to meet the specified design strength is an obvious and simple step. A more sophisticated step is incorporating complementary cementing materials (CCM) into the concrete mix as a substitute for cement. Properly graded aggregates will reduce cement requirements, and recycled aggregate can be used where appropriate, such as in sidewalks. Where quality and uniformity can be ensured and maintained, recycled aggregate can be used in structural concrete, also. Water reclaimed from concrete batch plant operations can be used in concrete production. Each of these engineering solutions is discussed below.

Mix design

The starting place for any concrete project, "green" or not, is a high-quality mix design. Engineers should have a solid understanding of what constitutes a good concrete mix design and what parameters they should specify or what is in the scope of the concrete supplier. Following the American Concrete Institute's *Building Code Requirements for Structural Concrete (ACI ACI 318-08) and Commentary (ACI 318R-08)* (ACI Committee 318 2008), the structural engineer is simply instructed that the mix shall be proportioned so that it meets the project requirements for workability, strength, and durability. For guidance on *how* to proportion the materials, ACI Committee 211 (Proportioning Concrete Mixtures) publishes a suite of guidelines giving standard practices for various types of concrete. *Standard Practice for Selecting Proportions for Normal, Heavyweight, and Mass Concrete* (1991) gives a good overview of the fundamentals. When durability and other environmental concerns are absent, it is normally allowable for the structural engineer to simply specify slumps, maximum aggregates sizes, and 28-day strengths. The materials and water/binder ratio that are needed to meet the slump and strength requirements are left in the hands of the concrete supplier. It cannot be overstressed that providing good durability should be a goal for every project. Furthermore, since it is relatively easy and usually cost-neutral to satisfy green criteria such as reduced CO_2 emissions, structural engineers should be proactive in improving the quality and decreasing the impact of the concrete they specify. The structural engineer must be more involved in the specification of the mix design and materials used.

When environmental considerations such as extending the service life and reducing the ecological footprint of a structure are design factors the structural engineer must have an active role in developing the mix design. With just a little background reading structural engineers can be a lot more knowledgeable about what does and does not make sense for a quality concrete mix. This education is imperative for a structural engineer to be a valuable member of an integrated design team and the point of contact with the concrete supplier. Provided here is a very brief overview of how to use concrete in the age of global warming.

Main goal — Specify elements of a mix design that will provide concrete with the needed strength, durability, and workability. This should be achieved with the most efficient use of resources and least environmental damage possible. In short, the goal is to figure out how to use the least amount of cement without compromising performance goals.

Steps to minimize the portland cement content include the following:

- *Reduce water content*: Using a lower water/binder ratio can provide the same strength with less binder. Using fly ash and superplasticizers help improve workability without increasing water.
- *Do not use portland cement as the only binder*: Using coal fly ashes, slags, natural pozzolans and ultrafines reduces the cement content without raising the water/binder ratio.
- *Reduce the paste volume (binders plus water)*: Using the largest maximum aggregate size suitable reduces the surface area the paste needs to cover. If possible use well-graded aggregates with coarse sand only.
- *Select proper strengths*: Choose target strengths (f'_c) at ages that realistically reflect the needs of the project, rather than generic design strengths at 28 days. This will reduce the cement required and allow for a greater flexibility in the use of fly ash.

Good mix design is synergistic — The strategies listed above reduce cement use while maintaining strength and workability and they will also improve the durability of the concrete and extend the service life of the structure.

Strength

Strength of a mix design depends upon a variety of factors.

Water/binder ratio (w/b) — The term *binder* is used instead of cement so that it is inclusive of cement and all other materials that contribute to the paste content that binds aggregates together. The relationship between the water/binder (w/b) ratio and strength is commonly known — the lower the w/b ratio, the higher the strength, to a point. In concrete with a low w/b ratio a higher percentage of the cement grains may never come into contact with water. Unhydrated cement does not form any binder products. In low w/b mixes, superplasticizers and water-reducing admixtures are effective at ensuring a higher portion of cement grains are hydrated.

Non-cement binders — Moderate and high strength concretes can and should be achieved using more than just portland cement. Pozzolans, slags, and ultrafines can be used in varying amounts to target specific strength needs. These complementary cementing materials and their uses are discussed in detail in the next section. The primary chemical function of pozzolans and slags is to react with the calcium hydroxide (CH) formed by portland cement and water. The secondary reaction product is calcium silicate hydrate (C-S-H), which provides a much stronger bond especially in the critical area around aggregates. C-S-H takes longer to develop and therefore design strength requirements should be adjusted as necessary. In many applications a 28-day design strength is merely convention and not a functional requirement. For these cases a 56 or even 90 day strength should be specified. If early strength (such as 7 day) is required, a mix using highly reactive pozzolans (silica fume or rice husk ash) and/or ultrafines can provide a significant boost before the later pozzolanic reaction starts.

Aggregates — Normally available aggregates are stronger than the surrounding hardened paste. Maximizing the aggregate content is consistent with economical, environmental and high strength design.

Durability

Similar to strength, the durability of a mix design depends upon a variety of factors.

Water/binder ratio (w/b) — The relationship between the w/b ratio and durability is at least as important as w/b and strength. The maximum w/b ratio that will *not* introduce voids is 0.32. This is derived from the simple facts that cement has a higher specific gravity than water (typically 3.14 vs. 1.0), and as water and cement combine the new volume of paste is the sum of their individual volumes. So every volume unit of water combined with the same volume unit of cement corresponds to a w/b = 1/3.14 or 0.32 (Mehta and Monteiro 2006). Any increase in water weight means an increase in water volume, which results in "free water." Free water is unbound water that creates unwanted voids in the concrete as it cures and contributes to drying shrinkage as it evaporates. Unwanted voids and shrinkage cracking negatively effect durability by providing conduits for corrosive ions to the interior of the concrete where steel reinforcement is put at risk.

Non-cement binders — As CH becomes C-S-H both the strength *and* the durability of the concrete will improve. It is important to note that there is only a favorable correlation between high strength and durability in concrete containing pozzolans and slags. C-S-H is a much denser product that CH, thus it makes a more impermeable and durable concrete. Further, non-cement binders such as pozzolans will lower the heat of hydration. This is crucially important especially in high ultimate strength concretes. High heats of hydration are associated with the development of thermal cracking, which will increase permeability and can dramatically limit service life. Specific durability issues such alkali-silica reactions are discussed below in complementary cementing materials.

The National Ready Mix Concrete Association provides a free software program, called Life-365, to help designers optimize the durability of their mix designs. In addition to w/b ratio, paste volume and types of binders, design parameters include exposure environments, time span, reinforcement (regular, epoxy coated, or stainless steel) and clear cover. The program calculates estimates for service life, repair schedules, and cost benefit analysis. It is a very useful tool to see the life cycle benefits of one mix against another, however this program is not a substitute for testing and should not be relied upon to generate a mix design. It can be downloaded at: http://www.nrmca.org/research/life365_instructions.asp

Aggregates — Where available aggregates have a history of alkali-silica reactions (ASR), a high portion of fly ash is recommended.

Workability

Workability of a mix design will depend upon the same factors as strength and durability.

Water/binder ratio (w/b) — Workability is the ability to successfully place or pump concrete. It is normally specified by the slump measurement. High w/b ratios generally mean higher slumps. The required slump depends on the element being formed and the degree of congestion of the rebars. The higher the slump, the looser the concrete mix is and the easier it is to place in forms and around rebar. If the slump is too high the aggregates will segregate (larger ones falling toward the bottom), which is detrimental to the integrity of the concrete. In some concrete operations slump is increased as needed by the addition of water (and usually more cement to maintain a prescribed w/b ratio). This unnecessarily increases the paste volume and is wasteful of cement. Water-reducers and superplasticizers can be used to increase workability without increasing water and cement contents. These admixtures are a good way to minimize water content and use cement more efficiently. The dosage used should follow the manufacturers' instructions, but a good rule of thumb is to limit the water-reducers or superplasticizers to 2 percent of the mass of the binders (this is determined using the mass of the solids portion of the admixtures). Too much of these admixture can cause segregation and excessive bleed water.

Non-cement binders — Fly ash should be included in mix designs to help enhance workability. Its spherical shape acts as a physical lubricant and thus aids in cement hydration. Studies dating back as far as 1952 find that for every 10 percent of fly ash added approximately 3 to 4 percent of the water can be reduced without sacrificing workability (Joshi and Lohtia 1996).

Aggregates — An excessive amount of fines can make a mix sticky to work with. Using coarser sands will reduce water demand and is the most appropriate choice for most applications.

Complementary cementing materials (CCM)

Formerly known as supplementary cementitious materials (SCM), a more current and correct terminology is complementary cementing materials (CCM).

Pozzolans are not cementitious, but they do complement cement hydration products with a secondary reaction forming calcium silicate hydrate (C-S-H) cementing compounds.

Overview — For every tonne of cement replaced by a carbon-neutral waste product, 0.9 tonnes of CO_2 emissions are avoided (Taylor et al. 2006). The practice of using CCMs in concrete has been growing in North America since the 1970s. Some of these materials are currently going to waste and using valuable space in landfills. The CCMs discussed here — fly ash, slag cement, silica fume, rice husk ash, and ultrafine minerals — are industrial by-products and, therefore, carbon neutral. These materials are considered pre-consumer recycled materials; they are not manufactured, but are sold, as the byproducts of an industrialized process.

The use of CCMs as a partial replacement for portland cement improves the environmental footprint of the concrete structure in the following ways:

- reducing its embodied energy content;
- reducing CO_2 emissions;
- reducing the amount of materials that are placed in landfill;
- reducing the environmental impacts caused by extracting virgin materials;
- reducing the environmental impacts that result from the manufacturing of portland cement clinker; and
- improving durability and extending service life.

Use — CCMs are used as a partial replacement for the portland cement in concrete and are frequently used in ready mixed concrete. Fly ash is commonly used at replacement levels up to 25 percent; slag cement up to 60 percent; and silica fume is commonly used at replacement levels up to 7 percent. The binder content of concrete is typically about 10 to 15 percent, it follows that CCM replacement of cement will range between 2 to 8 percent of the mass of the concrete.

There are two methods of inclusion for incorporating CCMs into concrete, batch mixing and blended cements. Most common in the United States is to simply specify the CCM (classified as a mineral admixture) as a separately batched ingredient. This means the CCM is added into the mix at the batch or ready mix plant. A second method (more common in Europe) is to use a blended cement in which the pozzolanic or slag material is either interground with portland cement or mechanically blended to "attain an intimate and uniform blend" (ASTM C595-08a). A third approach to incorporating CCMs is to use a combination of batch mixing and blended cements. Blended cements are discussed in detail later in this section.

Testing can determine the maximum amounts of CCMs that can be used to meet the project's performance properties specified for concrete. When CCMs are used in high proportions, test mixes should be performed earlier than usual to allow for mix design modifications. As with all mix testing, these tests are to demonstrate that the concrete mix design (using the actual project materials) satisfies project requirements.

Using CCMs is good for concrete structures and sustainable development alike, because most CCMs enhance the durability of concrete. Large proportions of pozzolans dramatically increase impermeability and thus durability. The most problematic aspect of most CCMs (type F fly ash in particular) is that curing times increase. For most projects this is not an issue, but for some ternary blend mix designs only minimal CCM inclusions are appropriate.

The properties of fly ash, slag, and most CCMs vary; the structural engineer, project contractor, and the concrete producer should use judgment, testing, and control procedures to ensure good concrete performance. The project specifications should explain the required concrete properties for each building element, the acceptable range of CCM content, and any other project-specific caveats such as when cold weather placement or exposure to de-icing chemicals is likely, or if a high pozzolan content is required to provide enhanced durability. Limits to CCM content may be set based on previous performance where applicable, and the performance of new concrete tests in the field or laboratory. Contact your local ready-mixed concrete suppliers to determine what classes of fly ash or other CCMs are available and to verify its performance in quality concrete. This may vary between suppliers. Anecdotal experience from several practitioners suggests that your local supplier may need to be encouraged to locate CCMs.

Fly ash

According to a report issued by the Portland Cement Association (PCA) "Fly ash is commonly used as a partial replacement for portland cement— or as an addition to portland cement — because it can enhance the placement, engineering properties, and durability of concrete (Marceau et al. 2002)."

Fly ash, shown in Figure 3.2-3, is a pozzolanic by-product of the combustion of pulverized coal in electric power generating plants. It is commonly used as a partial substitute for 15 to 25 percent of the portland cement in concrete. In the United States, fly ash is normally used as a mineral admixture and added to ready mixed concrete at the batch plant.

Figure 3.2-3. Fly ash (Meryman 2007)

Fly ash is the most abundant CCM worldwide and domestically. Fly ash is available throughout most of the United States; however, quantities are limited in some locations. The 2006 Coal Combustion Product (CCP) Production and Use Survey compiled by the American Coal Ash Association (2008) reports 65 Mtonnes of fly ash were generated in 2006, of which, approximately 45 percent were recycled and 35 percent were placed in landfills. Of fly ash produced, 17 Mtonnes, or 26 percent, was used in concrete products and cement. Not all fly ash is useable in concrete. Power plants with high NOx emissions controls are producing fly ash that is ammoniated. Fly ash with ammonia content greater than 100 ppm is considered a health hazard; to protect workers, contaminated ash is not acceptable for use in concrete. Several technological solutions exist that process the ash to remove the ammonia (Malhotra and Mehta 2008).

Benefits — "The use of fly ash in concrete can reduce the environmental impact of concrete and can actually improve the quality of the concrete (Marceau et al. 2002)."

Incorporating fly ash in concrete can enhance the properties of concrete. During placement, improvements to the properties of fresh concrete include the following:

- enhanced workability;
- reduced bleed water;
- resistance to segregation; and
- reduced slump loss.

For hardened concrete, the addition of fly ash provides the following benefits:

- increase long-term strength;
- reduce permeability;
- increase durability;
- reduce potential for sulfate attack; and
- reduce potential for alkali-silica reactivity.

Fly ash concretes generally have a slower rate of strength gain, due to a lower heat of hydration. This is desirable in mass concrete applications and when the atmospheric temperature is high. Lower heats of hydration correspond to a reduction in thermal micro-cracking and thus decreased permeability. As with all concrete constituents, proper use is necessary for successful concrete.

Composition and specifications — When considering fly ash, a structural engineer should understand the following:

Chemistry and mineralogy: Fly ash is primarily amorphous silicate glass containing silica, aluminum, iron, and calcium. Minor constituents are magnesium, sulfur, sodium, potassium, and carbon. Crystalline compounds are present in small amounts.

Physical properties: The relative density (specific gravity) of fly ash ranges between 1.9 and 2.8 and the color is gray or tan. It is useful to recognize, that since fly ash is lower in density than portland cement, replacement on a "per mass" basis increases the paste volume of concrete. This provides better coverage of aggregates and improves the cohesiveness and workability. Further, fly ash particles are spherical, which helps "lubricate" a mix during hydration; in effect increasing slump without increasing the w/b ratio. By holding slump and paste volume constant, these characteristics (shape and density) can be used to decrease the cement and water content of a mix, without lowering strength.

Class F fly ash: This type is a by-product of burning bituminous coal, which is generally found in the eastern portion of the United States. Class F materials are high in iron, silica, and alumina, but low in calcium (less than 10 percent CaO). Carbon contents are usually less than 5 percent.

Class C fly ash: This type is a by-product of burning the sub-bituminous coals and lignites found in western states. Class C materials are higher in calcium oxide (10 to 30 percent CaO) with carbon contents typically less than 2 percent. Due to the reactivity of the CaO content, Class C fly ashes are considered semi-cementitious. Concrete with Class C fly ash generally develops strength faster than concrete with Class F fly ash. Class C fly ash may be preferred to Class F fly ash where construction schedules demand a fast curing concrete.

Freeze-thaw: Both types vary in composition and carbon content. Fly ash used in concrete subject to freezing and thawing should have low levels of unburned carbon in order to achieve adequate air content — extra air entrainment agent may still be required because it gets absorbed and deactivated by carbon. Specifications typically limit the unburned carbon content to a maximum of 6 percent; however, market forces have typically limited this to less than 1 percent (Marceau et al. 2002).

Particle size: For optimum results a finer particle size is preferred. Particles large than 45μm are generally non-reactive. Pozzolanic activity has been shown to be directly proportional to the amount of particles finer than 10μm (Mehta 1985). ASTM C618-08a allows for a maximum of 34 percent of particles larger than 45μm as retained on a No. 325 sieve. However, it is recommended to limit this to value to a maximum of 15 percent.

Class F and Class C fly ashes meeting ASTM C618-08a, *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete,* are commonly used for general purpose concrete. ASTM C618-08a provides minimum values for the pozzolanic compounds, limits carbon content and particle size. ACI 232.2-03, *Use of Fly Ash in Concrete*, (ACI Committee 232 2003) provides an extensive review of fly ash.

Use — Fly ash often replaces cement at 15 to 25 percent by mass of binder material, that is, the total of cement, fly ash, and other complementary cementing materials. Replacement rates vary with the reactivity of the ash and the desired effects