APPENDIX A:

OVERVIEW OF PORTLAND CEMENT AND CONCRETE

Overview of Portland Cement and Concrete

Although the terms “cement” and “concrete” are often used interchangeably, cement is actually an ingredient of concrete. Cements are binding agents in concretes and mortars. Concrete is an artificial rock-like material, basically a mixture of coarse aggregate (gravel or crushed stone), fine aggregate (sand), cement, air, and water. The term portland cement is a general term used to describe a variety of cements used today. Portland cements are hydraulic cements, which means they will set and harden by reacting chemically with water through hydration.

Current (2004) world total annual production of hydraulic cement is about 2 billion metric tons (Gt), with production spread unevenly among more than 150 countries. This quantity of cement is sufficient for about 14 to 18 Gt/yr of concrete (including mortars), and makes concrete the most abundant of all manufactured solid materials. The current yearly output of hydraulic cement is sufficient to make about 2.5 metric tons per year (t/yr) of concrete for every person worldwide (van Oss, 2005).

Cement and Cement Manufacturing

Hydraulic cements are the binding agents in concretes and most mortars and are thus common and critically important construction materials. Hydraulic cements are of two broad types: those that are inherently hydraulic (i.e., require only the addition of water to activate), and those that are pozzolanic. The term pozzolan (or pozzolanic) refers to any siliceous material that develops hydraulic cementitious properties in the presence of lime [$Ca(OH)_2$]. This includes true pozzolans and latent cements. The difference between these materials is that true pozzolans have no cementitious properties in the absence of lime, whereas latent cements already have some cementitious properties, but these properties are enhanced in the presence of lime. Pozzolanic additives or extenders can be collectively termed supplementary cementitious materials (SCM). (van Oss, 2005)

Portland cement is the most commonly manufactured and used hydraulic cement in the United States (and the world). It is manufactured through the blending of mineral raw materials at high temperatures in cement rotary kilns. Rotary kilns produce an intermediate product called “clinker.” Clinker is ground to produce cement. By modifying the raw material mix and, to some degree, the temperature of manufacture, slight compositional variations in the clinker can be achieved to produce portland cements with varying properties

Similar varieties of portland cement are made in many parts of the world but go by different names. In the United States, the different varieties of straight portland cement are denoted per the American Society for Testing and Materials (ASTM) standard C-150 as:

- Type I: general use portland cement. In some countries, this type is known as ordinary portland cement.
- Type II: general use portland cement exhibiting moderate sulfate resistance and moderate heat of hydration.
- Type III: high early strength portland cement.

- Type IV: portland cement having a low heat of hydration.
- Type V: portland cement having high sulfate resistance.

For Types I, II, and III, the addition of the suffix A (e.g., Type IA) indicates the inclusion of an air entraining agent. Air entraining agents impart a myriad of tiny bubbles into the concrete containing the hydrated cement, which can offer certain advantages to the concrete, especially improved resistance to freeze-thaw cracking. In practice, many companies market hybrid portland cements; Type I/II is a common hybrid and meets the specifications of both Types I and II. Another common hybrid is Type II/V.

Blended Cements

Blended cements (called composite cements in some countries) are intimate mixes of a portland cement base (generally Type I) with one or more SCM extenders. The SCM commonly makes up about 5% to 30% by weight of the total blend, but can be higher.

In blended cements, the SCM (or pozzolans) are activated by the high pH resulting from the hydroxide ions released during the hydration of portland cement. The most commonly used SCM are volcanic ashes called pozzolana, certain types of fly ash (from coal-fired power plants), ground granulated blast furnace slag (GGBFS)—now increasingly being referred to as slag cement—burned clays, silica fume, and cement kiln dust (CKD). In general, incorporation of SCM with portland cement improves the resistance of the concrete to chemical attack, reduces the concrete's porosity, reduces the heat of hydration of the cement (not always an advantage), potentially improves the flowability of concrete, and produces a concrete having about the same long-term strength as straight portland cement-based concretes. However, SCM generally reduce the early strength of the concrete, which may be detrimental to certain applications (van Oss, 2005).

Blended cements either can be prepared at a cement plant for sale as a finished blended cement product, or by doing the blending within a concrete mix. In fact, most of the SCM consumption by U.S. concrete producers is material purchased directly for blending into the concrete mix. Concrete producers in the United States buy relatively little finished blended cement.

The designations for blended cements vary worldwide, but those currently in use in the United States meet either ASTM Standard C-595, C 989 or C-1157. ASTM Standard C-595 defines several types of blended cements. The main designations include (van Oss, 2005):

- Portland blast furnace slag cement (IS). Contains 25% to 70% GGBFS.
- Portland-pozzolan cement (IP and P). Contains a base of portland and/or IS cement and 15% to 40% pozzolans.
- Pozzolan-modified portland cement (I(PM)). The base is portland and/or Type IS cement with a pozzolan addition of less than 15%.
- Slag-modified portland cement (I(SM)). Contains less than 25% GGBFS.

- Slag cement (S).[1] GGBFS content of 70% or more. Type S can be blended with portland cement to make concrete or with lime for mortars; the latter combination would make the final cement a pozzolan-lime cement.

Chemical Composition of Portland Cement

Modern straight portland cement is a very finely ground mix of portland cement clinker and a small amount (typically 3% to 7%) of gypsum (calcium sulfate dihydrate) and/or anhydrite (calcium sulfate). Cement chemistry is generally denoted in simple stoichiometric shorthand terms for the major constituent oxides. Table A-1 provides the shorthand notation for the major oxides in the cement literature. Table A-1 also shows the typical chemical composition of modern portland cement and its clinker. For clinker, the oxide compositions would generally not vary from the rough averages shown by more than 2% to 4%. The oxide composition of portland cement would vary slightly depending on its actual gypsum fraction or whether any other additives are present.

Table A-1: Chemical Shorthand and Composition of Clinker and Portland Cement

Oxide Formula	Shorthand Notation	Percentage by Mass in Clinker	Percentage by Mass in Cement*
CaO	C	65	65.0
SiO_2	S	22	22.0
Al_2O_3	A	6	6.0
Fe_2O_3	F	3	3.0
MgO	M	2	2.0
$K_2O + Na_2O$	K + N	0.6	0.6
Other (including SO_3^-)	…(…$\bar{S}$)	1.4	3.6
H_2O	H	“nil”	1.0

* Based on clinker shown plus 5% addition of gypsum ($CaSO_4 \cdot 2H_2O$).

Source: van Oss, 2005

Mineralogy of Portland Cement and Its Clinker

The major oxides in clinker are combined essentially into just four cement or clinker minerals, denoted in shorthand: tricalcium silicate or ‘alite’ (C_3S); dicalcium silicate or ‘belite’ (C_2S); tricalcium aluminate (C_3A); and tetracalcium aluminoferrite (C_4AF). These formulas represent averages, ignoring impurities commonly found in actual clinker. It is the ratios of these four minerals (and gypsum) that determine the varying properties of different types of portland cements. Table A-2 provides the chemical formulas and nomenclature for the major cement oxides as well as the function of each in cement mixtures.

[1] True Type S cements are no longer commonly made in the United States. Instead, the name slag cement (but with no abbreviation) is now increasingly given to the unblended 100 % GGBFS product (van Oss, 2005). ASTM C989 now governs slag cement (GGBFS).

Table A-2: Typical Mineralogical Composition of Modern Portland Cement

Chemical Formula	Oxide Formula	Shorthand Notation	Description	Typical Percentage	Mineral Function
Ca_3SiO_5	$(CaO)_3SiO_2$	C_3S	Tricalcium silicate (‘alite’)	50-70	Hydrates quickly and imparts early strength and set
Ca_2SiO_4	$(CaO)_2SiO_2$	C_2S	Dicalcium silicate (‘belite’)	10-30	Hydrates slowly and imparts long term (ages beyond 1 week) strength.
$Ca_3Al_2O_6$	$(CaO)_3Al_2O_3$	C_3A	Tricalcium aluminate	3-13	Hydrates almost instantaneously and very exothermically. Contributes to early strength and set.
$Ca_4Al_2Fe_2O_{10}$	$(CaO)_4Al_2O_3Fe_2O_3$	C_4AF	Tetracalcium aluminoferrite	5-15	Hydrates quickly. Acts as a flux in clinker manufacture. Imparts gray color.
$CaSO_4 \cdot 2H_2O$	$(CaO)(SO_3) \cdot (H_2O)_2$	$C\bar{S}H_2$	Calcium sulfate dihydrate (gypsum)	3-7	Interground with clinker to make portland cement. Can substitute anhydrite ($C\bar{S}$). Controls early set.
$CaSO_4$	$(CaO)(SO_3)$	$C\bar{S}$	Anhydrous calcium sulfate	0.2-2	

Source: van Oss, 2005.

As indicated in Table A-2, some of the minerals in clinker serve different functions in the manufacturing process while others impart varying final properties to the cement. The proportion of C_3S, for example, determines the degree of early strength development of the cement. The “ferrite” mineral’s (C_4AF) primary purpose, on the other hand, is to lower the temperature required in the kiln to form the C_3S mineral, and really does not impart a specific property to the cement. Table A-3 presents the common mineralogical compositions of Types I through IV cements and the unique properties of each type.

Table A-3: Typical Range in Mineral Composition in Portland Cements

ASTM C-150 Cement Type	Clinker Mineral Percent*				Properties of Cement
	C_3S	C_2S	C_3A	C_4AF	
I	50-65	10-30	6-14	7-10	General purpose
II	45-65	7-30	2-8	10-12	Moderate heat of hydration, moderate sulfate resistance
III	55-65	5-25	5-12	5-12	High early strength**
IV	35-45	28-35	3-4	11-18	Low heat of hydration
V	40-65	15-30	1-5	10-17	High sulfate resistance

* Range of minerals is empirical and approximate rather than definitional.
** High early strength is typically achieved by finer grinding of Type I cement.

Source: van Oss, 2005.

Physical Properties of Portland Cement

Portland cement consists of individual angular particles with a range of sizes, the result of pulverizing clinker in the grinding mill. Approximately 95% of cement particles are smaller than 45 micrometers, with the average particle around 15 micrometers. The fineness of cement affects the amount of heat released during hydration. Greater cement fineness (smaller particle size) increases the rate at which cement hydrates and thus accelerates strength development. Except for AASHTO M 85, most cement standards do not have a maximum limit on fineness, only a minimum. The fineness of Types I through V portland cement are shown in Table A-4 (Kosmatka, 2002). Values are expressed according to the Blaine air-permeability test (ASTM C 204 or AASHTO T 153), which indirectly measures the surface area of particles per unit mass.

Table A-4: Fineness of Portland Cement

ASTM C - 150 Cement Type	Fineness (cm^2/g, Blaine)	
	Range	Mean
I	3,000-4,210	3,690
II	3,180-4,800	3,770
III	3,900-6,440	5,480
IV	3,190-3,620	3,400
V	2,750-4,300	3,730

The specific gravity of portland cement typically ranges from 3.10 to 3.25, with an average of 3.15. Bulk densities can vary significantly depending on how the cement is handled and stored. Reported bulk densities range from 830 to 1,650 kg/m^3 (Kosmatka, 2002).

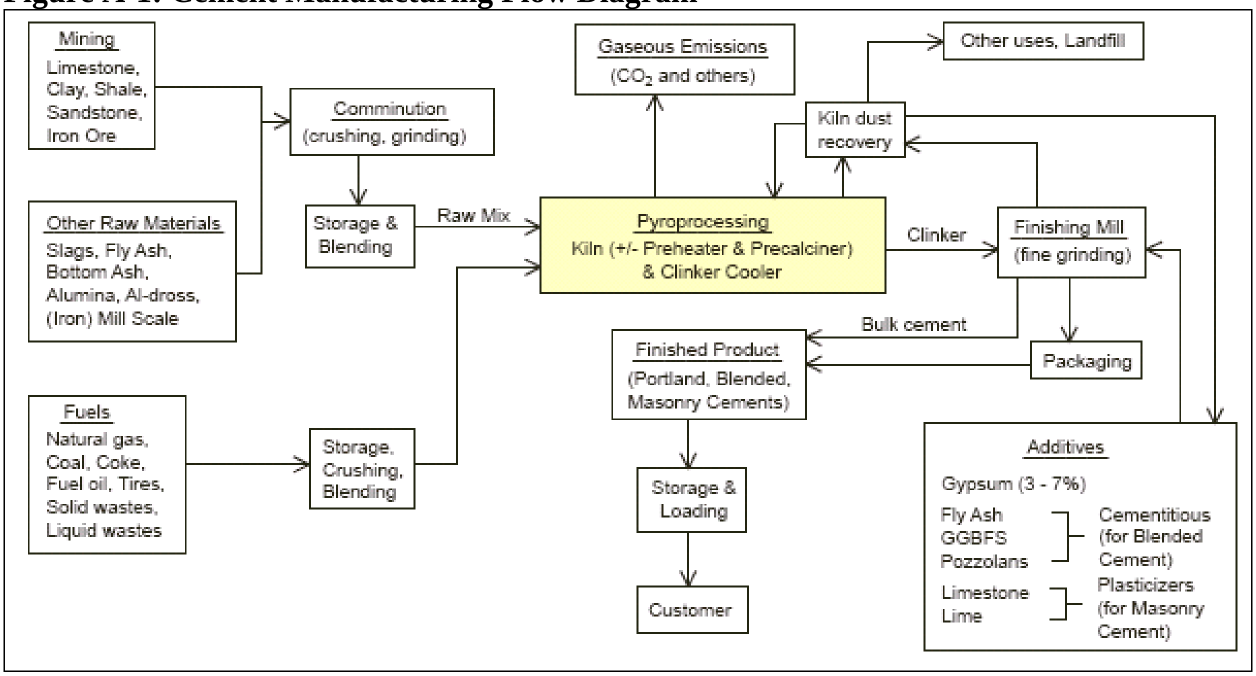
The Clinker Manufacturing Process

Portland cement manufacturing is a two-step process beginning with the manufacture of clinker followed by the fine grinding of the clinker with gypsum and other additives to make the finished cement product. Grinding can occur on site or at offsite grinding plants.

The first step in clinker manufacture is the quarrying, crushing, and proportioning of raw materials. Due to the low unit value of these raw materials, they typically are mined within a few miles of the cement plant. The cost of transport renders long-distance transport of these low-cost raw materials uneconomical.

Once the raw mix, or raw meal, is prepared, it is fed into a cement kiln and converted into the clinker minerals through a thermochemical conversion, referred to as pyroprocessing because it involves direct flame interaction. Figure A-1 provides a generalized flow diagram of the cement manufacturing process (van Oss, 2005).

Figure A-1: Cement Manufacturing Flow Diagram



The raw materials for clinker manufacture consist primarily of materials that supply four primary oxides: Calcium oxide (CaO), silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), and ferric oxide (Fe_2O_3). The composition of the raw mix typically includes about 80% calcium carbonate, about 10% to 15% silica, and small amounts of alumina and iron. Depending on the quality and quantity of these oxides available to the facility, other raw materials, referred to as accessory or sweetener materials, are added to correct for any deficiencies in the primary raw materials. Certain types of fuel burned in the cement kiln can also contribute oxides (e.g., ash from coal combustion contributes silica oxides, steel belts in waste tires contribute iron oxide).

Calcium oxide (CaO or simply C in shorthand) is the primary ingredient in clinker, comprising about 65% of clinker by mass. A cement plant typically examines its source of C (typically limestone, marl, or chalk) and determines what other oxides need to be added to achieve the desired clinker composition. Clay, shale, slate, or sand provide the silica and alumina component, while iron, mill scale, or other ferrous materials provide the iron content. Preparing the raw mix for clinker production requires constant sampling, chemical testing, and adjusting of the inputs to maintain the desired clinker composition.

On average, it takes about 1.7 tons of nonfuel raw materials to produce 1 ton of clinker. Of the 1.7 tons of raw materials, approximately 1.5 tons is limestone or calcium oxide rich rock (van Oss, 2005). The lost mass takes the form of carbon dioxide (CO_2) driven off by the calcination of limestone and the generation of CKD. Nearly one ton of CO_2 is produced for every ton of clinker manufactured (van Oss, 2005). The CKD that is produced during clinker manufacture is carried "up the stack" and captured by emission control devices. A large portion of the CKD, though not all of it, is returned to the kiln as part of the feed stream.

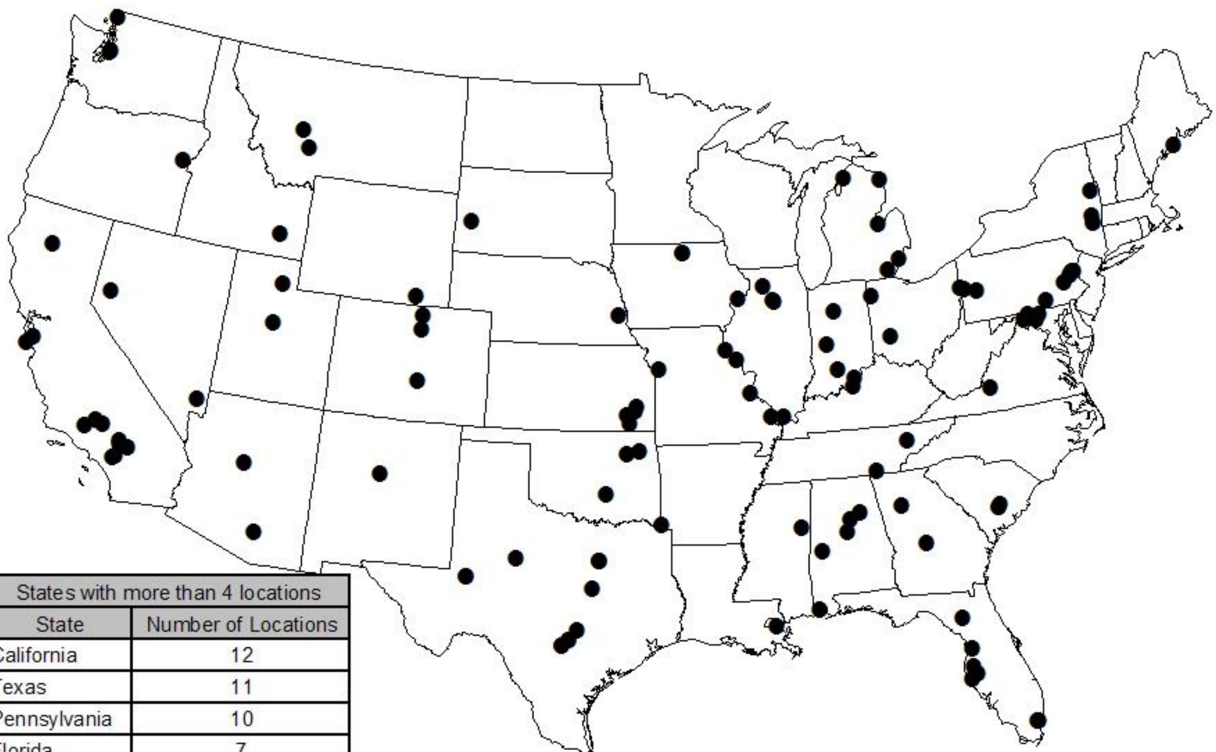
Manufacture of Finished Cement from Clinker

After clinker has been cooled to about 100°C, it is ready to be ground into finished cement in a grinding mill, more commonly referred to as a finish mill. Generally, separate grinding and/or blending finish mill lines will be maintained at a plant for each of its major product classes (finished portland cements, blended cements, masonry cements, ground slag). Additives that commonly require grinding at the mill include gypsum, limestone, granulated blast furnace slag, and natural pozzolans. Additives that generally do not require significant grinding include coal fly ash, GGBFS, and silica fume, but the finish mill does provide intimate mixing of these with the portland cement base.

Production

The U.S. Geological Survey (USGS) estimated that in 2005 approximately 97.5 million metric tons (Mt) of portland plus masonry cement was produced at 113 plants in 37 states in the United States. The reported final production of masonry plus portland cement was 99.3 Mt, with portland cement alone accounting for 93.9 Mt of this total (van Oss, 2007). Figure A-2 shows the locations of U.S. cement plants in 2005 based on information provided by the Portland Cement Association (PCA, 2006). Appendix C contains a listing of cement plants operating in the United States in 2005. The estimated value of cement production for 2005 was about $8 billion. The final reported actual value for portland plus masonry cement production in 2005 was $11.6 billion. Of this total, $10.9 billion was for portland cement alone (van Oss, 2007). Most of the cement was used to make ready mixed concrete (75%), while 14% went to concrete manufacturers, 6% to contractors, 3% to building materials dealers, and 2% to other users. Clinker production occurred at 107 plants, with a combined annual capacity of about 103 million tons. Actual U.S. cement imports in 2005 were reported at 30.4 Mt (excluding Puerto Rico), and clinker imports were 2.86 Mt (van Oss, 2007). Average mill prices for cement in 2005 were about $84 per ton. More than 172 million tons of raw materials were used to produce cement and clinker in the United States in 2004. Table A-5 summarizes U.S. cement statistics for the years 2000 through 2005 (USGS, 2001; 2002; 2003; 2004; 2005; 2006). Table A-6 summarizes raw materials used in the United States in 2003 and 2004 to produce cement and clinker (van Oss, 2004).

Figure A-2: U.S. Cement Plants



States with more than 4 locations	
State	Number of Locations
California	12
Texas	11
Pennsylvania	10
Florida	7
Alabama	5
Michigan	5
Missouri	5

Table A-5: U.S. Cement Statistics

Year	2000	2001	2002	2003	2004	2005
	--------------------------*million metric tons*----------------------------					
Estimated Cement Production	87.8	88.9	89.7	92.8	97.4	97.5*
Clinker Production	78.1	78.8	81.5	81.9	86.7	87.4
Imports of Cement	24.6	23.7	22.2	21.0	25.4	29.0
Imports of Clinker	3.7	1.8	1.6	1.8	1.6	2.8
Exports of Cement and Clinker	0.74	0.75	0.83	0.84	0.82	0.80
Average Price, Mill Value, $/ton	78.56	76.50	76.00	75.00	79.50	84.00

* Actual total masonry plus portland cement final production for 2005 is reported at 99.3 Mt, of which 93.9 Mt was for portland cement alone.

Table A-6: Raw Materials Used in Producing Clinker and Cement in the United States

Raw Materials	2003		2004	
	Clinker	**Cement**	**Clinker**	**Cement**
	-----------------------*thousand metric tons*-------------------			
Limestone	109,000	1,530	125,000	1,810
Cement rock	12,700	44	12,700	2
Cement kiln dust	289	149	333	165
Lime	22	27	24	29
Other calcareous	235	32	23	19
Clay	3,950	--*	4,740	--
Shale	2,630	8	3,700	29
Other aluminous	618	--	661	--
Ferrous, iron ore, pyrites, millscale, other	1,340	--	1,340	--
Sand and calcium silicate	2,860	2	3,150	--
Sandtone, quartzite soils, other	587	2	878	6
Coal Fly ash	2,250	39	2,890	77
Other ash, including bottom ash	1,100	--	1,050	--
Granulated blast furnace slag	17	333	104	345
Other blast furnace slag	214	--	189	--
Steel slag	448	--	401	--
Other slags	113	--	53	--
Natural rock pozzolans	--	25	--	6
Other pozzolans	129	49	114	19
Gypsum and anhydrite	--	5,000	--	5,300
Other, not elsewhere classified	70	68	106	98
Clinker, imported	--	4,240	--	7,530
Total	**139,000**	**11,500**	**157,000**	**15,400**

*-- Indicates none reported.

Concrete

Concrete is basically a mixture of two components: aggregate and cement paste. The cement paste, comprised of a binder (usually portland cement) and water, binds the aggregates (usually sand and gravel or crushed stone) into a rocklike mass as the paste hardens. The paste hardens because of a chemical reaction, called hydration, between the cement and water.

The National Ready Mixed Concrete Association (NRMCA) estimates that ready mixed concrete production in the United States was approximately 349 million cubic meters in 2005. NRMCA estimates that there are approximately 6,000 ready mixed concrete plants in the United States, and that annual ready mixed concrete production is valued at more than $30 billion. Table A-7 shows ready mixed concrete production by state in 2005 as reported by NRMCA. USGS estimates that total concrete production in the United States in 2005 was valued at more than $48 billion (USGS, 2006). Although there are no data available on the amount of concrete placed annually in the United States, based on U.S. cement sales it can be estimated to be nearly one billion metric tons per year.

Table A-7: Ready Mixed Concrete Production by State (2005)

State	Production (million cubic meters)	Percent of National Production	State	Production (million cubic meters)	Percent of National Production
Alabama	4.9	1.4%	Nebraska	3.8	1.1%
Alaska	0.5	0.1%	Nevada	7.3	2.1%
Arizona	13.1	3.8%	New Hampshire	0.6	0.2%
Arkansas	3.4	1.0%	New Jersey	5.5	1.6%
California	43.4	12.4%	New Mexico	2.5	0.7%
Colorado	7.3	2.1%	New York	8.9	2.6%
Connecticut	2.2	0.6%	North Carolina	8.2	2.4%
Delaware	0.6	0.2%	North Dakota	1.0	0.3%
District of Columbia	0.6	0.2%	Ohio	10.9	3.1%
Florida	31.6	9.1%	Oklahoma	4.5	1.3%
Georgia	12.4	3.6%	Oregon	3.5	1.0%
Hawaii	1.2	0.3%	Pennsylvania	9.3	2.7%
Idaho	2.0	0.6%	Puerto Rico	5.2	1.5%
Illinois	11.6	3.3%	Rhode Island	0.5	0.1%
Indiana	6.1	1.8%	South Carolina	5.0	1.4%
Iowa	5.4	1.6%	South Dakota	1.4	0.4%
Kansas	4.3	1.2%	Tennessee	6.0	1.7%
Kentucky	4.2	1.2%	Texas	40.8	11.7%
Louisiana	5.5	1.6%	Utah	4.3	1.2%
Maine	0.7	0.2%	Vermont	0.4	0.1%
Maryland	4.4	1.3%	Virginia	7.5	2.1%
Massachusetts	3.5	1.0%	Washington	6.3	1.8%
Michigan	8.2	2.4%	West Virginia	1.4	0.4%
Minnesota	5.7	1.6%	Wisconsin	6.6	1.9%
Mississippi	3.0	0.9%	Wyoming	1.3	0.4%
Missouri	8.0	2.3%	Other	1.2	0.3%
Montana	1.1	0.3%	**Total**	**348.8**	**100.0%**

The character of concrete is determined by the quality of the cement paste (i.e., the cement and water mixture). The water to cement ratio—the weight of the mixing water divided by the weight of the cement—plus the quality and type of cement determines the strength of the paste, and hence the strength of the concrete. High-quality concrete is produced by lowering the water-cement ratio as much as possible without sacrificing the workability of fresh concrete. Generally, using less water produces a higher quality concrete provided the concrete is properly placed, consolidated, and cured.

For a typical concrete mix, 1 metric ton of cement (powder) will yield about 3.4 to 3.8 cubic meters of concrete weighing about 7 to 9 metric tons (i.e., the density is typically in the range of about 2.2 to 2.4 metric tons per cubic meter). Although aggregates make up the bulk of the mix, it is the hardened cement paste that binds the aggregates together and contributes virtually all of the strength of the concrete, with the aggregates serving largely as low cost fillers. The strengths of the cement paste is determined by both the quality and type of the cement and the water-to-cement ratio (van Oss, 2005).