Basalt as an alternative to limestone in the production of Portland cement

Sophia L. Shapiro

Avenues: New York, 455 W. 23rd St. Apt 17 AB, New York, 10011, USA

sshapiro19@avenues.org

ABSTRACT: A wide range of environmental consequences will occur due to anthropogenic climate change caused by carbon dioxide emissions.[1] Cement production accounts for 6% of these carbon emissions, releasing around 2.25 x 10^9 tons of carbon dioxide annually.[2] When limestone is heated, it emits CO_2 into the atmosphere through a process called calcination, due to the prevalence of calcium carbonate.[3] Scientists are aware of this problem, however there is no sign that the cement industry will change. Cement is the primary ingredient in concrete, and concrete is the second most consumed substance on Earth after water.[4] This paper proposes the use of basalt as the primary ingredient in the production of Portland cement. Through the synthesis of cement with basalt and following calculations, the following paper concluded that if limestone were substituted for basalt, 3.9375 x 10^8 metric tons of CO_2 would be saved. These findings support the thesis that using basalt as the primary ingredient in cement would be a viable comfortable conservation solution.

KEYWORDS: Climate change; Carbon dioxide; Cement; Basalt; Calcination; Hydration

Introduction. In 2014, global CO_2 emissions from industrial processes were around 37.5 x 10^9 tons; 2.25 x 10^9 tons of which were from cement production.5 Half of these emissions were due to the burning of fossil fuels, while the other half is accounted for by the calcination process.[6] During the calcination process, limestone used in cement is heated, and the carbon present in the rock is released and oxidized to form CO^2 and quicklime:

$$CaCO_3 \rightarrow CaO + CO_2$$

While there are some existing solutions to this problem, none of them are comfortable conservation solutions. The term "comfortable conservation" is used to classify a type of solution that accomplishes the set goal without disturbing daily life, oftentimes even improving it. The method most often discussed involves blending other materials with limestone to reduce emissions from the limestone itself. This technique is called blended cement. Blended cement involves replacing a percentage of the limestone primarily with fly ash. Fly ash is produced when coal is heated to temperatures as high as 2800 degrees Fahrenheit.[7] In this way, fossil fuels must be burned to produce the fly ash. This method, however, does cost less than normal Portland cement.

Portland cement costs vary from around $50 to $75 per ton, while fly ash prices range from $15 to $40 per ton.[8] Unlike Portland cement, a major portion of the cost of fly ash is in transportation, as is demonstrated by the increased cost for fly ash in remote locations. The use of fly ash, however, is probably not a solution to decreasing carbon emissions. This technology has been around for years, but because of the transportation and the decrease in strength of the cement, many companies prefer to use limestone.[9]

Basalt and Portland Cement Chemical Composition. Basalt is a fine grained· igneous rock composed mostly of plagioclase and pyroxene minerals· Plagioclase is a term used to classify a group of minerals that are homogeneous mixtures of albite and anorthite· In addition· basalt also contains high levels of magnesium· silica· and iron.[10] Unlike the limestone used in cement· there is no exact chemical formula for the composition of basalt·

Portland cement is essentially composed of crushed and heated limestone. Limestone is chemically represented as $CaCO_3$. Lime (CaO) is derived from the limestone, and oftentimes silica, iron, and magnesium are added depending on the desired strength and composition. Calcium oxide is the largest component of cement, accounting for an average of 63.81% of its composition.[11]

In order to significantly reduce the emissions from calcination, basalt would be an ideal replacement for carbon-emitting limestone. Components of basalt such as iron, magnesium, and silica are all normally found in cement, but the lack of calcium carbonate makes it an appropriate substitute. Since all of the essential components to cement are present in this one igneous rock, only a small percentage of lime would be needed. However, about 50% of basalt is silica, which is often added to Portland cement to strengthen the mixture.[12] Since there is a lack of calcium carbonate in basalt, no carbon dioxide can be produced from its heating. However, supplemental lime would be needed to strengthen the cement.

The Production of Portland Cement. The process of cement production, demonstrated in **figure 1** below, begins

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with the extraction of limestone. The proposed solution would start with basalt instead. Once the natural rocks or minerals are extracted, they are sent to a production facility where they are crushed through a milling process and stored in large chambers called silos. This fine powder, known as raw meal, is then preheated and sent to a kiln. The kiln is heated between 950-1500 degrees Celsius. Chemical reactions take place during the heating process to form cement clinker. After being processed at such high temperatures, the initial oxides (CaO, SiO_2, Al_2O_3, and Fe_2O_3), then present in the form of mineral oxides: alite ($3CaO\bullet SiO_2$, C_3S), belite ($2CaO\bullet SiO_2$, C_2S), celite ($3CaO\bullet Al_2O_3$, C_3A), and felite ($4CaO\bullet Al_2O\bullet Fe_2O_3$, C_4AF).[13] The kiln itself is angled at 3 degrees allowing the clinker to pass through. Upon exiting, the clinker is cooled and then ground again to produce cement. A small amount of gypsum is usually added, which determines how the cement will set.[14] Without the addition of gypsum, C_3A will react quickly with water, resulting in the flash setting of concrete. Finally, the cement is packaged and transported to the desired locations.[15]

Hydration. These reactions are exothermic, and therefore generate heat.[16] During cement production, sources of calcium oxide and silica are finely ground, mixed, and pyro processed, or subjected to high temperatures. During this step, calcium oxide and silica react to form dicalcium silicate.[17] However, not all of the calcium oxide is consumed in the reaction and reacts with the intermediate dicalcium silicate to form Tricalcium silicate, leaving excess calcium oxide. Oftentimes, there is again excess calcium oxide remaining in the cement clinker, known as “free lime”.[18] During hydration, water reacts with this free lime to form calcium hydroxide, a preliminary reaction of the hydration process:

$$CaO + H_2O \rightarrow Ca(OH)_2$$

In addition to the hydration of free lime C_3S and C_2S will also hydrate, producing the binding materials that give concrete its strength.

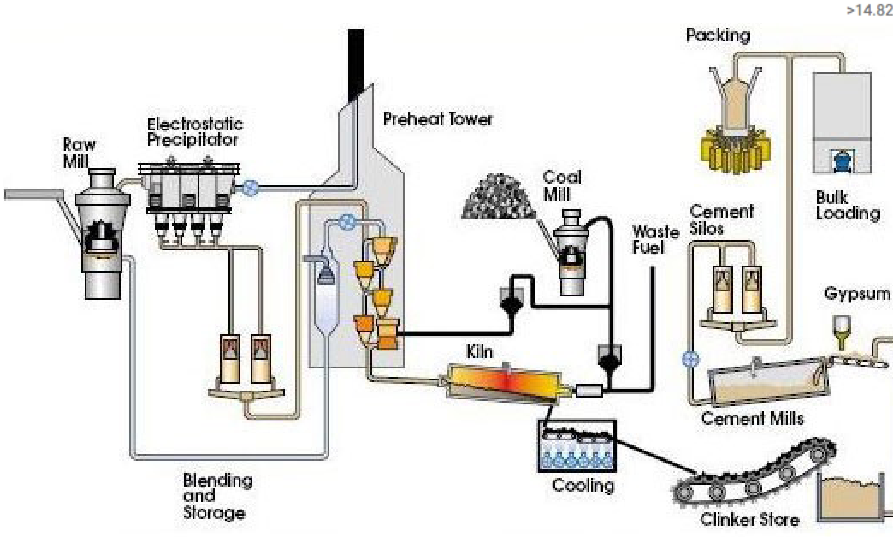

Figure 1. Cement production process.

When packaged, the Portland cement is anhydrous.[19] In order to produce concrete, the Portland cement is mixed with sand, gravel and water. When mixed with water, a hydration reaction occurs involving multiple reactions, where the products of the intermediates bond to form a solid mass.

Results and Discussion. Table 1 contains each sample with according ratio, and the pressure required to break the cement. These findings are graphed in Figure 3, which demonstrate the increase in strength with addition of lime. The dried cement samples, indented where the force probe was, are shown in Figure 4.

Sample #	Percent CaO	Percent Basalt	Percent Water	Pascals Required
1	5%	70%	25%	8.14MPa
2	5%	70%	25%	7.47MPa
3	10%	65%	25%	8.98MPa
4	15%	60%	25%	9.77MPa
5	20%	55%	25%	11.67 MPa
6	25%	50%	25%	>14.82MPa
7	60%	0%	40%	>14.82MPa

Table 1. Ratios tested and the according pascals required to break the cement.

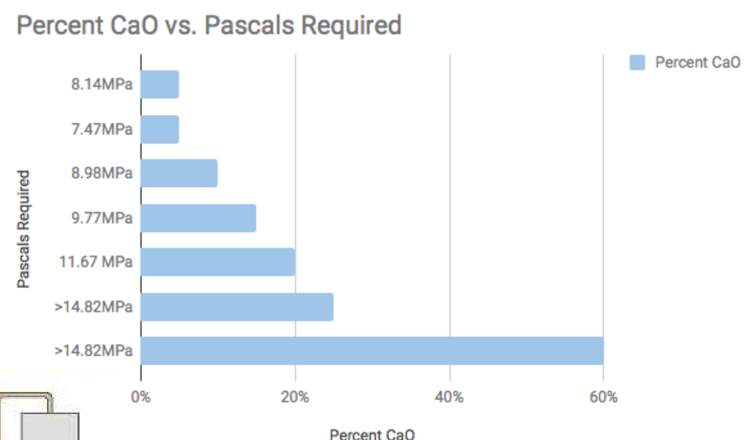

Figure 3. Relationship between the percentage of calcium oxide and the Pascals required to break the cement.

These results shown in both the table and graph demonstrate how the addition of lime strengthens the cement. However, after 25%, the samples require similar amounts of force to break, since basalt contributes an additional 10% CaO. If 25% of lime were used in the production of cement instead of the 60% found in Portland cement now, 3.9375 x 10[8] tons of carbon dioxide would be conserved, according to the following calculation:

$$(2.25x10^2)(0.35) = 3.9375x10^8 \text{ metric tons}$$

Conclusion. In conclusion, replacing the majority of limestone in cement with basalt would be

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Figure 4. Basalt and calcium oxide samples of varying ratios. Percent calcium oxide for top row left to right: 25%, 20%, 15%. Bottom row left to right: 10%, 10%, 5%.

an ideal way to combat climate change. While the proposed solution would greatly reduce carbon emissions, there is an urgent need for further research in this field. Basalt is currently used predominantly as an aggregate for construction projects, as well as cut into thin slabs for tiles and other stone objects, but so far has had limited use as the primary component of cement.[21] Research should be conducted on the carbon sequestration properties of basalt, and how this could both positively and negatively affect the outcome. While climate change will continue to progress, the use of basalt in cement would make a contribution that might mitigate the effects of climate change in the long term.

Methods and Materials. In order to validate the usability of basalt as an alternative to limestone, multiple experiments were conducted to establish valid ratios of basalt to calcium oxide. The basalt and calcium oxide were ordered online, from Alibaba group and Carolina Biological Supplies Company respectively. The goal of this experiment was to produce a strong cement with as little calcium oxide possible. To do so, five different ratios were tested, starting with 5% calcium oxide and increasing the amount by intervals of 5% until a suitable result was acquired. The water content was held at a constant 25% of the mixture, and the basalt changed according to the percent calcium oxide. Each sample was measured using a 1:1 ratio of grams to mL, the total amount being 100 per sample.

For the first sample, 5 grams of calcium oxide was weighed and then added to a plastic container. This was followed by 25 mL of water, and 70g of basalt. The sample was then mixed with a metal stirrer and poured into half a petri dish. Immediately after pouring, the samples were set aside to dry for 24 hours. These steps were repeated for all the ratios, weighing all the components accordingly as laid out in the table below. The samples were all compared to Portland cement, which has 60% CaO. [18]

In order to test the strength of the cement, Vernier dual range force sensors were used to measure the amount of force required to break each sample. After the samples were dry, pressure was applied to each sample by the head of the sensor, recording the amount of force applied. Constant and increasing force was applied, and the force required to break the sample was recorded. This step was conducted for every single sample. In order to convert the force applied into Pascals to measure pressure, the measured newtons were divided by the area of the head of the sensor. This area was estimated to be about $4 mm^2$.

The final amount of estimated carbon dioxide saved was calculated by dividing the original 2.25×10^9 tons of carbon dioxide by 2, to find the amount of carbon dioxide released from the calcination process. Then, 35% of this value was found to be the amount of carbon dioxide saved. This value was calculated under the hypothesis that using only 25% calcium oxide would save 35% of the total carbon dioxide emissions due to calcination.

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Author. Sophia Shapiro is an aspiring environmental engineer from New York City. She was awarded a bronze medal at Genius Olympiad, an international environmental science competition. In addition to sustainable cement, Sophia is also interested in sustainable lead filtration, computer programming, and entrepreneurship.