CEMENT - REDUCTION OF CO_2 EMISSIONS - SUSTAINABLE DEVELOPMENT

Supplementary Cementitious Materials (SCMs) in British Columbia

Simandl, G.J.[1] and Simandl, L.[2]

[1]British Columbia Ministry of Energy, Mines and Petroleum Resources, Victoria, BC [2]St. Michaels University School, Victoria, BC

For more information contact:
George.Simandl@gov.bc.ca

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Executive Summary

Portland cement production is an energy intensive process involving the use of fossil fuels. Cement plants are considered to be significant stationary sources of greenhouse gas emissions. The cement industry is succeeding in the reduction of *"Fuel-related" CO_2 emissions* per tonne of cement produced by increasing the efficiency of cement making equipment, increasing the use of biofuels and alternative fuels, and by reducing the use of Portland Cement through the increased use of blended cements (without sacrificing quality).

This poster introduces the cement-making process, describes how CO_2 is generated during Portland cement production, explains the blended cement concept, and demonstrates how the increased use of blended cement is resulting in substantial reductions of CO_2 emissions.

Blended cement has chemical and physical properties similar to those of traditional Portland cement (the main cementitious material used to make concrete); however, it commonly consists of 10-30% (in some cases up to 50%) additives that do not require, or require only low temperature calcining. These additives are *supplementary cementitious materials* (SCMs) or natural *pozzolans*. They include fly ash, silica fumes, volcanic ash, scoria, pumice, silica sinter, metakaolin, slags, zeolites, diatomaceous earth, rice husk ash, calcined shale and a number of other materials. As a result, the production of blended cement requires the combustion of a smaller quantity of fossil fuels than Portland cement. The reduction in the use of Portland cement also lowers the level of *raw material - related emissions* emitted by the calcination of limestone.

The most common secondary cementitious material in British Columbia (BC) is imported fly ash. BC has a variety of locally available secondary cementitious resources. Most of these resources are undeveloped and a lot of them remain untested.

In BC, the substitution of imported fly ash by domestically available pozzolans would not be without challenges, but if economically and technically viable, it could benefit the mining industry, help the environment by reducing CO_2 emissions and create employment.

Introduction

Cement is a major building block of the world's economy. The countries with the largest cement production capacities are China, India and the USA (Figure 1). On the world scale, Canada's cement production, approximately 14 million tonnes per year is negligible. British Columbia is the 3rd largest cement producing province (Figure 2). In terms of value, cement production in BC represents over $300 million (Figure 3). The province has three cement plants with combined total clinker and grinding capacities of 2.6 and 3.1 million tonnes/year. Lafarge Canada Inc. (Figure 4) and Lehigh Northwest Cement Limited plants, located in Richmond and Delta near Vancouver (southwestern BC) are modern operations. Both of these plants have clinker production capacities of 1.2 million tonnes/year. Lafarge plant has a grinding capacity in excess of 1.5 million tonnes/year, while Lehigh Cement's plant has a grinding capacity in excess of 1.2 million tonnes/year. Lehigh's Delta plant production is shared equally between customers in BC and the US Pacific Northwest. The third plant, located near Kamloops (central BC) produces approximately 220 000 tonnes of cement per year.

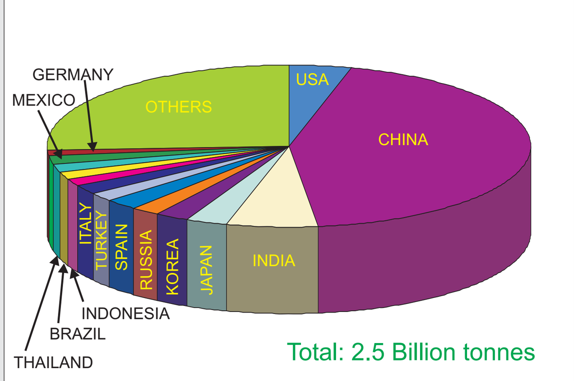


Figure 1. World cement production 2006. Data from van Oss (2007).

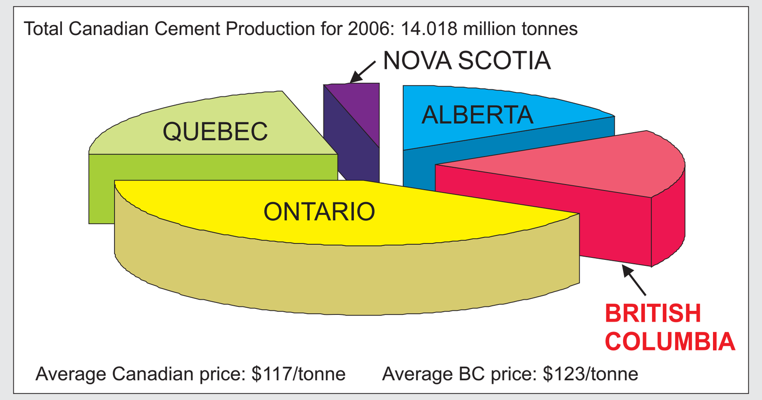


Figure 2. Canadian cement production for 2006 (Data from Panagapko, 2006).

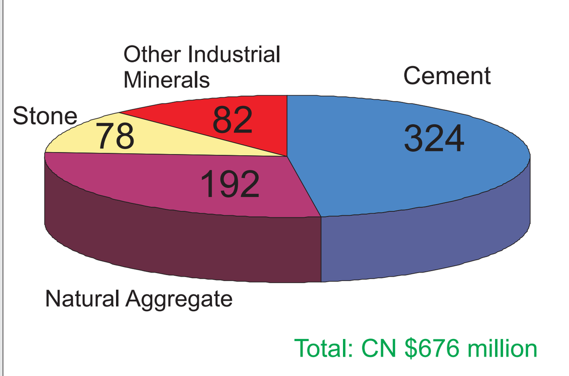


Figure 3. The value of cement, natural aggregate, stone and other industrial mineral products in British Columbia. (2006). From Simandl (2007).

Figure 4. Lafarge Canada Inc. plant, located in Richmond has a clinker and grinding capacities of 1.2 and 1.5 million tonnes/year.

Definitions

Portland cement is a basic ingredient in concrete, mortar and stucco (the most common type of cement worldwide). It is a powder produced by grinding and mixing together Portland clinker (> 90%), gypsum {$Ca(SO_4)\cdot 2(H_2O)$} that controls the cement's setting time (< 6 %), and other constituents (< 5%). At least two-thirds of ***Portland clinker*** consists of calcium silicates ($3CaO.SiO_2$ and $2CaO.SiO_2$). The remainder consists largely of alumina and of iron-containing clinker phases to a lesser extent. The CaO to SiO_2 ratio of Portland cement shall not be less than 2.0 and its MgO content shall not be less than 5.0% by mass. The content of alkali elements is kept as low as possible.

Blended cement is a mixture of Portland cement and a variety of additives. The main additives that are combined with the Portland cement are referred to as *supplementary cementitious materials* and/or as *pozzolans* (see definitions bellow). The addition of these materials to Portland cement results in a substantial reduction of fossil fuels during cement production (results in cost savings) and at the same time significant reductions in CO_2 emissions. In many cases, technical characteristics of blended cements are superior to those of Portland cement.

Supplementary cementitious materials (SCMs), unlike Portland cement (calcined at > 1450°C), do not need pre-treatment (except for calcined shale or metakaolin that require low temperature, < 700°C treatment). Yet, SCMs have cementitious properties when added to Portland cement. Depending on the type and quantity of SMCs added, they provide economic and/or ecological benefits. They also improve the characteristics of concrete by their pozzolanic and/or hydraulic activity.

Pozzolans are mostly natural materials consisting mainly of silica and/or alumina. When in a finely divided form and in the presence of moisture, pozzolans react with the calcium hydroxide that is released by the hydration of Portland cement, to form compounds possessing cementitious properties.

Many pozzolan deposits, some in the proximity of existing infrastructure, remain to be discovered and developed.

Production of Portland Cement

Portland clinker is produced by calcining a homogeneous mixture of raw materials that has a set chemical composition. The temperature within the cement kiln varies (Figure 5), but in the hottest portion of the kiln the gas can reach a temperature of up to 2000°C. Complex computer programs were designed to optimize and continuously adjust the composition of the feed that enters a modern kiln; however, to illustrate the concept of clinker-making to a non-specialist (Figure 6), we adopt the approach of Simandl (2007) and Manning (1995). The major raw materials (sources of CaO) are common limestone, chalk, marble or coquina. These materials consist mainly of calcite or aragonite. Sand, sandstone or quartzite are the primary sources of silica (SiO_2). Clays or shale and bauxite are the common sources of Al_2O_3 and to some extent silica. Iron oxides are not shown on Figure 5, to avoid the need for a complex three dimensional diagram. They act as fluxes and reduce the temperature required for clinker production. Iron oxides are most commonly introduced as iron ores or major components of slag. The raw materials are blended. The line that connects the two points representing the chemical compositions of typical limestone and shale is called the blending line. The final composition of the blend must fall within the red triangle (Figure 6) to meet industry specifications. When a cement kiln is fired by coal, the ash of the coal, depending on its chemical composition, may act as an important secondary source of Al_2O_3. This reduces the need for costly alumina and bauxite that are commonly used to correct the composition of the feed (Simandl and Brulé 2008). C_3S, C_2S and C_3A are abbreviations for stable synthetic minerals in Portland clinker. C_3S stands for tricalcium silicate (mineral alite {Ca_3SiO_5}), which is the main active component in Portland cement. C_2S is dicalcium silicate (belite {Ca_2SiO_4}) and C_3A is tricalcium aluminate {$Ca_3Al_2O_6$}, which is not known to occur in nature. From a metallurgist's point of view, the formation of clinker may be best approximated by the formation of slag.

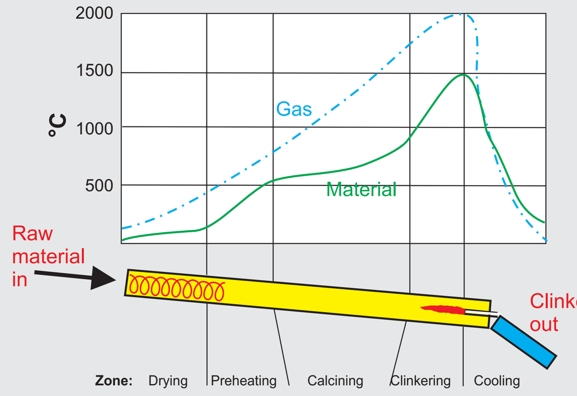


Figure 5. Principle of the cement kiln operation. After Manning (2005) and Simandl and Brulé (2008).

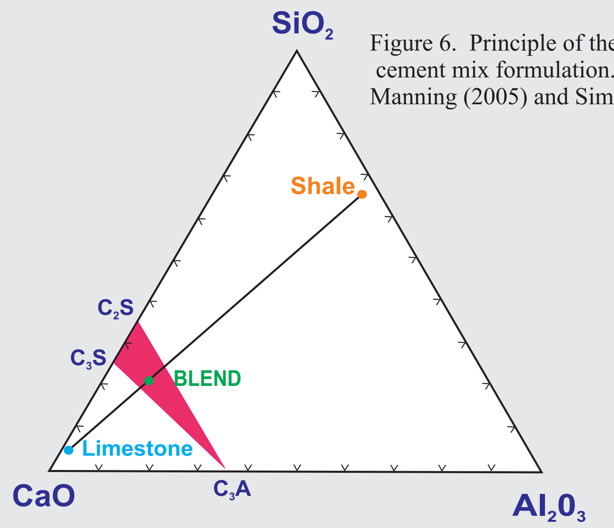


Figure 6. Principle of the Portland cement mix formulation. After Manning (2005) and Simandl, L.

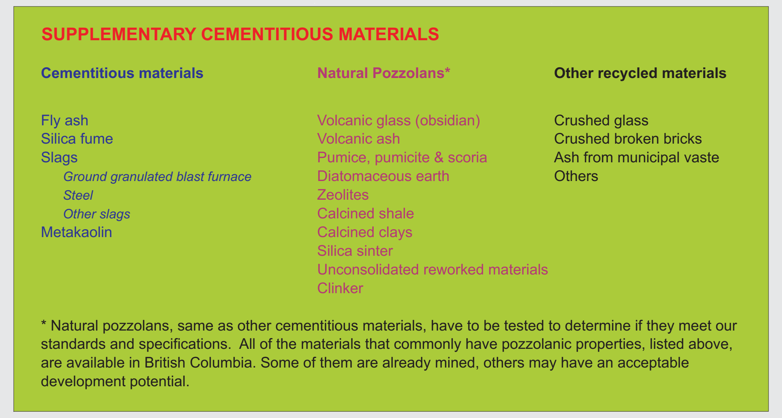
CO_2 Emissions Generated During Portland Clinker-Making

The cement industry is succeeding in the reduction of *"Fuel-related" CO_2 emissions* per tonne of cement produced by increasing the efficiencies of cement making equipment, increasing the use of biofuels and alternative fuels and by reducing the use of Portland Cement through an increased use of blended cements (without sacrificing quality). *Raw material-related CO_2 emissions* are directly linked to decarbonation reactions (see the mass balance bellow).

$$\underset{(100)}{3CaCO_3} + \underset{(20)}{SiO_2} \longrightarrow \underset{(76)}{Ca_3SiO_5} + \underset{(44)}{3CO_2} \text{ (Raw material } CO_2 \text{ emissions)}$$

Assuming that the calcination (decarbonation) is complete, we can see that for every 100 kg of limestone and 20 kg of silica that goes through the kiln, we obtain 76 kg of alite (the main active component in cement clinker) and we produce 44 kg of Raw material-related CO_2 emissions. This translates into approximately 58 kg of raw material-related CO_2 emissions per 100 kg of clinker (alite) produced.

Supplementary Cementitious Materials (SCMs)



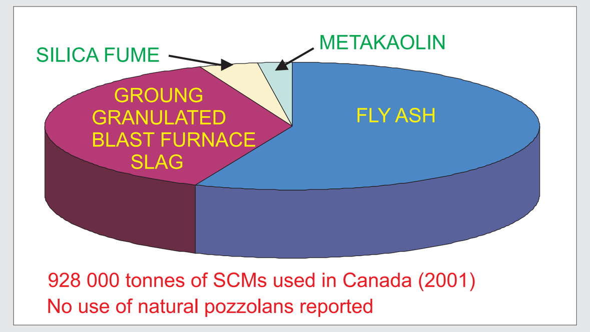


Figure 7. Supplementary Cementitious Materials used in Canada (Bouzoubaă and Fournier, 2005). In British Columbia, natural pozzolans and local slag may significantly displace some of the imported fly ash.

Acknowledgements

Dr. Suzanne Paradis of the Geological Survey of Canada in Sydney, BC improved the first version of this document. Critical review by Claude Brulé (optimization and environment manager) and Sean McCoy (environmental co-ordinator) of Lafarge Canada Inc. in Richmond is greatly appreciated. Comments from Larry Baloun of Lehigh Cement were helpful. Charles Nichols (Corporate Geologist) and Michaek Hrizuk (VP-Manufacturing) from Ash Grove Cement Company also read the earlier version of this document. Final edits by Alan Duffy of the British Columbia Ministry of Energy and Mines are acknowledged.

Potential Market for SCMs in British Columbia

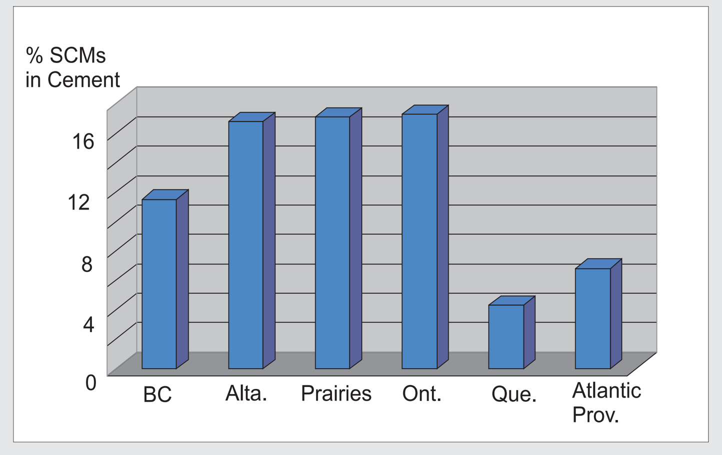


Figure 8. Percentages of supplementary cementitious material in average cement (wt%) in 2001. Ontario is the leader with 17.5%. Average cement in British Columbia contained 11.5% of cementitious materials, mostly imported fly ash (Bouzoubaă and Fournier, 2005). Our unofficial survey suggests that in 2008, the percentage of SCMs in BC probably reached 16% (wt.) This represents a substantial increase in the SCMs market since 2000.

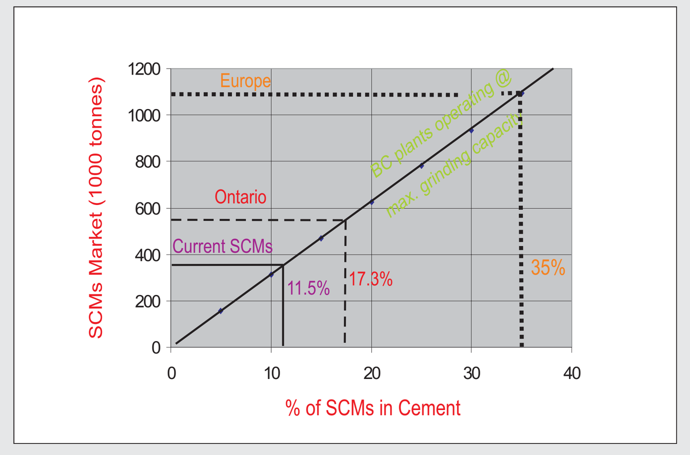


Figure 9. Conceptual evaluation of the market for SCMs and pozzolans in BC. We assume that the 3 local cement plants operate at their maximum combined grinding capacity. The 11.5% SCMs substitution level (Bouzoubaă and Fournier, 2005) corresponds to 350 000 tonnes/year. Assuming that BC can match Ontario's level of substitution (17.3%), the SCM market would reach over 550 000 tonnes. At 35% substitution level, the BC market would exceed 1.2 million tonnes. It remains to be established what substitution level can be achieved based upon realistic technical and economic constrains.

Estimate of Avoided CO_2 Emissions for British Columbia

This section aims to obtain a rudimentary estimate of the potential of SCMs to reduce cement-related greenhouse gas emissions in British Columbia. The accuracy and precision of our method depends on a number of technical and market assumptions. The main assumption is that the three BC cement plants will operate at their maximum grinding capacity reported in the past near 3.5 million tonnes per year (Panagapko, 2006). Other assumptions are that SCMs will be transported 1000 km to the plant and that 0.022 tonnes of CO_2 will be released per tonne of SMCs transported over a distance of 1000 km. It is also assumed that 0.1 tonne of CO_2 will be released per tonne of SMCs ground. These or similar factors are quoted by Bouzoubaă and Fournier (2005). Their validity remains to be verified. Since mills in BC use electric power, which is generated to a large extent by hydroelectric plants, the average mill-related emissions for BC pozzolan or cement producers may be much lower. In our projection, the tonnage of CO_2 avoided equals the tonnage of Portland cement substituted by SCMs multiplied by a factor of 0.87 (Humphreys and Mahasenan, 2002), minus the emissions released during the transportation of SCMs, minus emissions released during the grinding of SCMs. For simplicity, pozzolan mining-related emissions are assumed to be equal to emissions released by the mining of the limestone used in Portland cement-making.

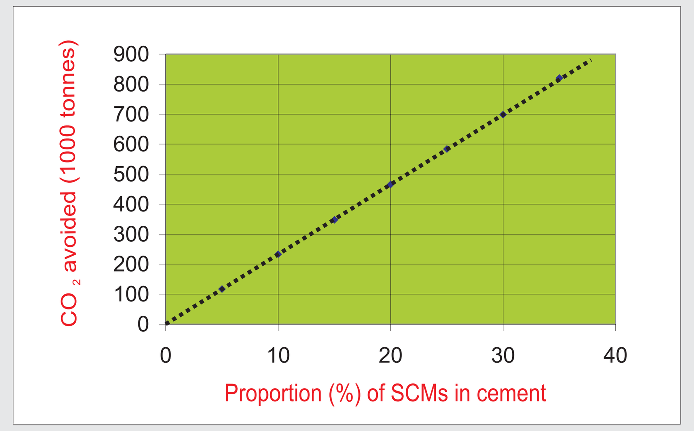


Figure 10. Conceptual evaluation of the CO_2 emission reductions by substituting cementitious materials for Portland cement. The vertical scale indicates corresponding levels of CO_2 emissions that were avoided. The horizontal scale represents the proportion of SCMs in blended cement. For example, at 10% and 35% substitution levels, there would be over 200 000 tonnes and over 800 000 tonnes of CO_2 emissions avoided respectively.

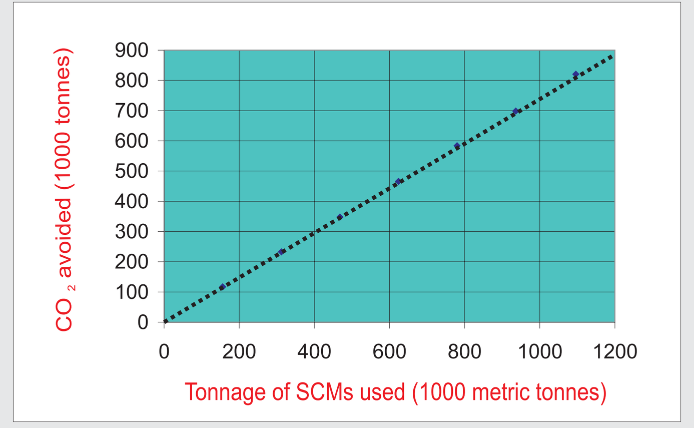


Figure 11. Conceptual evaluation of the CO_2 emission reduction for some of SCMs used in BC. The horizontal scale represents the tonnage of SCMs used. The vertical scale indicates corresponding levels of avoided CO_2 emissions. For example, the use of 800 tonnes of SCMs in the production of blended cements would avoid emissions of nearly 600 000 tonnes of Co_2.

Discussion and Summary

As a consequence of cutting fuel costs, the efficiency of cement plants increased and significant reductions in fuel-related CO_2 emissions per tonne of Portland cement were achieved over the past 25 years. The efficiency of conventional kilns was nearly maximized; consequently, additional reductions of fuel-related CO_2 emissions are costly to achieve. Experimentation with solar energy in lime calcining could be theoretically extended to cement-making; however, this technology is not likely to be commercialized in the foreseeable future.

An increased substitution of Portland cement by SCMs represents the most promising short to medium-term approach to reduce both, fuel and raw material related CO_2 emissions. Fly ash is the main SCM currently used in BC. Slag from historical and operating base metal smelter are important sources of iron for Portland clinker production; however, ungranulated slag rarely has cementitious properties. Some zeolite, volcanic ash, obsidian, pumice and scoria, burned coal-associated clays and high-alumina clays with good pozzolanic properties may (at least partially) displace imported fly ash. The use of local SCMs would have a positive impact on BC economy, but their introduction would be slow, unless the Ministry of Highways and British Columbia's architects put an emphasis on specifying blended, pozzolan-bearing cement as construction material. British Columbia Ministry of Energy Mines and Petroleum Resources may encourage the use of local pozzolans by identifying some of the sites worth testing. Long-term contracts between fly ash users and utilities owning coal-fired electricity generating plants, the potential inability of new pozzolan suppliers to produce homogeneous products and the resistence of builders/architects to SCMs for competitive reasons (in general, longer setting time of the cement) are some of the main obstacles.

On the positive side, electricity generating companies are currently under pressure to reduce their mercury (Hg) emissions at the stack. The injection of pulverized activated carbon (PAC) is one of the most effective methods for removing elemental mercury (Hg) from flue gas streams; however, the use of this method results in a higher carbon content of fly ash, making it unsuitable as a pozzolan for cement making. Cement-friendly methods to reduce Hg in flue gas are being developed (Lockert et al. 2005; Landreth et al 2007), but if they are not accepted by the industry, cement grade fly ash shortages may develop. Such shortages may result in increased demand for natural pozzolans.

The production of Portland cement without raw-material related emissions is technically possible (Simandl et al. in preparation). Unfortunately the raw materials, such as wollastonite, required to achieve this objective are not widely available at acceptable costs.

From a sustainability point of view, a variety of waste materials destined to landfills were turned into fuels. Example are: tires, used oil, non-recyclable plastics etc. (Simandl et al. In preparation). In some jurisdictions scientists are experimenting with sewer sludge as fuel for cement-making. British Columbia's cement and some other industrial mineral producers could benefit from trees killed in the pine beatle affected areas, as they represent renewable inexpensive fossil fuels. Coal rejects may be used, not only as a fuel, but also as a source of high alumina materials (Simandl and Brulé, 2008). Slags and in some cases mine tailings, could represent acceptable pozzolans; however, site by site testing is required.

The estimates presented above for the SCMs market and of the CO_2 emissions that could be avoided due to the use of SCMs are quite conservative. Firstly, major cement producers operating in British Columbia are committed to CO_2 emission reductions. Secondly, it is unlikely that BC cement producers will operate kilns at reduced clinker capacity unless they are forced to do so by severe construction slowdown. In the medium term, the most likely scenario is that they will operate the kilns at their designed (combined) clinkering capacity (2.6 million tonnes/year) and at same time increase the average proportion of the SCMs in cement to 20%. At that rate, there would be a market for more than 600 000 tonnes of SCM products in BC with a most likely delivered value in order of $60 million to $90 million (not considering potential CO_2 credits). Currently, Ready Mixed producers rely on Portland cement producers to test SCMs and the laboratory work that they perform is devoted entirely to quality control. At least some of the Ready Mixed producers would be willing to instal extra silos if this expense was justifiable by increased demand for blended cements containing natural pozolanic materials.

The use of SCMs will contribute to sustainable development of cement-materials and a reduction of CO_2

Potential Use of Local Pozzolans and Other SCMs

Apple Bay rock, mined by Electra Gold Ltd., is a source of silica and alumina, but it may have pozzolanic properties. **Monteith Bay** material has a similar composition.

Scorria from **NAZKO** has number of industrial uses. If product specifications are not available, this material should be also tested for pozzolanic properties.

Alumina-rich buchite, mined by Pacific Bentonite Inc. in the **Hat Creek** area, is a source of alumina and silica for cement making. It may be an excellent pozzolan.

	MATERIAL	SOURCE	SCM /Portland Cement cost	COMMENTS
STANDARD	Portland Cement	Local - Lower Mailand and central BC.	1	Principal cementitious material in use worldwide
Imported materials	Fly Ash	Washington State & Alberta	0.5 - 0.7	Off-the-shelf, fly ash-bearing cement formulations are available in BC
	Silica Fume	Quebec, USA, Norway	> 4.5	High cost limits its use
	Granulated Blast Furnace Slag			Its use in BC is not confirmed.
	Metakaolin	Imports from Washington State & Alberta; Northwest Pozzolan Ltd. is a new BC producer	> 4.0 (?)	High cost prevents widespread use.
	"Barren" Base Metal Slag	Teck-Cominco smelter in Trail (southestern BC)	>1	Component of cement additives in Alberta; finished products imported to BC.
Local materials*	Volcanic glass	Garibaldi Obsidian (15 km north of Squamish); Terrace Mountain area (south of Vernon and others).	<1	Garibaldi Obsidian is known to be pozzolanic; other obsidian/perlite deposits remain untested.
	Pumice, Pumicite, Scoria	NAZKO cone (near Quesnell Central BC) and Mount Meager area deposits (near Pemberton).	<1	Producing deposits. Transportation cost is the key factor.
	Volcanic Ash	Sherwood Creek and other occurrences (Deadman River Valley, Central BC)	<1	Pozzolanic properties tested and recognized
	Diatomaceous Earth	Microsil (Lot 906) and Clayburn Industries ("Quesnel"), Deadman Lake and other deposits (mainly in Central BC).	Variable, may be <1	Past producers and promissing prospects
	Calcined Shale**	Long Harbour (Salt Spring Isl.), Hillbank deposit (Vancouver Isl), Saturna (Saturna Isl.)	≈1	Kiln requires lower operating temperature than in Portland cement making
	Silica Sinter	Monteith Bay and Apple Bay silica/alumina deposits; in production (Vancouver Island - barging possible)	≈1 or <1	Used in cement, as source of silica and alumina. It is not known if these materials are pozzolanic.
	Zeolites	Sunday Creek & Zeo, Princeton area (southern BC); Ranchlands (Z1 and Z2) deposits in Cache Creek area (central BC)	<1	Past producers and advanced prospects - some deposits tested for pozzolanic properties
	Base Metal Slags, other than from Trail	Anyox (North Coast barging possible) , Greenwood and Grand Forks (Southern BC)	<1	Metal content may limit the use. Some of Grand Forks slag is granulated.
	Buchites***	Hat Creek area (Central BC)	<1	Used a source of alumina and silica (pozzolanic properties not determined)
	Partially consolidated, deposits	Example: WK claims near Clinton.	<1	Previously tested as potential source of pozzolanic materials.

*1970's study concluded that natural pozzolans cannot compete with fly ash in BC. This is questionable, a case by case comparison is needed.

** There is gray zone between the use of terms "metakaolin" and "calcined shale", in some cases they refer to identical Products (although starting materials may be very different).

***Buchites are produced by pyrometamorphism of rocks associated with burned coal seams (fused shales, clays or diatomaceos rocks). Under ideal circumstances buchites are natural equivalents of metakaolin or calcined shale.

Meta-diatomaceous earth, **Quesnel** area, used as pozzolan during the construction of the Hudson-Hope Dam.

Zeo Deposit near Princeton, is mined by Heemskirk Canada Limited. Clinoptilolite from this deposit has many uses, including specialty cement formulation for the oil and gas industry.

Mount Meager, pumice deposit (Great Pacific Pumice Inc.). Material is reported to have acceptable pozzolanic properties.

Granulated slag from **Grand Forks** and **Trail** may have acceptable cementitious or pozollanic properties. **Greenwood Slag** was not granulated and probably has higher trace element content than previously mentioned slag resources.

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