CHAPTER 1. Introduction

"Cementing a sustainable future"

XIII International Congress on the Chemistry of Cement.

Cement production has undergone a tremendous development from its beginnings some 2000 years ago. Today's annual global cement production has reached 2.8 billion tonnes, and **is expected to increase** to some 4 billion tonnes per year. At the same time, the cement industry is **facing challenges** such as cost increases in energy supply, requirements to reduce CO_2 emissions, and the supply of raw materials in sufficient qualities and amounts [Schneider et al, 2011]. Furthermore, there have been considerable efforts in waste **prevention and management** in the EU in recent years based on: waste prevention, recycling and reuse, and improving final disposal and monitoring. Unless properly regulated, the **disposal of waste** may have a serious **environmental impact** [Eurostat, 2010].

In 2008, about 2600 million tonnes of waste was generated in the EU, of which some 98 million tonnes constituted **hazardous waste**. Relative to the size of the population, the waste generated in the EU averaged 5300 kg per inhabitant. The largest waste streams in Europe originate from construction and demolition mining and quarrying, along with manufacturing activities. Most EU municipal waste is still sent to landfill (40%). However, waste management is improving and more and more municipal waste is recycled or composted (40%), or incinerated with energy recovery (20%). In EU, Greenhouse gas (GHG) emissions from landfills and waste incinerators have decreased by 34 % since 1990 [Eurostat, 2010].

Worldwide **cement manufacturing** represents **5% of man-made CO_2 emissions**. Overall, the resulting emissions are disproportionately large when compared to those produced by other industries.

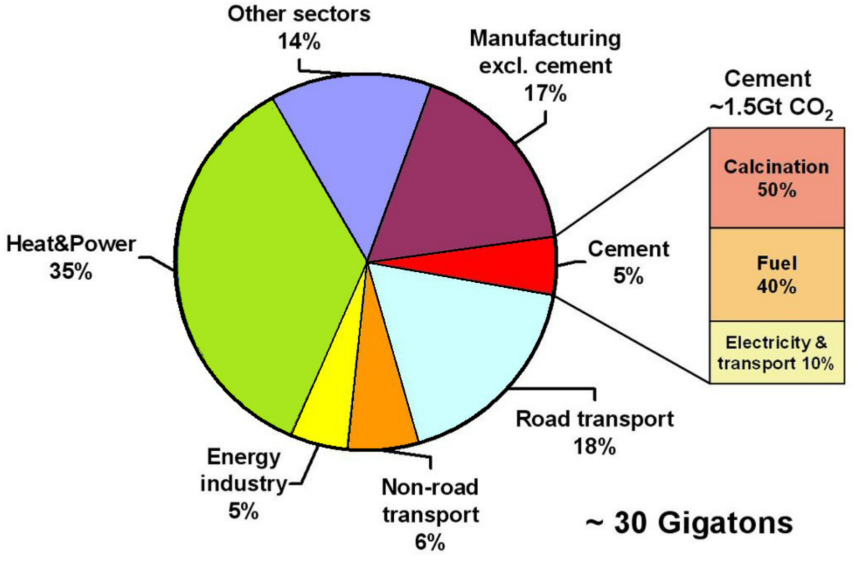

Figure 1.1. Global CO_2 production [Adapted from WBCSD, 2005].

As shown in Figure 1.1, carbon dioxide emissions from a cement plant are divided into two source categories: combustion and calcination. Combustion (burning fuel) accounts for approximately 40% and chemical process of clinker production (e.g. limestone calcination to obtain lime) accounts for 50% of the total CO_2 emissions from a cement manufacturing facility. Only 10% is related to electricity (for grinding) and transport. The combustion-generated CO_2 emissions are related to fuel use. The CO_2 emissions due to calcination are formed when the raw materials (mostly limestone and clay) are heated up to >1000ºC and CO_2 is liberated from the decomposed limestone [WBCSD, 2005].

According to the **Kyoto Protocol**, to avoid a substantial increase in risk to the consequences of climate change, by 2050 GHG emissions in developed countries should be extremely reduced, meaning significant **CO_2 reductions in all sectors**, and construction sector is not an exception [Solanas et al, 2009]. With currently available alternatives and the worldwide demand for cement increasing, investment in energy as well as CO_2-reducing technologies and processes in the cement industry represents a key opportunity. Significant challenges are to be ahead [IntertechPira, 2011].

Cement is often considered a key industry for a number of reasons. To begin with, cement is an essential input into the production of concrete, a primary building material for the construction industry. But, a part from emitting CO_2 to the atmosphere, cement industry has been always looked with disfavour for leading to environmental negative **impacts** as follows [Gaminde, 2009]:

- High natural resources consumption, associated to quarrying;
- Energy intensive consumption;
- Source of ambient pollution.

Over the past few decades the European cement industry has demonstrated an impressive record in continual environmental improvement within the context of the sustainable manufacture and use of cement. To conserve natural non-renewable resources, **wastes valorisation as raw materials** is highlighted for two main different purposes. Firstly, **partially substituting the clinker** with alternative materials in cement manufacture process. Secondly, for using **alternative fuels** reducing fossil fuels consumption, especially coal [Schneider et al, 2011].

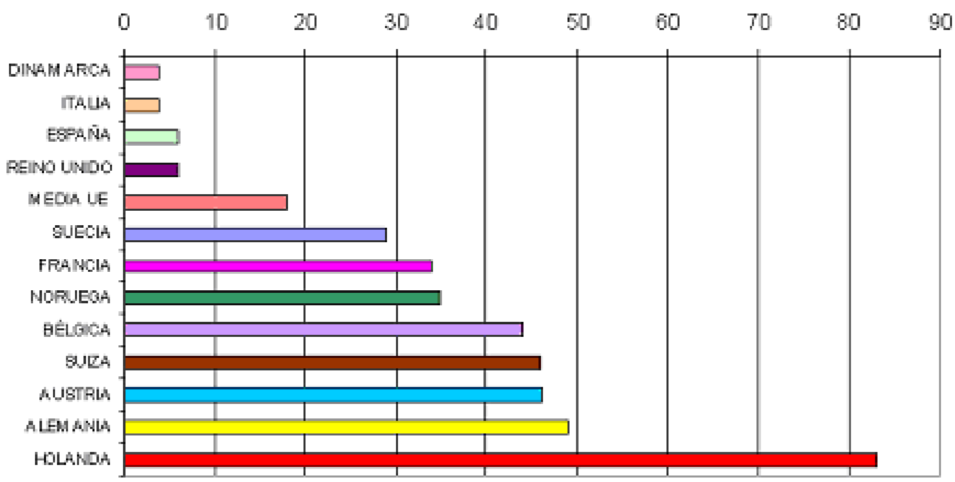

Figure 1.2. Recovery percentage of wastes in European cement industry [Gaminde, 2009].

Life cycle analysis shows that recycling these materials can be the answer: it **prevents unnecessary land-filling of wastes** while **reducing the environmental impacts** from extracting and processing virgin materials in new construction as well as **reducing wastes** to be treated [WBCSD and IEA, 2009].

Blended cements are produced by intimately and uniformly intergrinding or blending two or more types of fine materials. The primary materials are portland cement and SCMs, being all of them mixed with cement clinker. Such kind of cements is also called **sustainable** or **low-CO_2 cements**, substituting in large quantities the Ordinary Portland Cement (OPC) [PCA and Concrete Thinking, 2011].

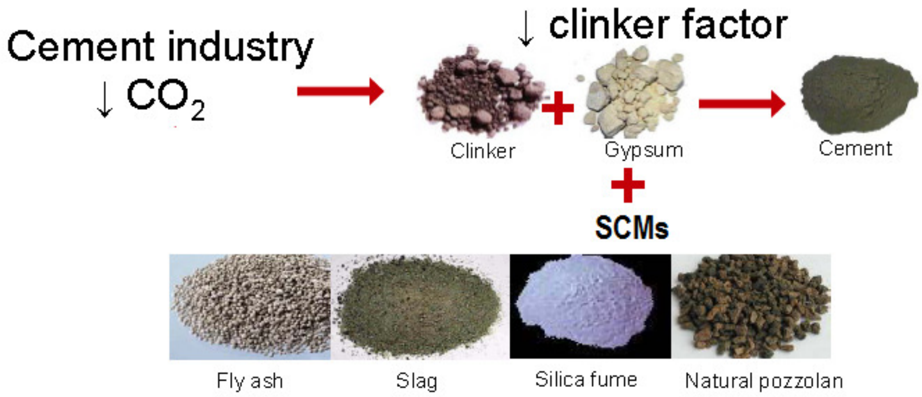

Figure 1.3. SCMs addition in cement manufacture [Adapted from Scrivener, 2010].

The practice of using **Supplementary Cementitious Materials (SCMs)**, also called mineral admixtures, in concrete has been growing since the 1970s. Nowadays, they are widely used in concrete either in blended cements or added separately in the concrete mixer (where no additional clinkering process is involved, emitting less CO_2 per ton of product) [Lothenbach et al, 2011]. They are comparable to cement raw materials' composition and react chemically with calcium hydroxide released from the hydration of portland cement to form cement compounds being often added to concrete to make concrete mixtures more economical, reduce permeability, increase strength, etc. However, the blending of SCMs with Portland cement leads to a more complicated system and CSH or portlandite (main hydration products) formation may be influenced. Typically used by-products are the following [PCA, 2011]:

- **Fly ash**; most commonly used pozzolan in concrete, is a finely divided residue that results from the combustion of pulverized coal and is carried from the combustion chamber of the furnace by exhaust gases.
- **Slag**; essentially of silicates, aluminosilicates of calcium, and other compounds that are developed in molten conditions.
- **Silica fume**; also called microsilica, and is a finely divided residue from the production of elemental silicon or ferro-silicon alloys released through exhaust gases.

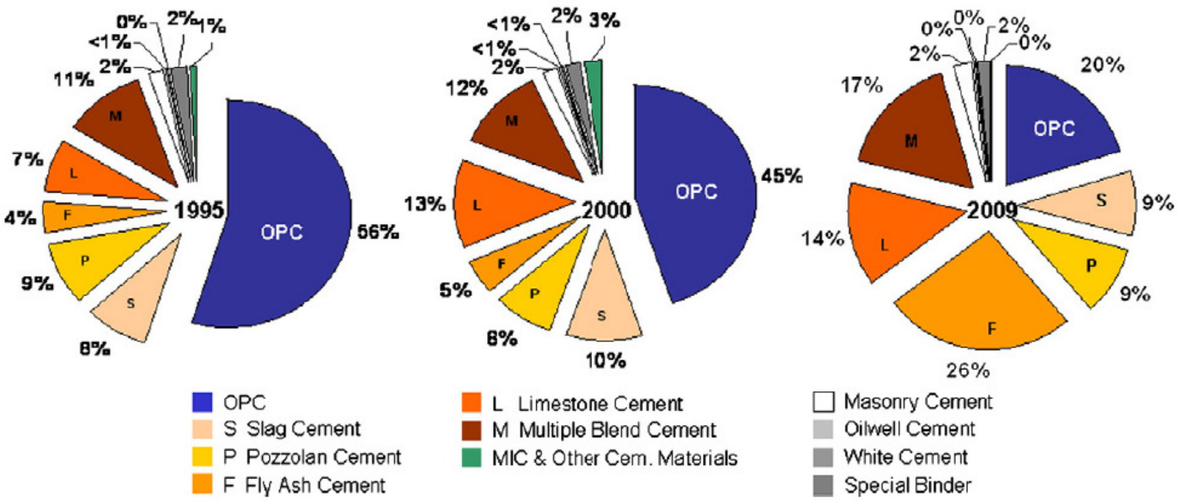

Figure 1.4. Cement types produced by Holcim 1995-2009 [Schneider et al, 2011].

According to the WBCSD, over the decade of the 1990s, global cement production increased around 20% while unit-based cement industry CO_2 emissions decreased by approximately 1.5%, meaning that efforts realised by cement manufacturers lead to positive environmental consequences [WBCSD, 2005].

A part from producing less contaminant materials, cementitious systems can also be well considered for hazardous wastes immobilization, especially heavy metals, considering its high production in nowadays society. Currently, **cementitious solidification/stabilization** –S/S- is recognized as the best demonstrated available technology by the US Environmental Protection Agency (USEPA) for the disposal of most toxic elements, trying to reach more chemically stable wastes (stabilization) or easier to transport, classify and process (solidification) [Kundu and Gupta, 2008]. Sooner or later, S/S waste will contact water and leaching might cause a (partial) remobilization of toxic elements. It is thus extremely important to understand the leaching behaviour of different elements. Depending on process parameters, like pH (highly alkaline in cement-based systems), different processes may occur, e.g. surface complexation, dissolution/precipitation, sorption and incorporation to a mineral phase. **Leaching tests** and subsequent **geochemical modelling** are typically used to investigate pollutants' leaching behaviour [Martens et al, 2010].

Naturally, **trace elements** are introduced into the clinker burning process via both raw materials and fuels. The use of SCMs substitutes for an equivalent proportion of natural constituents but also containing trace elements, whose concentrations can be much higher. Therefore, it's of utmost importance to study these additional elements' **effects on hydration and microstructure of cementitious materials** [VDZ, undated].

Past research initiatives and the legislation in waste management have focused on contaminants of high concentration and toxicity such as Cu, Cd, Hg, Pb and Zn whereas **oxyanionic species** have received considerably less attention because of their much lower total solid phase concentrations. However, they are often found in relatively high concentrations in leachates compared to the cationic species due to their **high solubility**. Interest in the **leaching behaviour** of As, Cr, Mo, Sb, Se, V and W has been growing over the last years. Most of these elements are redox sensitive and some oxidation states can form oxyanions (negatively charged species containing O) in solution, forming a range of different species depending on both pH and redox potential. Therefore, in order to comply with legislation, it is necessary to develop techniques to control oxyanion leachability [Cornelis et al, 2008]. Leaching tests combined with geochemical modelling support the development of regulatory criteria [Van der Sloot et al, 2008].

Vanadium is a heavy metal that can be found at high concentrations in commonly used SCMs, particularly in fly ash and slag from steel industry. **Vanadium behaviour** in cementitious systems is **ill-known** and, as a result, **literature** about this element is **not well defined** and vanadium presence is linked to an **environmental risk**. According to previous works [Glasser, 1997], additional wastes may slow cement chemical reactions, having influence in leaching tests results at early ages, considering that pastes' behaviour improves when maturing.

Consequently, this study wants to contribute to understand how vanadium behaves in this kind of systems because, if it can be immobilised in cement matrix, a really sustainable fate for oxyanionic species would be achieved, as alternative to landfill deposition.

Therefore, the **present study** aims to understand **vanadium retention mechanisms** by which could be immobilised in the cement, a fact that could have immediate positive effects for the environment.