

## Analysis of possible use of sewage sludge in cement based composites mix design

Final Degree Project Building Engineering

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### **Acknowledgments**

To finish my Bachelor on Building Engineering I had to perform my Final Project, with this aim I went to Prague in September 2013.

This project was done thanks to the Erasmus Programme, which allowed me living in Prague last 9 months researching in Czech Technical University in Prague. I must say that thanks to this year abroad I have learnt lots of things, not only at university studying and extending my knowledge about cement and building materials, I could feel what is Erasmus, experiences which cannot be explained only with words, it is something more and recommended for everyone.

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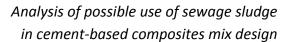
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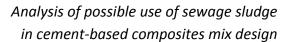






<<The veracity of building materials: concrete, brick and stone, will be maintained in all buildings constructed or to be constructed>>

*Le Corbusier (1887-1965)* 











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### **0.- Introduction**

#### 0.1. - Objectives. The importance of cement nowadays

Cement is one of the most important materials in construction nowadays and, probably, it will be used for a long time. It is the main component of concrete, which is the most used material in building structures, and it is essential in prefabrication industry.

Concrete is in constant evolution, lots of investigation groups are studying this interesting building material. It is necessary not only for improve the strength resistance of structures with less sections in columns or beams, but also to improve the characteristics against the external factors like CO2, sulphates, chlorides, pure water, acid water... increasing the life of structures and prolonging the life of cities.

Cement manufacturing is relatively easy because we can find limestones and clays (main cement components) in some place. However, the concerns are in the environmental because of the limestones and clays after 1500°C in the oven generates CO<sub>2</sub>.

The study of cement, and the knowledge about macroscopic and microscopic properties of additions and his relation with the concrete is a good starting point to satisfy my curiosity about this topic.

In these times, the sustainability is one of the most important factors in the building industry; we have to admit that cement manufacturing is not a clean process with the environment; **cement manufacturing is the source of 5% of global CO2**, for this reason we have to change something. In this project, my main aim is analyse the possibilities to recycle sewage sludge from waste water treatments plants, cooperating with the environment but we cannot and must not forget the cement properties, decreasing its characteristics to a large degree.

The production of sewage sludge generates a high volume of waste, a very important reusing way for sludge is in agricultural practices. However, the properties of sewage sludge depend on the quality of wastewater, for example industrial wastewaters containing heavy metals, in most of cases, cannot be used in agriculture. A possible solution to this problem would be using in cement, where metals are converted into highly insoluble salts, which do not leach at appreciable rates.





#### 0.2. - Summary by chapters

The aim of this project is to present an analysis of possible use of dried sewage sludge in cement-based composites mix design, performing my own analysis taking into account the last articles and publications about the issue.

It consists of nine chapters, the first one is the <u>Chapter 1</u> on cement, making a brief review to the history of this historical material and its production, how is manufactured Portland cement nowadays, with pictures and schemes explaining all steps to get the Portland cement as we know it, assessing its environmental impact, CO2 emissions, etc.

This is followed by the <u>Chapter 2</u> on sewage sludge, history of these sewage sludge and the origin of wastewater treatment plant are discussed. In addition in this Chapter are explained the different steps to remove most of pollutants from wastewater and the procedure to establish and removing all unwished organisms before storage to know how is generated the sludge which we have used in this project.

The <u>Chapter 3</u> deals with the legislation in Europe about the sewage sludge use, addressing the legislation related to treatment, disposal and recycling of sewage sludge, ISO/CEN standards to apply the sludge in agriculture or in other routes, and finally, we can also see the comparison between Europe legislation with Spanish regulations we can find.

Sewage sludge in depth is the title of the <u>Chapter 4</u>, where we study all aspects of dried sewage sludge that we must to know. Definition and types of sewage sludge, treatments and stabilisation, characteristics and components, analysing their possible applications to recycle it and avoiding the incineration or landfilling that increase the Greenhouse gases emissions.

We continue with <u>Chapter 5</u>, Supplementary cementing materials (SCM) are discussed, firstly with a brief introduction about SCM with definition and some examples of concrete cement-based application before exposing a classification of supplementary cementing materials, discussing the most known and used SCM nowadays according to its definition, history, effects on cement-based concrete properties, chemical and physical properties, applications and types. Finally the possible place that would take the sewage sludge as cement replacement is commentated.

The <u>Chapter 6</u> deals with Sewage sludge in cement mix design, the laboratory tests to analyse the sludge in cement mix design performed are described (previous work, making cement samples and testing cement samples). This point is the most relevant in the research because of with these results we can get scientific and real results to analyse them. We have tested mechanical and physical properties with specimens made with different percentages of sludge (10%, 20%, 30% and 40%) about cement weight.

The <u>Chapter 7</u> includes the role of sewage sludge on Sustainable Development, exposing the environmental advantages in the use of the sludge from wastewater treatment plants. Today, researching on the reusing of possible supplementary materials in cement mix





design is absolutely essential, saving money and energy, getting better cements and concretes with improved physical and chemical characteristics.

Finally, the <u>Chapter 8</u> are final conclusions about the possible use of sewage sludge in cement-based composites mix design, after knowing the results from all tests performed in the laboratory, all publications read about the issue and all information given in the chapters of this project relating to dried sewage sludge.





## 1.- Cement: History & production

#### 1.1. - Cement history

Historical data indicate that some mortars and concretes were used in Egyptians and Chinese civilizations about 3000 B.C., who used gypsum and limestones for give stabilization to his stones, later the Grecians (500 B.C.) added clays in the mix.

However, it was the Romans who used their famous mortar fabricated with limestones and volcanic soil additions from Pozzuoli, coastal town situated at the foot of Vesuvius on the east of Italy, in Naples.

#### About pozzolana...

<<There is also a Kind of powder from which natural causes produces astonishing results. This substance, when mixed with lime and rubble, not only lends strength to buildings of other kinds, but even when piers are constructed of it in the sea, they set hard under water>>

(Vitruvius, "The Ten Books of Architecture" Dover Publications, 1960)

With this material, which had cementing properties due to its alumina and silica, they built numerous constructions, we can highlight the public baths of Rome, the theatre of Pompeii the Pont du Gard or the Pantheon.

It was not until 1756 when **John Smeaton** (1724-1792), an engineer from Leeds, used mortars obtained by calcination of limestone and clay mixtures which harden under water to rebuild the Eddystone Lighthouse, at the Cornwall coast, it was finished in 1759 and its foundation still endures.

Figure 1: Eddystonne Lighthouse

Developed studies performed by French aristocrat **Lavoisier** (1743-1794) and the engineer **Vicat** (1786-1861) in general chemistry allowed to **James Parker** and **Joseph Aspdin** improve significantly the mix of clay and limestones.

We can say that the first parent cement was Louis Vicat; he proposed the manufacture system that we use nowadays in 1817. He was an important French researcher; in 1818 he published "Recherches experimentales" and "Mortiers et ciments calcaires" in 1928. In this works he indicates how to produce cement using limestones and clays with the correct proportions and grounded together.







Figure 2: Souillac Bridge

Taking this as his starting point, Louis Vicat designed the first bridge with mass concrete, "Souillac Bridge" which was built between 1812 and 1824 over the Dordogne River.

It is 180 metres length and it has 7 spans with 22 metres length.

Portland cement was patented in October 21, 1824 by Joseph Aspdin. It was named

"Portland cement" because of its colour because its colour resembled the stone quarried on the Isle of Portland off the British coast. The invention was to bake in an oven at high temperatures a milled mixture of charcoal and clay, really similar to the current form. Using this cement, in 1828 Isambard K. Brunel scored concrete which was used to repair several gaps appeared in the famous Thames Tunnel in London.



Figure 3: Thames Tunnel

Cement manufacturing as we know nowadays is due to Isaac Johnson, who in 1845 achieved temperatures high enough to get clinker hydraulically active from the mixture of clay and limestone used as raw material. Johnson improves the process developed by Aspdin, giving lots of information about the manufacturing with parameters of design and amounts.

The intense development of the construction of railways, bridges, ports, dams, etc... in the second half of the XIX century, gives great importance to cement factories, beginning to spread everywhere.

It is from 1900 when the Portland **cements are imposed on engineering** and when it begins a rapid decline in the consumption of natural cements.

#### 1.2. - Cement manufacturing process

The cement manufacturing process is a mix of traditional chemistry and high technology equipment to make the cement used in buildings around the world. The process consists on various steps, which will be explained below.



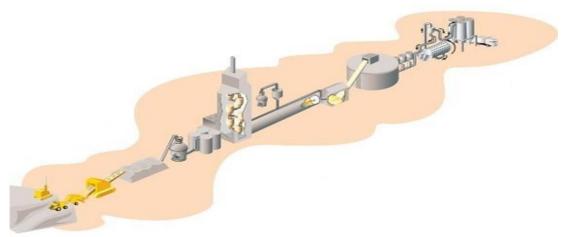


Figure 4: Cement manufacture process

#### 1.2.1. - Extraction and quarry of raw materials.

The raw materials needed to produce cement (calcium carbonate, silica, alumina and iron ore) are extracted from limestone rock, chalk, shale or clay. These raw materials are won from the quarry either by extraction or through blasting. Huge power shovels are used to load dump trucks or small railroad cars for transportation to the cement plant, which is usually nearby. This saves the extra fuel cost and makes cement somehow economical.

#### Examples of raw materials for Portland cement manufacture

Calcium	Silicon	Aluminum	Iron
Limestone	Clay	Clay	Clay
Marl	Marl	Shale	Iron ore
Calcite	Sand	Fly ash	Mill scale
Aragonite	Shale	Aluminum ore refuse	Shale
Shale	Fly ash		Blast furnace dust
Sea Shells	Rice hull ash		
Cement kiln dust	Slag		

Table 1: Raw materials for Portland cement manufacture

The ingredients listed above include both naturally occurring materials such as limestone and clay, and industrial by-product materials such as slag and fly ash. From table it may seem as if just about any material that contains one of the main cement elements can





be tossed into the kiln, but this is not quite true. Materials that contain more than minor amounts of metallic elements such as magnesium, sodium, potassium, strontium, and various heavy metals cannot be used, as these will not burn off in the kiln and will negatively affect the cement.

Another consideration is the **reactivity**, which is a function of both the chemical structure and the fineness. Clays are ideal because they are made of fine particles already and thus need little processing prior to use, and are the most common source of silica and alumina. Calcium is most often obtained from quarried rock, particularly limestone (calcium carbonate) which must be crushed and ground before entering the kiln. The most readily abundant source of silica is quartz, but pure quartz is very unreactive even at the maximum kiln temperature and cannot be used.

These materials are crushed through a milling process. At this stage, additional minerals are added to ensure the correct chemical composition .These minerals can be obtained from waste or by-products of other industries, such as paper ash. After milling, the raw meal is transported to the plant where it is stored.

#### 1.2.2. - Analyzing, blending and grinding.

The raw materials from quarry are now in plant laboratory, where they are analyzed and proper proportioning of limestone and clay. Usually, **limestone is 80% and clay 20%.** There are some indicators to know the correct dosage of mix (clay and limestone). With these formulates the manufacturers keep the correct proportions of calcium carbonates, silica, alumina, iron ore, etc. Le Chatelier and Michaelis proposed the following:

Le Chatelier; 
$$\frac{CaO + MgO}{SiO_2 + Al_2O_3} = 3$$

Michaelis; 
$$\frac{CaO}{SiO_2 + Al_2O_3 + Fe_2O_3} = 1.8 - 2.3$$

When the raw is mixed, plant grinds it with the help of heavy wheel type rollers and rotating table. Grinding produces a fine powder (known as raw meal) which is stored in a prehomogenization pile.





#### 1.2.3. - Pre-heating and burning raw material.

The material is ready to enter in the pre-heating chamber. Pre-heater chamber consists on series of vertical cyclone from where the raw material passes before the kiln. Pre-heating chamber utilizes the emitting hot gases from kiln reaching a temperature less than 800°C. Saving energy is really good for reduce the length of kiln, from 180 to 80 meters approximately, and it is essential to make a plant environmental friendly.



Figure 5: Preheaters

Kiln is a huge rotating furnace also called as the heart of cement making process. In the Kiln, raw material is heated up to 1500°C, this temperature begins decarbonation. The kiln itself is angled by 3° to the horizontal to allow the material to pass through it, over a period of between 20-30 minutes. The series of chemical reactions between calcium and silicon dioxide compounds form the primary constituents of cement. When material reaches the lower part of the kiln, it forms the shape of clinker.

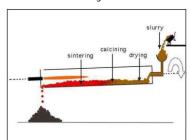
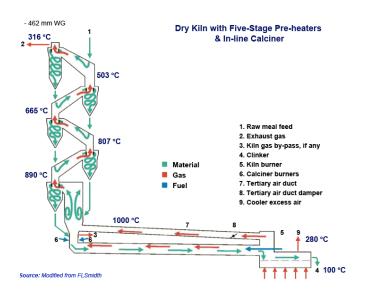


Figure 6: Kiln



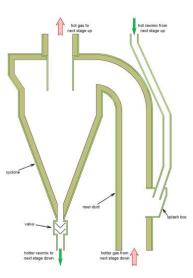


Figure 7: Preheaters schemes





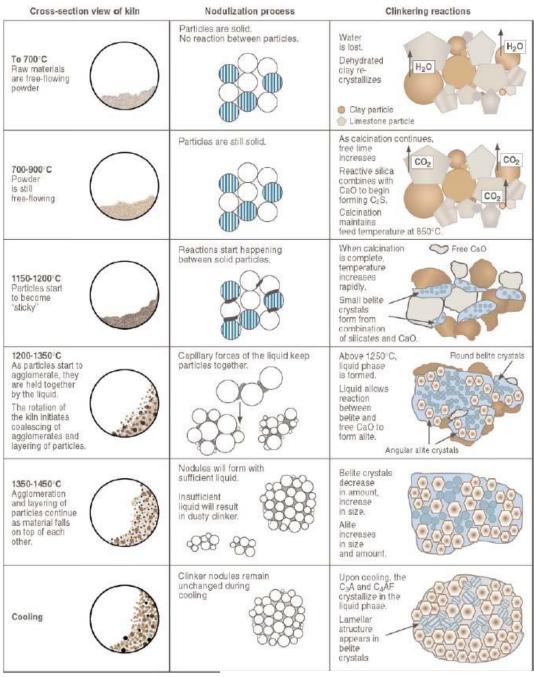


Figure 8: Clinker evolution in the kiln

#### 1.2.4. - Cooling and final grinding

After passing out from the kiln, clinkers are cooled by mean of forced air. Clinker released the absorbed heat and cooled to lower temperature. This step is essential due to  $C_3S$  (Alite) generated in the kiln is highly unstable.





When clinker is cool, we ground it using a ball mill. This is essentially a large rotating drum containing steel balls. The drum rotates approximately once every couple of seconds.

The drum is generally divided into two or three chambers with different size grinding media.

Grinding systems are either "open circuit" or "closed circuit". In an open circuit system, the feed rate of incoming clinker is adjusted to achieve the desired fineness. In a closed circuit system, coarse particles are separated from the finer product and returned for further grinding.



Figure 9: Interior view of ball mill

As part of the grinding process, **calcium sulphate is added (3-5%) as a set regulator**, usually in the form of gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O). Since the clinker gets hot in the mill due to the heat generated by grinding, gypsum can be partly dehydrated. It forms hemihydrate, or plaster of Paris (CaSO<sub>4</sub>·1/2H<sub>2</sub>O). On further heating, hemihydrate dehydrates further to a form of calcium sulphate known as soluble anhydrite (CaSO<sub>4</sub>).

The relative proportions and different solubilities of these various types of calcium sulphate are of importance in controlling the rate of C₃A hydration and consequently of cement set retardation. For set regulation, the most important feature of aluminate is not necessarily the absolute amount present, but the amount of surface which is available to water for reaction.

#### 1.2.5. - Packing and shipping

The last step in the cement making process is packing and shipping, cement is stored in silos (large storages tanks of cement) before being shipped in bulk or in bags. Most of cement is shipped in bulk quantities by rails or ships, remaining cement is packed in 20-40 kg bags for customers whom need is very small.



Figure 10: Bulk quantities cement transport







Figure 11: Bags cement transport

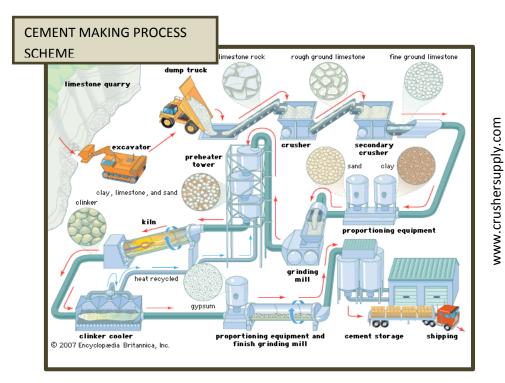


Figure 12: Cement manufacture process II

#### 1.3. - Environmental impact

#### CO<sub>2</sub> and cement making process

60% of emissions are due to the transformation of raw materials at high temperatures and the remaining 40% result from the combustion required to heat the cement kilns to 1500°C.





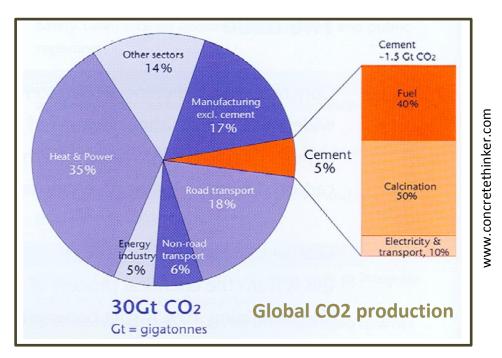


Figure 13: Global CO2 production

#### Cement not only generates CO2, but it reabsorbs CO2 in carbonation process.

During the life of a concrete structure, the concrete carbonates and absorbs the CO2 released by calcination during the cement manufacturing process. Once concrete has returned to fine particles, full carbonation occurs, and all the CO2 released by calcination is reabsorbed. A recent study indicates that in countries with the most favourable recycling practices, it is realistic to assume that approximately 86% of the concrete is carbonated after 100 years. During this time, the concrete will absorb approximately 57% of the CO2 emitted during the original calcination. About 50% of the CO2 is absorbed within a short time after concrete is crushed during recycling operations. (Nordic Innovation Centre Project 03018).





# 2.- Sewage sludge: History & production

#### 2.1. - Sewage sludge history

It is essential to know how are produced sewage sludge; because of there are lots of types of sludge. Also, learning about the wastewater treatment plants history and production becomes in an important point in the project to continue with its possible uses in cement manufacturing.

Wastewater treatment plants have grown the last century. The first signs of plumbing date back as far as 8000 B.C. in Scotland, and 4000 years later in Iraq appeared vertical cesspits under the homes. 3000-2000 B.C. the inhabitants of Mohenjo-Daro (Pakistan) began designed a separate room in the house to be a latrine room, here drains were connected to a sewer in the street, where the wastes went to either the Indus River or to large cesspits.



Figure 14: Mohenjo-Daro

The Romans were the best architects in water transport in the history. The Cloaca Maxima, in Rome, is the main wastewater collector and presumably flows the course of an old ditch which was used at about 500 B.C. although his building began 235 years before.

Following the Middle Ages and Fall of Rome, infrastructure building came to a near halt and was not resurrected for centuries. Wastes were thrown into the streets, from windows. It became polite for the gentleman to walk on the outside of a lady when walking down a street. The gentleman would be more in the line of fire from wastes being thrown from overhead.

After this period of stagnation, cities become to develop and regain its glory in the sixteenth and seventeenth centuries. In the second half of the eighteenth century the industrial revolution, in which the largest set of socioeconomic, technological and cultural transformation in the history of humanity is experiencing, from the Neolithic occurs.

In 1806 starts working in Paris the largest water treatment plant known so far. There sediment water for 12 hours before filtration, the filters consisted of sand and coal.





Today, we have modern wastewater treatment plants from Atotonilco WWTP (Mexico), the biggest WWTP in the world, to modern UV system, which is a physical process that instantaneously neutralizes microorganisms as they pass by ultraviolet lamps submerged in the effluent. The process adds nothing to the water but UV light, and therefore, has no impact on the chemical composition or the dissolved oxygen content of the water. In that respect, it ensures compliance with ever-tightening wastewater effluent discharge regulation.



Figure 15: Atotonilco WWTP

Taking this as our starting point, we can begin with the sewage sludge production, explaining all necessaries steps to get the sludge in a typical wastewater treatment plant. Wastewater treatment plants (WWTP), also called sewage treatment plants or water pollution control plants, remove most pollutants from wastewater before it is released to local waterways. Those plants clean the water with biological and physical processes which are normal in rivers, lakes, etc. Those plants work quickly, taking about 6-7 hours to remove most of pollutants from the wastewater. In the natural environment this process could take many weeks, so it would be impossible to clean all wastewater from big cities.

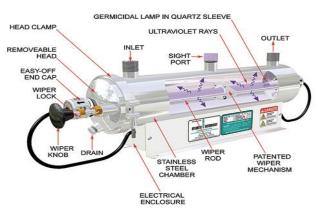


Figure 16: Germicidal lamp





#### 2.2. - Steps to remove most of pollutants from wastewater

#### 2.2.1. - Previous treatment

Wastewater flows into the plants from sewers connected to homes and businesses. Physical processes are the first step in the wastewater treatment. This wants to say that things are physically removed from the waste. The incoming wastewater, called "influent", passes through screens consisting of upright bars, spaced 3 to 100 cm. These bars remove large pieces of trash like newspaper, bottles, plastic cups or similar protecting the main sewage pumps and other equipment. The garbage is transported to landfills.



Figure 17: Screening

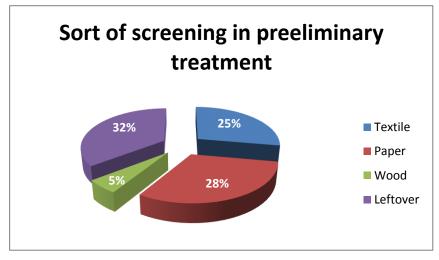
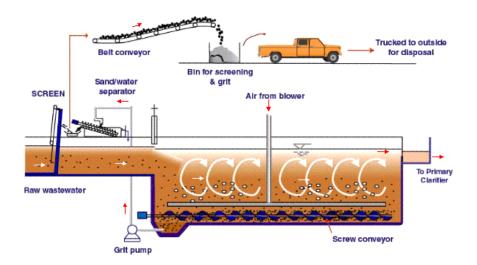


Figure 18: Sort of screening in preliminary treatment





After the liquid passes through bar screens, it enters a large settling tank, sometimes called a grit chamber. The influent flow is slowed so any heavy solids (such as sand and gravel) that remain settle to the bottom of the basin. The solids that fall to the bottom of the basin are removed from the treatment process.



SCHEMATIC OF HEADWORKS (Screen & Aerated Grit Chamber)

Figure 19: Settling tank

#### 2.2.2. - Primary treatment

Particulate organic matter is removed by primary clarifiers. From the grit chamber, the liquid is often pumped to another basin called a "primary clarifier" or "primary sedimentation tanks". The main purpose of the primary stage is to produce a generally homogenous liquid capable of being treated biologically and a sludge that can be separately treated or processed.

Clarifiers are typically a circular sedimentation basin. Clarifiers allow further slowing of the wastewater so that heavier organics fall to the bottom. In primary treatment, a mechanical process also takes place; a skimmer (sometimes called a rake) slowly skims the top of the water to remove the fats, oils, and greases that float to the top.

The fats, oils and greases that are scraped off the top are diverted to the digester, which will be explained later. The solids that fall to the bottom of the basin are removed from further treatment. Depending on the facility, these solids could be moved to a digester, to a sludge press or to a drying bed.





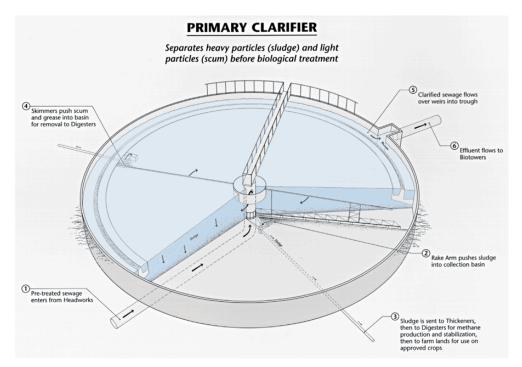


Figure 20: Primary clarifier

After the fats, oils and greases have been removed from the top and the organics materials have fallen to the bottom, the remaining water flows over weirs, moving on to the next step in the treatment process.

Weirs collect remaining small particles floating fats scum, greases, and help oxygenate the water to help the biological process.



Figure 21: Primary clarifier picture





#### 2.2.3. - Secondary treatment

Secondary treatment is called the activated sludge process. This is because air and sludge from the plant treatment process are added to the wastewater to break it down further. Air pumped into large aeration tanks mixes the wastewater and sludge to create an environment for beneficial microorganisms and other tiny organisms that are naturally present in the sewage to grow. These beneficial microorganisms consume most of the remaining organic materials that are polluting the water and this produces heavier particles that will settle later in the treatment process. Wastewater passes through these bubbling tanks during three to six hours.

These microorganisms, also called a "bugs", continue to consume (treat) any

remaining dissolved organic material in the water. There bugs get their name from the fact that they are so small and you need a microscope to see them.

The process of microbes eating waste products actually begins in the sewer pipes along the way to the plant. However, aeration basins provide the perfect environment for maximum consumption of the organic wastes.



Figure 22: Aeration tank picture

The process of using microbes to consume wastes in this oxygen-rich environment is called "activated sludge".

Activated sludge looks like dark mud. It is rich with active ("live") microbes; bacteria and protozoans. The bacteria and protozoans require oxygen to live and thrive, just like other living organisms. The aeration basin gives the extra oxygen so they will grow and consume the waste.

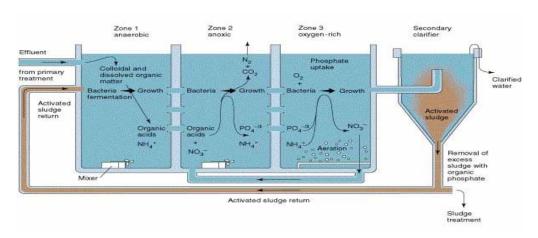


Figure 23: Aeration tank scheme





The aerated wastewater then flows to the final settling tanks (second clarifier) which are similar to the primary settling tanks. Here the heavy particles and other solids settle to the bottom as secondary sludge. Some of this sludge is re-circulated back to the aeration tanks as "seed" to stimulate the activated sludge process. The returned sludge contains millions of microorganisms that help maintain the right mix of bacteria and air in the tank and contribute to the removal of as many pollutants as possible.

The food chain is a continual cycle. In the aeration basins, the microbes digest and break down organic material and then die out when they reach the end of their life cycle. Since new wastewater, carrying new organic material is added all the time, the cycle continues and new microbes are born. When the microbes die, their dead cells stick together in clumps.



Figure 24: Secondary clarifier picture

#### 2.2.4. - Disinfection

For this stage can be used two methods:

#### Chlorination / Dechlorination

Even after primary and secondary treatment, disease causing organisms may remain in the treated wastewater. To disinfect and kill harmful organisms, the wastewater spends a minimum of 20 minutes in chlorine-contact tanks mixing with sodium hypochlorite, the same chemical used in common household bleach.

The treated wastewater, or effluent, is then released into local waterways. In large facilities, the chlorination process is followed by dechlorination, which is the removal of chlorine, to minimize any potentially toxic effect of the disinfectant.

#### **Ultraviolet Light**

Ultraviolet systems can destroy 99.99% of harmful microorganisms without adding chemicals. UV disinfection of water consists of a purely physical, chemical-free process. UV-





C radiation attacks the vital DNA of the bacteria directly. The bacteria lose their reproductive capability and are destroyed.

Because of concerns about high chlorine levels in the disinfected water, some wastewater systems are now using ultraviolet light as an alternative to using a chemical disinfectant being the main inconvenience the consumption of electrical power, more expensive than chlorination/dechlorination process.



Figure 25: UV light in water

#### 2.2.5. – Abstract Scheme

#### WASTEWATER TREATMENT PROCESS. SEWAGE SLUDGE GENERATION.

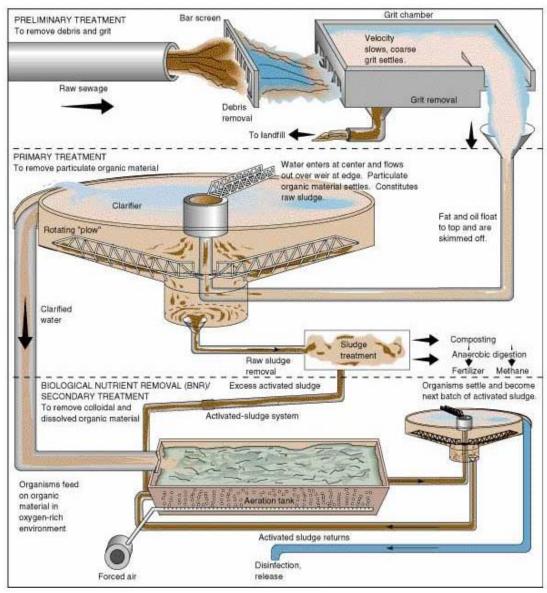


Figure 26: Wastewater treatment process





#### 2.3. - Sludge treatment process



#### 2.3.1. – Thickening

Thickening is the first step for reducing the sludge volume by removal of free sludge water. Thin sludge is concentrated to thick sludge. Thick sludge has a higher viscosity, but must still be pumpable.

Sludge settles in gravity thickeners and is compressed by the weight of its own solids. Due to their higher specific density, primary and digested sludge can be better gravity-thickened than secondary sludge. Secondary sludge is preferably thickened mechanically, separate from primary sludge. Polymers are added to the thin sludge for flocculation. Generation of large and strong flocs depends on the right choice and dosage of polymers, and on intensive mixing of polymers and sludge. Sludge water is released between the flocs and drains by gravity through a filter where flocs are retained thereon.

An alternative to gravity thickening is dissolved- air flotation. In this method, air bubbles carry the solids to the surface, where a layer of thickened sludge forms.

#### 2.3.2. – Digestion

Sludge is sent to large, heated and enclosed tanks called "digesters". The environment in the digester is anaerobic, which means it is completely free of dissolved oxygen. By-products of anaerobic digestion include methane gas, ammonia, and hydrogen sulphide. Sludge digestion is a biological process in which organic solids are decomposed into stable substances. Digestion reduces the total mass of solids, destroys pathogens, and makes it easier to dewater or dry the sludge. Digested sludge is inoffensive, having the appearance and characteristics of a rich potting soil.

Most large sewage treatment plants use a two-stage digestion system in which organics are metabolized by bacteria anaerobically. In the first stage, the sludge, thickened to a dry solid content of about 5 per cent, is heated and mixed in a closed tank for several days. Acid-forming bacteria hydrolyze large molecules such as proteins and lipids, breaking them into smaller water-soluble molecules, and then ferment those smaller molecules into various fatty acids. The sludge then flows into a second tank, where the dissolved matter is converted by other bacteria into biogas, a mixture of carbon dioxide and methane. Methane





is combustible and is used as a fuel to heat the first digestion tank as well as to generate electricity for the plant.

#### 2.3.3. – Dewatering

Dewatering reduces the liquid volume of sludge by about 90%. Digested sludge is sent through large centrifuges that operate like the spin cycle of a washing machine. The force from the very fast spinning of the centrifuges separates most of the water from the solids in the sludge, creating a substance known as biosolids. The water drawn from the spinning process is then returned to the head of the plant for reprocessing.

These processed biosolids can be applied directly on land as a fertilizer (in an agricultural setting), sent to the landfill or used to make compost mixtures for people to purchase for lawn and garden use.

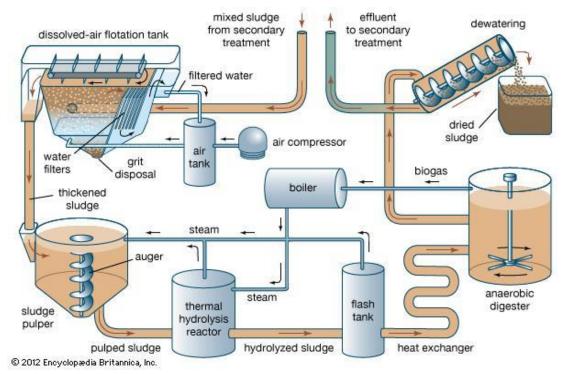


Figure 27: Sludge treatment process

#### 2.4. - Environmental impact assessment of sludge production

Greenhouse Gases of Concern from Wastewater Treatment Plants are:

- -CO<sub>2</sub>
- -CH<sub>4</sub>
- -N<sub>2</sub>O





The greenhouse gas emitted from wastewater treatment plants depend on the treatment technology employed. The paragraphs below detail the emissions sources of a particular Greenhouse gases (GHG) from a wastewater treatment plant.

#### Carbon Dioxide (CO2)

CO<sub>2</sub> production is attributed to two main factors; treatment process and electricity consumption. During anaerobic process the BOD (Biochemical oxygen demand) of wastewater is either incorporated into biomass or it is converted to CO<sub>2</sub> and CH<sub>4</sub>. A fraction of biomass is further converted to CO<sub>2</sub> and CH<sub>4</sub> via endogenous respiration. Other emission sources of carbon dioxide are sludge digesters and from digester gas combustion.

In the aerobic process CO<sub>2</sub> is produced through the breakdown of organic matter in the activated sludge process and some through the primary clarifiers.

#### Methane (CH<sub>4</sub>)

Wastewater as well as its sludge components can produce CH4 if it degrades anaerobically. The extent of CH4 production depends primarily on the quantity of degradable organic material in the wastewater, the temperature, and the type of treatment system. With increases in temperature, the rate of CH4 production increases. This is especially important in uncontrolled system and in warm climates.

#### Nitrous Oxide (N2O)

N2O is associated with the degradation of nitrogen components in the wastewater. Domestic wastewater includes human sewage mixed with other household wastewater, which can include effluent from shower drains, sink drains, washing machines, etc.

After being processed, treated effluent is typically discharged to a receiving water environment (river, lake, etc.). Direct emissions of N2O may be generated during both NDN (Nitrificacion-DeNitrification) of the nitrogen present. Both processes can occur in the plant and in the water that is receiving the effluent.

Nitrification is an aerobic process converting ammonia and other nitrogen compounds into nitrate (NO3-), while denitrification occurs under anoxic conditions (without free oxygen), and involves the biological conversion of nitrate into nitrogen gas (N2). N20 can be an intermediate product of both processes, but is more often associated with denitrification.

The most GHGs are produced during the anaerobic digestion and the sludge reuse, shown in figure below.





#### The contribution of processes in a WWTP to GHG emissions.

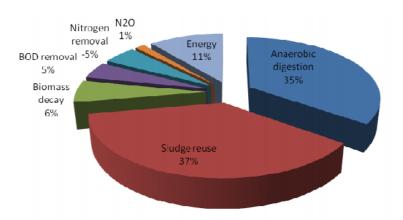


Figure 28: The contribution of processes in a WWTP to GHC emissions

#### Greenhouse gas emissions of a wastewater treatment plant

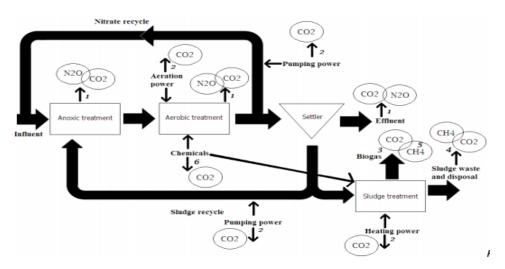


Figure 29: Greenhouse gas emissions of a wastewater treatment plant





# 3.- Legislation in Europe about the sewage sludge use

#### 3.1. – Introduction

Last decade in Europe a progressive increase in production of sludge from municipal wastewater treatment plants, (from 8\*10<sup>6</sup> tonnes in 1998 to 10<sup>7</sup> tonnes in 2007) had been revealed and a continuous raise of the cost for landfill disposal has been verified.

Many researchers assume that the production of sewage sludge will increase in the next years because of treatment requirements connected to actual regulations, (mainly in Europe) and new wastewater treatment plants constructions in emerging countries.

## 3.2. - Legislation related to treatment, disposal and recycling of sewage sludge

The legal framework established by the European Commission and regulating the various sludge routes is mainly composed of Directives which have to be transposed into national legislation by Member States. The ones most relevant to sludge management are the following:

- The Council Directive 86/278/EEC on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture. This Directive sets minimum quality standards for the soil and sludge used in agriculture, and defines monitoring requirements when sludge is spread on agricultural land. The limit values defined in this Directive concern heavy metals concentration for sewage sludge as well as for soil when sewage sludge is used on land and maximum annual heavy metals loads through the application of sewage sludge.
- The Waste Framework Directive (91/156/EEC amending 75/442/EEC on waste) conforms the waste management hierarchy already outlined in the Communication on Community strategy for waste management. According to this hierarchy preference has to be given to waste prevention followed by waste reduction, reuse, recycling, and energy recovery. This Directive establishes principles for the use and disposal of waste, waste management plans, approval procedures and monitoring. In addition, this Directive provides the definition for the term "waste". A list of the different type of waste is provided by the Commission Decision 2001/118/EC which amends Decision 2000/532/EC.





- The Council Directive of 21 May 1991 concerning urban waste water treatment (91/271/EEC), known as the Urban Waste Water Treatment Directive, is aimed at protecting the environment from the adverse effects of waste water discharges. This Directive sets minimum sewage treatment standards to be achieved in stages by the end of 2005, and provides for advanced wastewater treatment for the removal of nitrogen and phosphorus from sensitive areas. Sensitive areas are defined as: areas particularly susceptible to eutrophication, surface waters intended for the abstraction of drinking water with high nitrate levels, and other waters that require a higher standard of treatment to satisfy the requirements of other Directives.
- The Council Directive 91/676/EEC of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources, known as the nitrates Directive, requires identification by Member States of Nitrates Vulnerable Zones. These zones are defined as areas where water quality has or will exceed EC drinking water standard in terms of nitrates concentration (defined in Directive 75/440/EEC concerning the quality required of surface water intended for the abstraction of drinking water in Member States).

Finally, the Commission Decision 98/488/EC establishing the ecological criteria for the award of the Community eco-label to soil improvers, specifies that these products must not contain sewage sludge.

The Directive on the landfill of waste 1999/31/EC will contribute to making disposal of sludge to landfill more difficult, as this Directive aims at reducing the quantity of biodegradable waste going to landfills, and prohibits the landfilling of both liquid and untreated wastes.

Directive on the Incineration of Waste 200/76/EC sets limit values for emissions of pollutants to air due to waste incineration.

#### 3.3. - Standardization ISO/CEN

In addition to the legal framework, the ISO and CEN committee establish international standards and set out recommendations on sludge management. In particular, CEN/TC 308 on characterisation of sludge has published or is in the process of producing reports and standards on good practices on:

- Good practices for the use and disposal of sludge.
- The standard vocabulary
- The determination of the various elements in sludge





CEN has published a report on "Characterisation of sludge – Guide to preserve and extend sludge utilisation and disposal routes" (CR 13846)

The standards which have been published by CEN concerning characterisation of sludge are in the Appendix 1.

#### 3.4. - Specific requirements for the use of sludge in agriculture

#### - Limit values for heavy metals in sludge

According to Directive 86/278/EEC, national legislation which has been established in the Member States prohibits the use of sludge in agriculture if the heavy metals concentrations exceed specific limit values (Member States have to choose between Annex I B and Annex I C). In addition, the Directive specifies that sludge may not be used on land when the soil concentration exceeds the limit values set out in the same Directive and that Member States have to ensure that the limit values are not exceeded as a result of the use of sludge (Annex I A).

The Directive 86/278/EEC specifics limit values for these heavy metals:

- Cadmium
- o Copper
- Nickel
- Lead
- o Zinc
- Mercury
- o Chromium

Below we can see Annex I A, I B and I C from Directive 86/278/EEC compared with R.D. 1310/1990 (Spanish regulation).

ANEXO I A

Valor límite de concentración de metales pesados en los suelos
(mg/kg de materia seca de una muestra representativa de los suelos
tal como la define el anexo II C)

	Valores limite	
Parámetros	Suelos con Ph menor de 7	Suelos con Ph mayor de 7
Cadmio	1	3.0
Cobre	50	210,0
Níquel	30	112,0
Plomo	50	300,0
Zinc	150	450,0
Mercurio	1	1.5
Cromo	100	150,0

Table 2: Annex IA RD. 1310/1990

ANNEX I A

LIMIT VALUES FOR CONCENTRATIONS OF HEAVY METALS IN SOIL

(mg/kg of dry matter in a representative sample, as defined in Annex II C, of soil with a pH of 6 to 7)

Parameters	Limit values (1)	
Cadmium	1 to 3	
Copper (2)	50 to 140	
Nickel (2)	30 to .75	
Lead	50 to 300	
Zinc (2)	150 to 300	
Mercury	1 to 1,5	
Chromium (3)		
	Kerson Maria	

Table 3: Annex IA Directive 86/278/EEC





#### ANNEX I B

## LIMIT VALUES FOR HEAVY-METAL CONCENTRATIONS IN SLUDGE FOR USE IN AGRICULTURE

#### ANEXO I B

### Valor límite de concentración de metales pesados en los lodos destinados a su utilización agraria

(mg/kg de materia seca)

	Valores limite	
Parámetros	Suclos con Ph menor de 7	Suelos con Pi mayor de 7
Cadmio	20	40
Cobre	1.000	1.750
Niquel	300	400
Plomo	750	1.200
Zinc	2,500	4.000
Mercurio	16	25
Cromo	1.000	1.500

(mg/kg of dry matter)

20 to 40 1 000 to 1 750
300 to 400
750 to 1 200
2 500 to 4 000
16 to 25

<sup>(1)</sup> It is not possible at this stage to fix limit values for chromium. The Council will fix these limit values later on the basis of proposals to be submitted by the Commission within one year following notification of this Directive.

Table 4: Annex IB R.D.1310/1990

Table 5: Annex IB Directive 86/278/EEC

#### ANNEX I C

#### LIMIT VALUES FOR AMOUNTS OF HEAVY METALS WHICH MAY BE ADDED ANNUALLY TO AGRICULTURAL LAND, BASED ON A 10-YEAR AVERAGE (kg/ha/yr)

#### ANEXO I C

Valores límites para las cantidades anuales de metales pesados que se podrán introducir en los suelos basándose en una media de diez años

(kg/Ha/año)

Parámetros	Valores límite
Cadmio	
Cobre	12.00
Niquel	
Plomo	15,00
Zinc Mercurio	30.00
	0,10
Cromo	3,00

Table 6: Annex IC R.D.1310/1990

Parameters	Limit values (1
Cadmium	0,15
Copper	12
Nickel	3
Lead	15
Zinc	30
Mercury	0,1
Chromium (2)	

(\*) Member States may permit these limit values to be exceeded in the case of the use of sludge on land which at the time of notification of this Directive is dedicated to the disposal of sludge but on which commercial food crops are being grown exclusively for animal consumption. Member States must inform the Commission of the number and type of sites concerned. They must also ensure that there is no resulting hazard to human health or the environment.

(2) It is not possible at this stage to fix limit values for chromium. The Council will fix these limit values later on the basis of proposals to be submitted by the Commission within one year

tollowing notification of this Directive

Table 7: Annex IC Directive 86/278/EEC

#### Limit values for pathogens in sludge

The Directive 86/278/EEC does not include specific requirements for pathogens content in sludge used in agriculture. However, in order to reduce possible health risks related to pathogens, several national regulations have added limitations on pathogens content to standard requirements on sludge quality. The most common pathogens which are addressed by legislation are salmonella and enteroviruses.





In this case, Spain does not provide any limit values or requirements for pathogens in sludge.

#### Limit values for organic compounds in sludge

Directive 86/278/EEC does not provide any limit values or requirements for organic compounds in sewage sludge. In this case, several national regulations on the use of sludge have added specifications on organics compounds.

Spain, in the Royal Decree 1310/1990, neither provides any limit values or requirements for organic compounds.

#### - Limit values for soil to which sludge is applied

National Regulations on the use of sludge specify limit values for heavy metals in soil, which are in most cases similar or lower than the requirements set in Directive 86/278/EEC. Some countries, like Spain, have defined limit values for several categories of soil pH, while others countries, like Poland have distinguished several categories of soil based on their granulometric content.

We can find in several Member States limitations about the maximum annual load of heavy metals to agricultural land, on a ten year basis, for example in Finland, France or Luxembourg.

When limit values are exceeded, generally sludge cannot be used, however the regulation in some countries (United Kingdom or Luxembourg) specify special place where can be spread.

In Spain, through Royal Decree 1310/1990 specify limit values of heavy metals on sludge with similar values provided in Directive 86/278/EEC as we can check on the follow tables.

ANNEX I A

LIMIT VALUES FOR CONCENTRATIONS OF HEAVY METALS IN SOIL

(mg/kg of dry matter in a representative sample, as defined in Annex II C, of soil with a pH of 6 to 7)

10.100000000	Limit values (1)
Cadmium	1 to 3
Copper (2)	50 to 140
Nickel (2)	30 to .75
Lead	50 to 300
Zinc (2)	150 to 300
Mercury	1 to 1,5
Chromium (3)	190 <u>—</u> 3
of sludge but on which comme exclusively for animal con- inform the Commission of	rective is dedicated to the disposal ercial food crops are being grown sumption. Member States must the number and type of sites seek to ensure that there is no ealth or the environment.

Table 8: Annex IA Directive 86/278/EEC





# ANEXO I A Valor limite de concentración de metales pesados en los suelos (mg/kg de materia seca de una muestra representativa de los suelos tal como la define el anexo II C)

	Valores limite	
Parámetros	Suelos con Ph menor de 7	Suelos con Pr mayor de 7
Cadmio	1	3.0
Cobre	50	210.0
Níquel	30	112,0
Plomo	50	300,0
Zinc	150	450,0
Mercurio	1	1,5
Cromo	100	150,0

Table 9: Annex IA R.D. 1310/1990

#### - Obligations for treatment

The Directive 86/278/EEC specifies in that "sludge shall be treated before being used in agriculture". The definition of treated sludge is provided in Article 2 as "sludge which has undergone biological, chemical or heat treatment, long-term storage or any other appropriate process so as significantly to reduce its fermentability and the health hazards resulting from its use". However, the use of untreated sludge is possible according to the same Directive "if it is injected or worked into the soil"

In fact, most countries have transposed these provisions into national legislation, however, some countries like Spain prohibit the use of untreated sludge (in agriculture), while other countries have no specific requirements concerning the treatment of sludge.

#### - Surfaces on which use of sludge is prohibited

The Directive 86/278/EEC in the Article 7 provides restrictions concerning the spreading of sludge on grazing and pastureland, and on land on which vegetable and fruits are grown.

Spain also prohibits the spreading of sludge in the same conditions that the Directive 86/278/EEC, however most countries like Belgium have introduced higher delays before spreading or some countries have introduced restrictions on specific crops, like Austria.

#### Further quality related restrictions

#### Certification and information requirements

Information requirements provided in Directive 86/278/EEC have been transposed in national legislation.





In case of Spain, the Royal Decree 1310/1990 defines the same information requirements as the Directive 86/278/EEC, which are provided in Article 6 and 10 as we can read below.

Article 6(b): "sewage sludge producers shall regularly provide users with all the information referred to in Annex II A".

Article 10: "1. Member States shall ensure that up-to-date records are kept, which register:

- a) The quantities of sludge produced and the quantities supplied for use in agriculture.
- b) The composition and the properties of the sludge in relation to the parameters referred to in Annex A
- c) The type of treatment carried out, as defined in Article 2(b)
- d) The names and addresses of the recipients of the sludge and the place where the sludge is to be used
  - 2. The records shall be available to the competent authorities [...]"

In other cases, national legislation requires additional analysis, like Germany or Denmark. The frequency of analysis is variable too, for example, in Denmark, Finland, France, Luxembourg, Italy and Sweden depends on the size of sludge treatment plant.

Producer responsibility has for the moment remained limited to complying with information requirements provided by Article 10 of Directive 86/278/EEC. Although countries like Denmark the producer is also responsible for ensuring that information on quality accompanies the sludge.

#### Codes of practice and guides

In most countries, no codes of practice or guides on the use of sewage sludge have been developed. Ireland, Sweden and United Kingdom have developed national codes which provide technical guidance and details on the steps to follow when using sludge in agriculture. On the other hand, in Austria and Spain the codes are regional.

In Spain, concretely in the region where I live exists the "Strategic Plan about waste in Region of Murcia", which address about the practice on the use of sewage sludge.

Voluntary agreements on disposal and recycling of sewage sludge

In Europe, only Sweden and United Kingdom have voluntary agreements on the use of sludge. In Sweden is called "Sewage Sludge Agreement", while in United Kingdom is called "Safe Sludge Matrix". In Spain we cannot find any voluntary agreement.





## 3.5. - Specific requirements or legislation for other route (not agriculture)

#### Silviculture (plantation)

Only some countries have national legislations on sewage sludge with specific requirements on the use of sludge in silviculture like Denmark, Germany, Netherlands or Sweden. In addition, in most of cases the term "forest" or "forest soil" is mentioned without specifying whether it covers silviculture, natural forest or reforested areas.

Spain is one of the countries which have not any requirements on the use of sewage sludge in silvicultre.

#### Natural forest

Austria, Belgium and Germany prohibit the use of sludge in natural forest while Spain, Portugal or Sweden don't give any information about the use of sludge in natural forest. However several countries like France the use of sludge in forest areas is authorised, under certain conditions.

In the United Kingdom, the use of sludge in natural forest and reforested areas is addressed by a "Manual of Good Practice for Use of Sewage Sludge in Forestry"

#### Land reclamation

It does not exist specific requirements for the use of sludge in land reclamation in most national legislation. Only Austria Belgium, France and Poland mention the use of sludge in land reclamation in their national regulations.

#### - Green areas

Use of sludge on green areas is prohibited in Germany and Netherlands, however some countries provide additional requirements like Denmark, Sweden, Poland or Estonia. In case of Denmark, sludge must be pasteurised before its use.

The Spanish regulation, as most of nations in Europe, does not address the use of sewage sludge on green areas.

#### Incineration

Normally, we cannot find on National regulations requirements on the incineration of sewage sludge because is covered by general regulations on the incineration of waste. In Netherlands, for example, we can find the "Air Emissions Waste Incineration Decree" in 1993.

In Spain, the Royal Decree 653/2003 establishes limit values in its Annex V about general waste incineration, we cannot find nothing in exclusive about sewage sludge incineration.

#### Disposal to landfill





Disposal to landfill of sludge should progressively be reduced, in application of the Directive on the landfill of waste (1999/31/EEC), which recommends reducing the quantities of biodegradable waste going to landfills, and prohibits the landfilling of both liquid wastes and untreated wastes.

National regulations on sludge do not contain requirements on the disposal to landfill of sewage sludge. Disposal to landfill of sludge is covered by other legislation on landfill. In Spain, disposal to landfill is regulated by Royal Decree 1481/2001, which prohibits the landfilling of liquid wastes and untreated wastes but it does not address about sludge although it recommends reducing the quantities of biodegradable waste.

#### Cement manufacture?

It does not exist any European requirements or legislation about the use of sludge in cement mix design. In any case, the analysis and characterisation of sludge is strongly recommended before including it in the mix.

The scheme below shows an abstract of requirements on sludge uses in Europe.

3.6. - Abstract scheme.





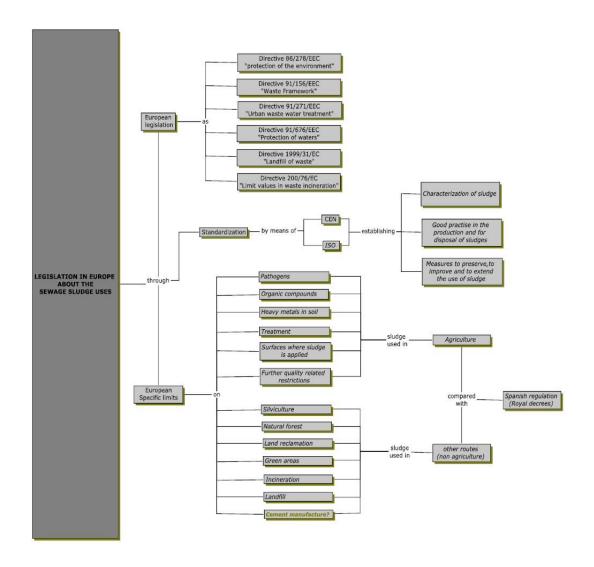


Figure 30: Legislation in Europe about the sewage sludge uses scheme





# 4.- Supplementary cementing materials: Sewage sludge

<< If we are going to produce structures that have a service life of at least 100 years, HFA concrete and concrete with high volumes of other pozzolans such as slag, rice hull ash and metakaolin, will be the concrete of choice. Straight Portland cement concrete is being replaced by a superior concrete product. >>

**Burt Lockwood** 

# 4.1. - Introduction and definition of partial Portland cement replacement

As I said before some times, sustainability is an important issue all over the world. Carbon dioxide emission has been a serious problem in the world. Nowadays, we need to reduce the CO2 emissions which produce the famous greenhouse effect, In cement industry there is a big problem due to it generates about 5-7% of CO2 produced in the world. We must work on it.

The main advantage of using cement replacement materials is that the total volume of clinker required to produce a certain amount of cement would decrease. This would result in a substantial amount of energy saving in the production of cement, reducing the consumption of natural raw materials and the fuel needed in the kiln for production of clinker would be reduced (3000KJ/Kg clinker).

Using supplementary cementing materials (SCM), manufacturing cements with optimum content of cement, improving concrete durability and participating in the good future of our Earth Planet. In this spot I will try to explain the main characteristic of this special materials and particularly sewage sludge as cement replacement material.

Supplementary cementing materials are special types of naturally materials or industrial waste products as sewage sludge that can be used in cement mixes to partially replace some of Portland cement.

When properly used, the Supplementary Cementing Materials can improve the following properties of concrete:

- Less alkali-aggregate reactivity
- Less permeability and absorption of water and other fluids.
- More long term resistance





- Increase the resistance to chloride ions
- Increase the resistance to sulphate attack
- Increase the resistance to acid attack
- Decrease the corrosion rate of steel
- Less segregation of fresh concrete
- Lower the heat of hydration
- Improve rheological properties making it easier to pump, place and finish concrete

However, we have to take into account that the performance of SCM concrete is influenced by:

- The type of SCM (physical and chemical properties)
- The level of replacement used
- The nature of the Portland cement (alkali content)
- The quality of the concrete
- Curing (The slower reaction of some SCM increases the sensitivity of the concrete to curing)

Some publications warn that SCM are not a panacea for all forms of deterioration, they have to be used properly to get good results.

In the following pictures we can see real examples of the SCM use.



Figure 31: Queen Elizabeth II Bridge

Queen Elizabeth II Bridge, which was erected with 70% slag cement in support pies and 50% in deck and towers.



Figure 32: Medway Viaduct

Medway Viaduct (Rail), built with 60% slag in bridge decks, 70% in piles and slipform piers and 80% in pile caps and caissons.





#### 4.2. - Types of supplementary cementing materials (SCM).

Cements can be classified into blended, Ternary Blends and Quaternary Blends. Blended cements have been used for the production of concrete for years, these cements are produced by intergrinding Portland cement clinker with various SCMs or by blending Portland cement with varying quantities of SCMs. Ternary systems consist of Portland cement and two additional SCMs, while quaternary systems contain Portland cement and three SCMs.

SCMs can be divided into two categories based on the type of reaction; hydraulic or pozzolanic. Hydraulic materials react directly with water to form cementitious compounds, while pozzolanic materials chemically react with calcium hydroxide (CH) (Portlandite) to form compounds possessing cementitious properties in the presence of moisture at room temperature.

The most-commonly used cement replacement materials are the following;

#### 4.2.1. - Natural Pozzolans

#### History

Structures built of limestone include the pyramids of Egypt. Long before the invention of Portland cement in 1824, mortars and concretes composed of mixtures and fillers and raw or heat-treated lime were used for construction throughout the world. The pozzolan was volcanic ash produced from two volcanic eruptions; one between 1600 and 1500 B.C. on the Aegean Island of Thera, now called Santorin, Greece; and the other in 79 A.D. at Vesuviuous on the bay of Naples, Italy.

The Greek discovered pozzolan-lime mixtures sometime between 700-600 B.C. and later passed their use of concrete along to the Romans in about 150 B.C. During 600 years of Roman domination, the Romans discovered and developed a variety of pozzolans throughout their empire.

#### **Definition**

Pozzolans are materials containing reactive silica and/or alumina which on their own have little or no binding properties, however when mixed with lime in the presence of water, will set and harden like a cement.

Pozzolans are an important component in the production of more ecological and cheaper Portland cement (OPC). A wide variety of siliceous or aluminous materials may be pozzolanic. In this paragraph we will discuss the most extended. Pozzolans can be classified into two groups: natural pozzolans such as volcanic ash and diatomite, and artificial pozzolans such as calcined clays, pulverized fuel ash and ash from burnt agricultural wastes. They can be blended with ordinary Portland cement (OPC) to improve some characteristics such as





long-term strength, resistance to sulphate attack, among others things, in addition they reduce costs of OPC.

#### Effects on cement-based concrete properties

In Portland cement-based concretes pozzolans are used to replace up to 30 per cent of OPC for use in structural applications and up to 50 per cent for non-structural purposes. As I said before, adding pozzolans in OPC save a considerably amount of money, but using pozzolans as supplementary cement material means improving its technical characteristics, in fresh and hardened concrete as we can see below;

#### Fresh concrete

- Improved water retention (lower bleeding)
- Improved workability
- Extend the time of setting (with reduced content of Portland cement)

#### Hardened concrete

- Lower permeability
- Reduced heat of hydration
- Improved resistance to alkali aggregate reaction
- Higher strengths at later ages
- Increased resistance to attack from sulfates
- Reduced Efflorescence
- Resistance to freeze-thaw

But we do not have only advantages; the main problem of pozzolans is its early strength, lower than OPC. This may delay the dismantling of formwork one or two days. However, some important engineers have recognized these technical and economic advantages and the disadvantages are a small problem if we compare it with the positive side of using pozzolans such as cement replacement material.

#### Chemical and physical properties

The chemical composition of pozzolanas varies considerably but the following can be taken as a guide;

Silica (SiO<sub>2</sub>) + Alumina (AL<sub>2</sub>O<sub>3</sub>) + Iron Oxide (Fe<sub>2</sub>O<sub>3</sub>)-> Not less than 70%

Other Oxides and alkalis-> Not more than 15%

Loss on ignition-> not more than 15%

Silica is normally considered to be the most important active oxide and should not normally fall below 40% of the total, some of the best pozzolans have silica contents above





90%. Carbon contents should be controlled, it should be as low as possible, below 12%. Higher carbon contents can be tolerated but will result in lower strength cements.

When a mixture of Portland cement and a pozzolan reacts, the pozzolanic reaction progresses like an acid-base reaction of lime and alkalis with oxides of the pozzolan.

The reason of the increase of long-term strength is due to the pozzolanic reaction has place in the cement-arid interface, the "weak area" in cements, improving the density and the compression strength. Calcium hydroxide (Portlandite) is produced in hydration of Portland cement and when it reacts with Silica and Alumina, which are present in pozzolanas in presence of water generate Calcium Silicates and Aluminates hydrated, getting cementing properties. The scheme of pozzolanic reaction:

The factors that affect the activity of pozzolans are:

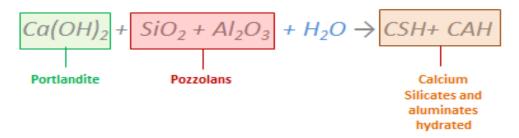


Figure 33: Pozzolanic reaction

- $SiO_2 + Al_2O_3 + Fe_2O_3$  content
- The degree of amourpheness of its structure (for chemical reaction, pozzolans must be amorphous)
- Fineness of its particles (more fineness, more pozzolanic activity)

#### **Applications**

#### Concrete pipes

Pozzolans provide several advantages in the manufacture of concrete pipes. Correctly proportioned mixtures with pozzolans improve the permeability of concrete, making pipe more resistant to acids and sulphates. In addition, a lower heat of hydration got with pozzolans reduce the cracks on the inside surface of pipe.

#### Mass concrete

Using natural pozzolans in mass concrete, it is easy to achieve a lower temperature rise without incurring in the undesirable effects like bleeding, bad workability or segregate.





Others possible applications are located in concrete masonry units or prestressed concrete products.

#### Examples of natural pozzolans:

#### Volcanic ash

Deposits of volcanic ash are found wherever there are active or recently active volcanoes. The place changes considerably their pozzolanic reactivity, although volcanic ashes do not require heating to improve their pozzolanic reactivity, it is possible that they need a little grinding.

Others examples of natural pozzolans are volcanic tuff and Pumicite.

4.2.2. - Fly ash

#### History

Fly ash was first used in concrete in the United States in 1929 for the Hoover Dam, where engineers found that it allowed for less total cement, controlling the heat of hydration. The first comprehensive study was explained in 1937 by R. E. Davis at the University of California and the first major practical application was reported in 1948 with the publication of data on the use of fly ash in the construction of the Hungry Horse Dam (120.000 tonnes of fly ash).

However, we can say that the fly ash history begins 2000 years ago when Romans built the Coliseum in the year 100 A.D. The ash generated from Volcanoes was used extensively in the construction of Roman structures. Coliseum is a classic example of durability achieved by using volcanic ash. Only difference is the fly ash is generated in artificial volcanoes, not in coal fired.



Figure 34: Coliseum

In these years, the most important structure built with fly ash added in concrete as cement replacement is Burj Dubai, the tallest building in the Earth with more than 800 metres.



Figure 35: Burj Khalifa





#### Definition

Fly ash is a by-product of the combustion of pulverized coal in thermal power plants. Power plants produce millions of tons of fly ash, which is disposed to landfills. However, today these plants have dust collector system which remove the fly ash, as a fine particulate from the combustion gases.

These dust collectors can be mechanical or electrostatic precipitators, but these second are the most extended and the best fly ash is obtained from plants using electrostatic precipitators due to mechanical collectors are coarser. The shape of fly ash particle is spherical, from  $0.5~\mu m$  to  $100~\mu m$ .

#### Effects on cement-based concrete properties

#### Fresh concrete

- Retard the setting of cement
- Improve the workability, pumpability
- Reduction in the temperature
- Improve the finish

#### Hardened concrete

- Higher final compressive strength
- Decrease of permeability (more durability)
- Lower creep and shrinkage

#### Disadvantages

It is really important to know the possible disadvantages that we can find in the use of sly ash as cement replacement material. The quality of fly ash is essential, poor quality fly ash can have a negative effect on concrete. The principle advantage of fly ash is reduced permeability at a low cost; however poor quality fly ash can increase permeability. Retarding the setting time if fly ash is used, but it can be perceived as a disadvantage when it could be really beneficial reducing thermal stress.

We can observe below the effect of fly ash in one cubic metre of mass concrete with and without after 8 years exposed to the environment.



Figure 36: Concrete blocks with/without fly ash





#### Chemical and physical properties

The chemical composition of fly ashes depends on the characteristics and composition of the coal burned in power stations. Generally, we can consider that the following elements are the most frequent in fly ashes;

SiO2, Al2O3, Fe2O3 and CaO are the major constituents of most fly ashes, although we can include other elements as MgO, Na2O, K2O, SO3, MnO, TiO2 and C.

As we can see in the following table it exists the same components in fly ash than Ordinary Portland Cement (OPC). However, in fly ash the components are amorphous by nature and in Portland cement is crystalline structure. The main difference is the quantity of each component, while in Portland cement is rich in limestone, in fly ash not too much. On the other hand, in fly ash we can find high amount of reactive silicates and low amount in cement. Mixing both components we get a better concrete product with the best of both.

Component	Fly ash (F)	Fly ash (C)	OPC
SiO	54,9%	39,9%	22,6%
Al <sub>2</sub> O <sub>3</sub>	25,8%	16,7%	4,3%
Fe <sub>2</sub> O <sub>3</sub>	6,9%	5,8%	2,4%
CaO	8,7%	24,3%	64,4%
MgO	1,8%	4,6%	2,1%
SO <sub>3</sub>	0,6%	3,3%	2,3%
Na <sub>2</sub> O & K <sub>2</sub> O	0,6%	1,3%	0,6%

Table 10: Fly ash components

High-calcium fly ash (C) has self-hardening properties, while Low-calcium fly ash, which has very little of no self-cementing properties, hydrates when alkalis and Ca(OH)2 are added. As more Ca(OH)2 is supplied, more of it fixed by silica and alumina in fly ash.

	Pozzolanic	Hydraulic
Silica Fume	XXXXX	
Low-CaO Fly Ash	XXXX	
Moderate CaO Fly Ash	XXXX	X
High-CaO Fly Ash	XXX	ХX
Slag	X	XXXX

Table 11: Pozzolanic/Hydraulic activity of different SCM







Figure 37: Cement /Fly ash picture

#### **Applications**

Fly ash can be used on other ways, not only cement or concrete manufacture (we can see the difference between both materials up). Below are described some of the several possible use for this industrial by-product.

- Structural fills
- Road base
- Synthetic aggregate
- Soil stabilization

#### Types of fly ash

 Class C fly ash (High calcium fly ashes): Produced from lignite of subbituminous coals.

SiO2+Al2O3+Fe2O3>50%

 Class F fly as (Low calcium fly ashes): Produced from anthracite or bituminous coals.

SiO2+Al2O3+Fe2O3>70%

Class C fly ash is considered a pozzolan material, however Class F requires a cementing agent to form concrete. Class C is typically considered the best type.





#### 4.2.3. - Granulated ground blast furnace slag

#### History

Granulated ground blast furnace slag is not a new product. It has been proven its advantages in its use all over the world since the mid-1800s. In 1862 Emil Langen proposed a granulation process to facilitate removal and handling of iron blast-furnace slag.

Michaelis, Prussing, Tetmayer, Prost, Feret and Green investigated about glassy iron blast-furnace slags, their investigation, along with Pasow, who introduced the process of air granulation, played an important part in the development of iron blast-furnace slag as a hydraulic binder. A cause of these researching, the first commercial use of slag cements was in Germany in 1865, while in Paris it was used to build the underground metro system.

#### Definition

Granulated ground blast furnace slag is a by-product of the production of iron in a blastfurnace where iron, limestone and coke are heated to about 1500°C. Then, two products are produced; molten iron, and molten slag. The molten slag is lighter and floats on the top of the molten iron. Silicates and alumina from the original iron ore, combined with some oxides from the limestone are contained in molten slag.

Secondly, the process of granulating the slag generates particles no larger than 5mm in diameter, resulting granular material with 95% non-crystalline calcium-aluminosilicates. Finally, the material is processed and ground to a very fine powder called Ground granulated blast furnace slag.

#### Effects on cement-based concrete properties

#### Fresh concrete

- Improved workability
- Extended time of setting
- Bleeding: when GGBF is finer than Portland cement, bleeding is reduced, but if it is coarser, bleeding may increase.

#### Hardened concrete

- Strength: Lower early compressive resistance but better long-age compressive strength
- Same modulus of elasticity
- Greater creep and shrinkage
- Influence of curing: The proper moisture and temperature is really important to obtain a correct cured.
- Light colour
- Reduced heat of hydration
- Reduced permeability





- Increase resistance to sulphate attack
- Reduction of expansion due to alkali-silica reaction
- Resistance to freezing and thawing: The same
- Resistance to the corrosion of reinforcement: Reduce concrete permeability, so improve the corrosion resistance.

#### Chemical and physical properties

Generally, silicon, calcium, aluminium, magnesium and oxygen constitute 95 % or more of the blast-furnace slag as we can see in the table below;

Constituents	%
SiO <sub>2</sub>	32-42
$Al_2O_3$	7,0-16
CaO	32-45
MgO	5-15.0
S	0.7-2.2
Fe <sub>2</sub> O <sub>3</sub>	0.1-1.5
MnO	0.2-1.0

Table 12: Granulated ground blast furnace slag components

To maximize hydraulic properties, the molten slag must be cooled rapidly as it leaves the blast furnace. This rapid cooling minimizes crystallization, if the cooled is slow, it produced a crystalline structure and do not possess significant cementitious properties.

Another process, the molten slag passes over a vibrating feed plate, where it is expanded and cooled by water sprays, then passes into a rotating, finned drum, which throws it into the air where it rapidly solidifies to spherical pellets. The resulting product can be used as a cementitious material, or as lightweight aggregate.

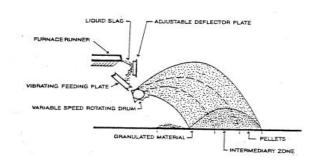


Figure 38: Granulated ground blast furnace slag pelletization process





#### **Applications**

The most important applications of GGBF is the improvement of cements.

#### Types of granulated ground blast furnace slag

They can be classified by their strengths when they are blended with the same mass of Portland cement based on hydraulic activity.

#### 4.2.4. - Silica fume

#### History

Silica fume was first mentioned in a US patent from 1944 of James William Sharp. James noted that bleeding was reduced and also observed an important increase of strength concrete. Few years later, in 1952 Carl Johan Bernhardt worked with silica fume as cement replacement up to 30%, publishing the first known published technical paper on silica fume in concrete. He reported a significant increase in strength and the improvement in freezethaw and sulphate resistance.

Silica fume was not available in big amount, it was the reason of the blockage in the researches with this by-product. Only the implementation of harder environmental laws during the 70s did silicon smelter begin to capture and collect the silica fume, the objective was to find uses for it instead of landfilling the material and the tests performed by the professor Bernhardt were taken into account.





Spring 2001

Spring 2002

Xibei Ferroallovs. China

Figure 39: Before/after silica fume collection

The sales in concrete industry started in Norway in the early 70s. The first documented used in structural concrete was a silo roof slab cast in 1971 at the Fiskaa plant in an environment with corrosive gases.





#### Definition

Silica fume is a by-product of producing silicon metal or ferrosilicon alloys. Silicon metal and alloys are produced in electric furnaces, with quartz, coal and woodchips. The smoke generated from kiln is collected and sold as silica fume. From this time, the development of silica fume as cement replacement has had an exponential growth.

#### Effects on cement-based concrete properties

#### Fresh concrete

- Increase of workability (very often are used plasticizers due to the more water consumption of silica fume)
- Reducing the bleeding and segregation
- Lower shrinkage and cracking

#### Hardened concrete

- High compressive strength.
- Lower impermeability (transition zone between hydrated cement paste and the aggregate)

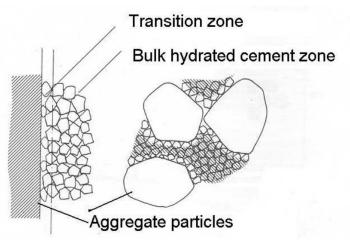


Figure 40: Cement replacement material in cement

#### Chemical and physical properties

As I told in "Definition", Silica fume is an inherent co-product of silicon and ferrosilicon, but silicon is not found in nature, and is normally produced from silica (SiO2) and carbon (C), The reaction is the following;

 $SiO_2+2C = Si + 2CO$ 





Where  $SiO_2$  is quartz, C is a mix of coal, coke and wood chips and for ferrosilicon an iron source is added, for example, iron oxide.

The production takes place in large electric kilns at temperatures above 2000°C.

#### **Applications**

- Shotcrete
- Oil well grouting
- Refractory materials
- Polymers and elastomers.

#### Types of silica fume

We can divide silica fume according to its colour (dark grey or light grey), and according to their commercially forms;

- As-produced: Extremely fineness and low bulk density, so it has really handling problems. It is difficult to transport and it generates lots of dust.
- Slurry Silica-fume: To solve the problems associated with transporting and handling the as-produced silica fume, some suppliers have concentrated supplying silica fume as a water-based slurry
- Densified (compacted): The most used as cement replacement, as produced silica fume is compacted, improving the handling and reducing the dust related to the as-produced silica fume.
- Pelletized silica fume: It is not used in cement, the silica fume is pelletied by mixing the silica fume with a small amount of water and often a little cement.
   This process form pellets that must be disposed of in landfills.

#### 4.2.5. - Meta-kaolin

#### History and definition

The name of kaolin is derived from Chinese term "kao-ling", meaning high ridge, the name of a hill near Jauchau Fu where this material was mined centuries ago for ceramics. The firs used documented was in 1962, when it was incorporated in the concrete used in the Jupia Dam in Brazil (227.300 tonnes)

Metakaolin is a calcined product of the clay mineral kaolinite, which calcine between 600 and 850 $^{\rm a}$ C is transformed to an amorphous phase called metakaolin, this mineral is activated and now has pozzolanic properties, above 900 $^{\rm a}$ C mullite (Al $_6$ Si $_2$ O $_{13}$ ) is produced and





it is now a no pozzolanic material. Meta-kaolin particles are 1.5-5 microns in diameter, like silica fume particles.

#### Effects on cement-based concrete properties

#### Fresh concrete

- Alkali-sand reaction is reduced
- Extend the setting time
- Pasticizer or water reducer have to be added (Lower workability)
- Increases Heat of hydration

#### Hardened concrete

- Reduce the pore size (lower permeability, more strength and more acid resistance)
- Sulphate resistance
- Reduced efflorescence
- More freeze-thaw resistance
- White concretes (coloured concretes)

#### Chemical and physical properties

The main constituent, kaolinite is a hydrous aluminium silicate of composition; generally contains 50-55% SiO<sub>2</sub> and 40-45 Al<sub>2</sub>O<sub>3</sub>. Other oxides present in small amounts include Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, CaO and MgO.

Meta-kaolin; 2H<sub>2</sub>O· Al<sub>2</sub>O<sub>3</sub>· 2SiO<sub>2</sub>.

#### **Applications**

- Shotcrete
- Mortars
- Geoloymers
- White concrete

#### Types of meta-kaolin

There are not different types of meta-kaolin, however in several publications, when the reaction from kaolinite to meta-kaolin is performed, it is divided in the temperatures of heating (from 600-850°C).





#### 4.2.6. - Rice husk ash

#### History and definition

Rice milling generates a by-product known as husk. Rice husk is the outer cover of paddy and it is removed during rice milling. Each ton of paddy produces about 200 kg of husk, and when this husk is burnt in the kiln, about 55 kg of RHA is generated.

This rice husk ash contains around 85-95% amorphous silica, being successfully used as a pozzolana in commercial production in several countries as Columbia, Thailand and India due to limited supply of silica.

India is an important rice producing country, about 18-22 million tons of rice husk is generated annually. Rice is grown in large quantities in many Third World countries including China, the Indian sub-continent, South-cast Asia and some regions of Africa and South America.

#### Effects on cement-based concrete properties

#### Fresh concrete

- Workability (need more water → plastifiziers)
- Reducing the bleeding and segregation
- Lower shrinkage and cracking
- Lower heat of hydration

#### Hardened concrete

- Lower density
- Increase of compressive strength
- Reduced water absorption considerably

#### Chemical and physical properties

Chemical composition of rice husk ash when it is burnt is:

Components	%
Fe <sub>2</sub> O <sub>3</sub>	0.54
K <sub>2</sub> O	0.1 - 2.54
SiO <sub>2</sub>	62.5 - 97.6
CaO	0.1 - 1.31
MgO	0.01 - 1.96
Na₂O	0.01 - 1.58
$P_2O_5$	0.01 - 2.69





SiO <sub>3</sub>	0.1 – 1.23
Carbon	2.71 – 6.42

Table 13: Rice husk composition

#### **Applications**

Due to its pozzolanic properties, this product can be used in several applications like;

- Insulation material
- Improvement of soil.
- Fuel for power generation
- Absorbents for oils and chemicals
- Pesticides
- Insecticides and bio fertilizers
- Refractory materials
- Ceramic glaze
- Specially paints

#### Types of rice husk ash

The rice husk ash can be categorized according to the type of burning in the kiln, rice husk combustion technology has developed from <u>open air burning</u> in the field (around 70s) to combustion using liquidized layers method (around 90s).

#### 4.2.7. – Limestone: (CaCO<sub>3</sub>) as filler.

#### History and definition

It is known that calcium carbonate has been used from Neolithic, nowadays it continues being used in the most important building material; cement. Limestone is calcareous sedimentary rocks formed at the bottom of lakes and seas with the accumulation of shells, bones and other calcium rich goods. It is composed by calcite (CaCO<sub>3</sub>), which is extracted from rocks in all over the world, not only from limestone, but chalk, travertine are rich in calcium carbonate.

#### Effects on cement-based concrete properties

#### Fresh concrete

- Fineness; Accelerate hydration of alite and aluminates of cement and densify the interfacial zone between the aggregate and cement paste.
- Consistency: Improve the workability

#### Hardened concrete

- Compressive strength is increased at early ages.
- Lower permeability





#### Chemical and physical properties

Physically, is hard (3 on Moh's Scale), compact (2.5 to 2.7 g/cm3), fine , resistant to weather impact and low porosity (water absorption less than 1%).

Chemically, limestone are more than 95% CaCO<sub>3</sub>.

#### Applications and types

Limestone is very common in our life, can be known as a material of a thousand uses due to is present in the most of house hold product, from tooth paste to the adhesive in the bathroom tiles. The table below shows the most common uses for limestone (including cement) according to the type of limestone.

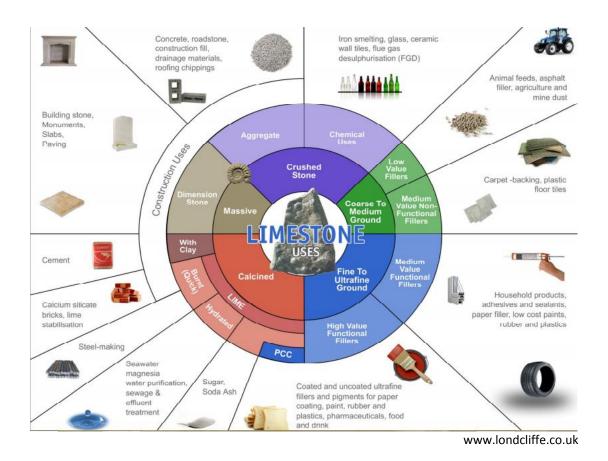


Figure 41: Limestone applications

Finally, I must warn that the slower reaction of some SCMs increase the sensivity of the concrete to curing. The picture below is the application of a polymeric-based curing membrane.





Figure 42: Polymeric curing membrane application

#### 4.3. - Sewage sludge as supplementary cementing material.

After describing the main materials used as cement replacement, talking about sewage sludge as supplementary cementing material is essential, this graphic explains perfectly where is situated the sludge about its components compared with the others famous cement replacement materials.

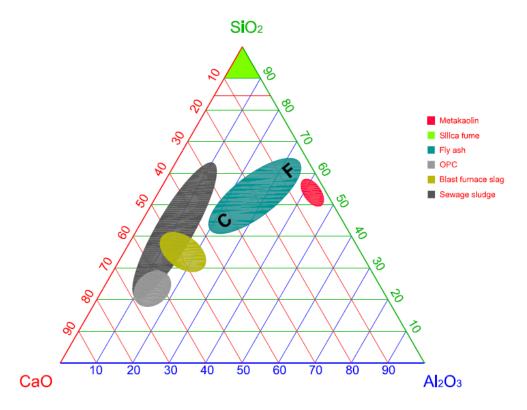


Figure 43: SCM pozzolanic components

To situate sewage sludge in the table above has been chosen the following amount of components according to several publications:

SiO<sub>2</sub>: 18 – 30%
 CaO: 23 – 27%
 Al<sub>2</sub>O<sub>3</sub>: 6 – 13%



The reason for the elongated shape of sludge is the low content in SiO<sub>2</sub>, CaO and Al<sub>2</sub>O<sub>3</sub>.

Sewage sludge as recyclable material is analysed in the next chapter called <u>"Sewage sludge in depth"</u>, where the subject is treated heavily, as well as on the chapter 6 titled <u>"Sewage sludge in cement mix design"</u> the sludge is described as cement replacement material by means of the test performed in the laboratory and summarizing others publications in science books and webs.





## 5.- Sewage sludge in depth.

#### 5.1. - Definition

According to Directive 86/278/EEC, the term "sludge" as:

- Residual sludge from sewage plants treating domestic or urban waste waters and from other sewage plants treating waste waters of a composition similar to domestic and urban waste water
- ii. Residual sludge from septic tanks and other similar installations for the treatment of sewage
- iii. Residual sludge from sewage plants other than those referred to in i) and ii).

...and "treated sludge" as:

Sludge which has undergone biological, chemical or heat treatment, long-term storage or any other appropriate process so as significantly to reduce its fermentability and the health hazards resulting from its use.

In Spain, Royal Decree 1310/1990, transposing Directive 86/278/EEC, defines sludge like the Directive, while the Spanish Minister of Environmental defines it as:

Water and solids mix separated from waste water, as result of natural or artificial processes.

Finally, the Code of Federal Regulations, Title 40: Protection of Environment, Part 503: Standards for the use or disposal of sewage sludge notes:

Sewage sludge is solid, semi-solid, or liquid residue generated during the treatment of domestic sewage in a treatment works. Sewage sludge includes, but is not limited to, domestic septage; scum or solids removed in primary, secondary, or advanced wastewater treatment processes; and a material derived from sewage sludge. Sewage sludge does not include ash generated during the firing of sewage sludge in a sewage sludge incinerator or grit and screenings generated during preliminary treatment of domestic sewage in a treatment works.

From my point of view, we can summarize the above definitions in the next one;

Sewage sludge is by-product solid, semi-solid, or liquid material with origin in industrial, urban or domestic waste waters treatment plants through natural or artificial processes (primary or secondary treatment). It can be treated with biological, chemical or heater treatment to reduce the health hazards resulting from its use and its applications are being researched all over the world, with agriculture, incineration or landfills as main destination.





#### 5.2. - Types of sludge

Wastewater treatment plants produce different sorts of sludge depending on each process step. Below is explained rigorously the types of sludge generated in the wastewater treatment processes

#### 5.2.1. – Pre-treatment

On the previous treatment (2.2.1) it is removed the voluminous items, sands and grease. The residues from this step must not be called sludge and they are disposed directly to landfills.

#### 5.2.2. – Primary sludge

Primary sludge is taken from the primary clarifiers (2.2.2); the sludge amassed at the bottom of the sedimentation basin is collected to its treatment. This sludge can have several compositions according to the catchment area, but in most of cases the primary sludge consists on a high percentage of organic matters as vegetables, fruits or textiles taken as a fluid with a water percentage above 90%.

#### 5.2.3. – Secondary sludge / Activated sludge

On Secondary treatment (2.2.3) it is got the secondary sludge or more known as "activated sludge". Activated sludge is produced in the aeration tank (or basin) where bacteria are kept in suspension in the tank in aerobic conditions as it has been explained. At the end of the process, the treated water goes to the second clarifier where activated sludge is collected from the bottom.

After this, a portion of the biomass is recycled back to the aeration basin with the aim of maintain the desired concentration of organisms in the basin, this is called "return activated sludge". The remaining sludge (excess sludge) is pumped from the system, usually by pumping for final disposal.

#### 5.2.4. – Mixed sludge

Some experts called "Mixed sludge" to the mixed primary and secondary sludge described above.

#### 5.2.5. – Tertiary sludge

This sludge is only present in wastewater treatment plants where extremely highquality effluent is wished such as direct discharge to a drinking water source.





It consists on remove remaining unwanted nutrients such as nitrogen and phosphorus by means of bacterial or chemical processes and disinfection by means of chlorination/dechlorination.

#### 5.2.6. – Digested sludge

Last type of sludge is the digested sludge, which is produced after water treatment during the digestion process described further in some parts of this report (2.3.2 and 5.3). This sludge has a black colour and smells earthy and it has an organic portion of the solid from 45 to 60%.

#### 5.2.7. – Abstract scheme

In the scheme below is clearly shown the types and phases of sewage sludge generation with its treatment steps.

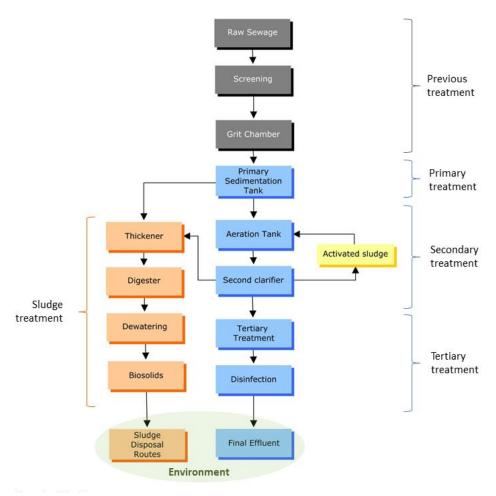


Figure 44: Types of sewage sludge and treatment steps



#### 5.3. - Sludge treatments and stabilisation



The treatments and stabilisation of sewage sludge aims at reducing the fermentation of the putrescible matter present in the sludge and the emission of odours. In addition, disinfection consists of eliminating pathogens, in this spot it is explained the most important sludge treatments used in Europe not only to remove pathogens or removing odours but reduce its water content or its volume and global mass.

#### 5.3.1. – Anaerobic digestion

It consists of confining the sewage sludge in a tank at a temperature about 35°C, this method is used in thickened sludge to reduce, stabilise and partially disinfection of the treated volume of sludge. The process of anaerobic digestion is the following:

- In this step is produced the decomposition (hydrolysis) of plant or animal matter. The organic material is broken down to usable-sized molecules such as sugar.
- Decomposed matter is converted on organic acids from these small compounds.
- The acids are converted to methane gas.

As I told before, the process temperature affects the rate of digestion and should be maintained in the range 35-40 °C. The picture below shows how the anaerobic digestion works.





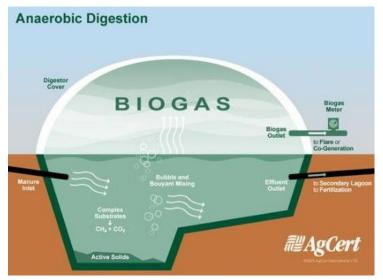


Figure 45: Anaerobic Digestion

It is important to know that the biogas produced is reused in boilers, to maintain the temperature around 35°C as we want, although it can be also used to produce electricity on the plant. An essential advice is save the sludge in the tank more than 20 days to obtain guarantees about the stabilisation and disinfection of the sludge.

#### 5.3.2. – Aerobic digestión

Sludge is placed in tanks with aerobic micro-organisms. Heat is generated when these bacteria degrade organic matter in oxygen-rich environments. During oxidation process, pollutants are broken down into carbon dioxide ( $CO_2$ ), water ( $H_2O$ ), nitrates, sulphates and biomass (microorganisms) in accelerated process by means of aerators.

The temperature can rise to over 70°C, by subjecting sludge to these high temperatures for a particular period of time (5 or 6 days), most harmful organisms are destroyed. In these conditions we can reduce volatile matter about 40%, the process is simple but it has a high energy cost, at least 5 times more than anaerobic digestion.

#### 5.3.3. – Long term liquid storage

Long-term storage of sewage sludge has a disinfecting property, reducing the amount of viruses and bacteria in sludge, its efficiency depends on the duration of the storage. In addition, this method regulates the flows of sludge and homogenising its composition.

#### 5.3.4. – Composting

Composting is an aerobic bacterial decomposition process where sludge is mixed with a co-product such as sawdust or animal manure. We can find three types of processes;





- Windrow: The sludge is mixes with a bulking agent and set out in piles, to introduce air and prevent excessive temperatures the composting material is turned mechanically, the disadvantage of this method is the large area which is necessary.
- Aerated static piles: The sludge mixed with the bulking agent is laid over perforated pipes where the air is blown.
- Tanks systems: This is a "closed" system because it has place in a closed tank where the air is injected and the sludge is introduced at the top of the tank.

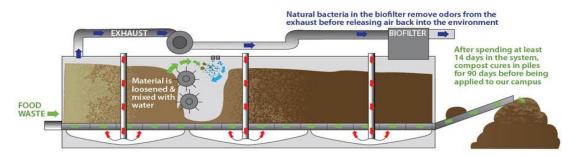
On the following pictures we can see the difference between each one:



Figure 46: Windrow



Figure 47: Aerated static piles



An in-vessel unit controls temperature, aeration, and moisture to accelerate decomposition of organic waste

Figure 48: Tanks systems

The optimum conditions for composting are a moisture content of about 50%, a carbon to nitrogen ratio of about 2530, and temperature of 55°C. Due to wastewater sludge is rich in nutrients, its carbon to nitrogen ratio is low (5-10) and high in moisture, addition of





dry sawdust, which is very high in carbon to nitrogen ratio can adjust both the moisture and carbon to nitrogen ratio, although other materials can be used for this purpose such as newspaper or garden wastes.

#### 5.3.5. - Lime treatment

Calcium hydroxide is an alkaline compound that can create pH level as high as 12. With high pH and increased temperatures, cell membranes of harmful pathogens are destroyed. The high pH also prevents flies and other insects from infecting treated biological waste. The treatment helps disinfecting sludge, increasing its dry matter content and making handling easier.

If we use quicklime (CaO) with water, an exothermic reaction occurs. The temperature of the biological waste can increase to 70°C, which provides effective pasteurization. Even the high pH will precipitate most metals present in the waste and reduce their solubility and mobility.

In addition, the solubility of calcium hydroxide provides free calcium ions, which react and form complexes with odorous sulphur species. As a result of this reaction, the biological waste odors are destroyed.

#### 5.3.7. – Pasteurisation

Pasteurisation cannot be used as a stabilisation process in itself, but it reduces the amount of pathogens in the sludge. This method consists of heating the sludge a minimum of 30 minutes at 70°C or minimum of 4 hours at 55°C, it must be followed in all cases by primary anaerobic digestion.

#### 5.4. - Components.

Sewage sludge is made of compounds with agricultural value such as organic matter, nitrogen, phosphorus, potassium, calcium, sulphur and magnesium, and it is also made of pollutants categorized in heavy metals, organic pollutants and pathogens.

#### 5.4.1. – Organic matter

Organic matter is really good to soil improvement. It is known the benefits of organic matter in soil, not only to improve the physical properties such as retention capacity of minerals an water or the strength, but increasing the soil content in compounds of agricultural value (N, S, Mg, etc.).





The sludge with more percentage of organic matter is the sludge from aerobic digestion and composting.

#### 5.4.2. – Nitrogen and phosphorus content

Nitrogen is typically found under organic form in sludge, even in ammoniac form (in lesser extent). The quantities of nitrogen in sludge depend on treatments carried out on sludge, during the operation of the WWTP and the sludge storage conditions.

Related to Phosphorus, it is used by the plant, the amount of phosphorus available in sludge depends on the treatments carried out. The phosphorus content in sewage sludge is not reduced after storage, contrary to nitrogen.

#### 5.4.3. – Calcium

Lime is added to sewage sludge to stabilise it as I explained in the before paragraph (5.3). It provides better structure and permeability of the soil and increasing on pH values. It is recommended add about 30% of lime to the dry matter, but it is necessary analyze sludge before use.

#### 5.4.4. – Other compounds of agricultural value

Potassium, sulphur, magnesium, sodium and oligo-elements as boron or cobalt may be of interest in crop production, it depends on their availability in the sludge.

#### 5.4.5. – Heavy metals

A big amount of heavy metals are in sludge. Heavy metals affect plant health and growth, soil properties and micro-organisms, human health, etc. Cadmium, Chrome, Cooper, Zinc, Plumb or Mercury are the most known heavy metals present in sludge.

The origins for heavy metals in sewage sludge are domestic effluents and industry, the proportion of each heavy metal depends on the origin, in industry it is really important the industrial situation of the country, for example.

#### 5.4.6. – Organic pollutants

Organic pollutants can be found in sludge, they affect soils, animals and human health, with the relevant environmental impact.

#### <u>5.4.7. – Pathogens</u>





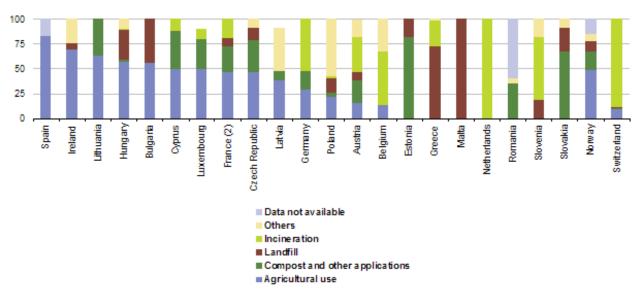
Pathogens are present in sewage sludge as micro-organisms, mainly when biological treatments are carried out. The pathogens usually taken into account are viruses, bacteria, protozoa and helminths. I treat how to remove these pathogens in the paragraph 5.3.

#### 5.5. - Applications. Solving the sludge problem



The sludge has several recycling possibilities or disposal routes, in this spot we will treat the most important and extended routes.

The graphic below from European Commission shows the distribution of sludge disposal in Europe last 2009.



(1) Belgium, the Czech Republic, Germany, France, Luxembourg, the Netherlands and Austria, 2008; Ireland, Cyprus, Latvia, Hungary and Slovakia, 2007; Switzerland, 2006; Denmark, Italy, Portugal, Finland, Sweden and the United Kingdom, not available.

(2) Based on a total excluding the category of other types of treatment. Source: Eurostat (online data code: env\_watq8)

Figure 49: Sludge disposal in 2009





#### 5.5.1. - Agricultural use

Agricultural use of sewage sludge is the most extended and the cheapest route in Europe, but its use is decreasing because of current legislation, with hard limits values. The land spreading is completely regulated in European Directives to ensure that chemical or pathogenic contaminants present in sludge do not cause adverse effects as it was explained in spot 3.

Sewage sludge has valuable agronomic properties in agriculture, its application to soil enables the recycling of nutrients and may eliminate the need for commercial fertilizers in cropland, the reason is that the sewage sludge is an organic fertilizer. However it is important the control of quality of the soil and ground water because although sewage sludge can improve bulk density or porosity some heavy metals and pollutants present in sewage sludge may be dangerous for the humans.

#### 5.5.2. - Silvicultural use

Sludge used in silviculture is a valuable way to recycle sludge. The organic matter present in sludge is applied as supply of fertilising compounds to soil. In addition the addition of pollutants in the food chain is low.

The main concern about the use of sludge in silviculture is soil contamination, but on the other hand, the main advantages are the low cost of the outlet and the minimum sanitary risks, one use may be to Christmas tree plantations.

#### 5.5.3. – Land reclamation

Sewage sludge can be used in land reclamation, the organic matter content in soil is really important to ensuring the maintenance of good water retention properties, sludge can be used to maintain, restore or create soil fertility. This route does not affect foodstuff and it has not the problems with the population as the agricultural use.

The main advantages of this disposal route are the following;

- Recycling organic matter
- o Low cost
- Reduced sanitary risks
- Low amount of pollutant in the food chain

But there are some disadvantages as:

- o Soil contamination
- o Groundwater contamination





Summarizing, the use of sludge into other components on derelict land produces a good growing medium with really good properties of soil structure, workability and moisture retention, improving the vegetation growth.

#### 5.5.4. – Landfilling

Landfilling has been a widely used disposal route for sludge, however it has several disadvantages. The main problem is that It does not allow recycling organic material of sludge and it has the disadvantage of wasting its fertilising value as other disposal routes. In addition, in Europe the Landfill Directive 1999/31/EC aims at reducing the total amount of biodegradable wastes to landfill, these reasons can decrease the landfill as an option for sludge.

This route is still an important disposal route for sludge, mainly because, in some cases, it is the only possibility. This is the case of Sweden, where the boycott of sewage sludge by farmers has caused that only a small portion of sludge can be used for agriculture. Also this route presents very low risks for health, being this the most advantage for the population.

#### 5.5.5. – Incineration

Incineration is the most expensive way and with more controversy. On the one hand, it is known that sludge incineration requires important investments, personnel and large energy supplies. It is considered as an expensive outlet for sludge, in addition this route does not allow recycling of the organic content of sludge and the use of its fertilising value.

On the other hand, Environment protection associations are strongly opposed to incineration, mainly due to gas emissions generated in the process. However, the requirements on agricultural use of sludge and disposal to landfill are increasing, without forgetting that food companies and consumer associations are opposed to use it in agriculture to exclude potential pollutants present in sludge from the food chain.

Finally, all actors agree in the advantages of incineration, which can be summarized as;

- Reduction of sludge volume (about 90%)
- o Thermal destruction of toxic organic compounds
- Minimization of odor generation

It can be expected that there will be an increase in the incineration in the long term due to this advantages and legal limitations concerning landfilling and agricultural use which we have talked before.

#### <u>5.5.6. – Sea disposal</u>

The sludge dumping at sea today is not a possible route to sludge removal; it is banned in Europe from December 31, 1998 by the Directive 91/271/CEE.





The risk of repetition of problems such as the Minamata affair, in which hundreds of people were affected by excessive concentrations of methyl mercury in the marine food chain, have pushed to ban this outlet.

#### <u>5.5.7. - Experimental uses. Cement manufacture</u>

The sludge use as cement replacement material is real not only as raw material in cement manufacture, but fuel for the kiln which generates the cement clinker. Several studies over the world like this address the properly use of this by-product from wastewater treatment plants.





# 6.- Sewage sludge in cement mix design

#### 6.1. - Introduction to laboratory tests with sewage sludge

To achieve better knowledge about sewage sludge as cement replacement material was essential testing in the laboratory this by-product in cement based composites mix design. The tests described below study the viability of using sewage sludge in cement, analyzing mechanical and physical properties comparing the results of reference cement (without cement replacement) with different percentages of sewage sludge as partial Portland cement replacement.

The tests has been developed for 4 months in the laboratory using samples which were designed by replacement of 10,20,30 and 40% of cement in cement pastes composition by sludge, while the water/binder ratio was the same for all the mixtures (0.4). In the next pages are explained in detail this abstract from the collection of sludge to the analysis of the results obtained. In the point 6.6 is shown a scheme summarizing all steps performed.

#### 6.2. - Previous work

#### 6.2.1. - Sewage sludge collection and dried

The previous work starts with the collection of sewage sludge, to this aim I went to one of the most big wastewater treatment plant en Czech Republic for the sole purpose of get dried sewage sludge to make my samples.



Figure 50: Wastewater treatment plant location







Figure 51: Collection of sludge

The plant was in Prague, near to the University and like most of wastewater treatment plants, next to the river, in this case the Moldova River. The plant as we can see in the picture above is a typical wastewater treatment plant and we can identify all steps described in the second chapter (2.2) from the screener and preliminary treatment to aeration tanks and clarifiers. Also we can observe the tanks for the sludge digestion which we know widely.

Once I talked to the head of the plant, who was very kind with me giving me permission I went into the plant accompanied by a worker and I got 2-3 kilograms of centrifuged sludge to perform my samples.

Although this sludge could not be used directly in the cement mix samples, the water content it was approximately about 80% water, so it was dried in the oven for 6 hours at up to 700 degrees.

In the graphic below we can see the evolution of temperatures which were reached by sludge in the oven for 6 hours before its use in the cement samples.

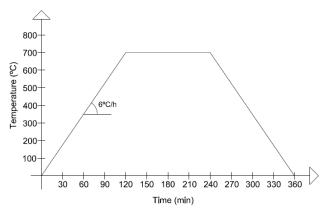


Figure 52: Temperature evolution in the oven

The temperature in the oven increased 6°C per hour for 2 hours until reach the top of temperature about 700°C for 2 hours to decreasing until 0°C when it is collected to its use in the cement based mix samples. We can observe the final aspect of dried sludge in the following picture.







Figure 53: Sewage sludge appearance

#### 6.2.2. - Size distribution

Particle size distribution was measured by means of laser diffraction principle using the device Analyssete 2 Micro Tec plus due to the grain size it was too big to use sieves testing. This device used allows measurement of grain size up to 2 mm.

Laser diffraction works measuring the angular variation in intensity of light scattered as a laser beam passes through a sample. Large particles scatter light at small angles relative to the laser beam while small particles scatter light at large angles as we can see in the following illustration. Then the angular scattering intensity data is analyzed to calculate the size of the particles to report a particle size as a volume equivalent sphere diameter.

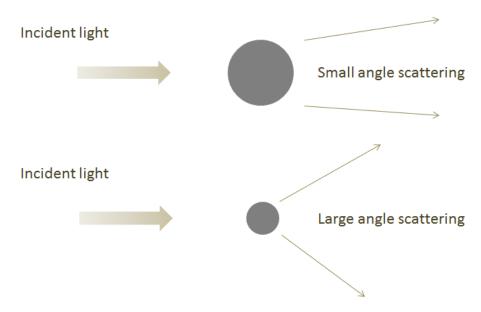


Figure 54: Size distribution performance scheme

The device has the following appearance and its complete results are found in Appendix 3.







Figure 55: Analysette 2 Micro Tec

The device scans the sample three times to obtain greater precision in the results, as follows we can observe these three "laps", which are summarized on the average of them.

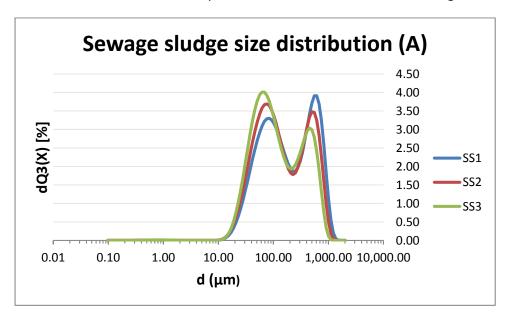


Figure 56: Sewage sludge size distribution

The results obtained were interesting compared with cement distribution, which was measured too by laser diffraction. It is really important the size distribution of the cement replacement material because big size particles decrease the velocity of pozzolanic reaction while a small particle size improves significantly the pozzolanic reaction with better short-time resistances, filling up large capillary pores and improving the impermeability.



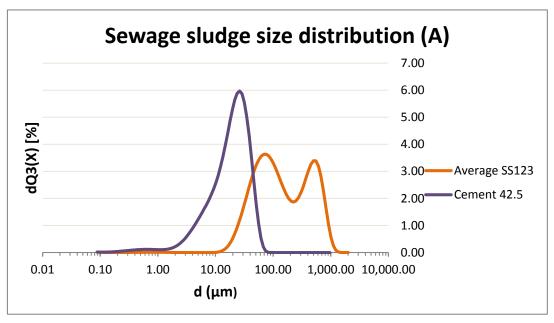


Figure 57: Cement and sludge size distribution

I analyzed these results in the following graph with both size distributions (sludge and cement) estimating the percentages of each zone.

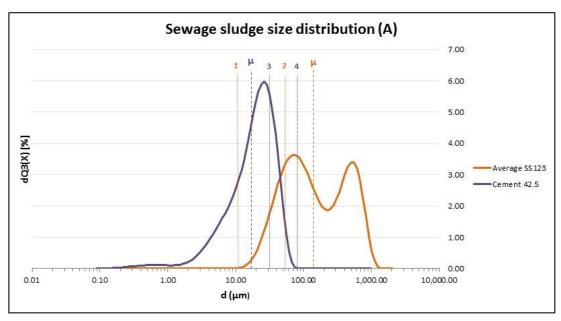


Figure 58: Cement and sludge size distribution analysis

To calculate the areas we have used relative frequences given by the device which you can find in the <u>Appendix 1</u>, adding together the corresponding relative frequencies between the points we want the area (%).

Cement quantity coinciding with sludge.





I measured the cement area from 3 to 4 (look at the graphic above). The area of cement coinciding with sludge on the left of 3 is compensated with the area of cement out of sludge on the right of 3.

This area is about 25% of cement content.

Cement quantity with bigger than sludge particle size.

I cannot found cement with bigger particle size than sludge.

Cement quantity with smaller than sludge particle size

I measured the sludge area on the left of 3 (look at the graphic above). The area of sludge on the left of 3 is compensated with the cement area out of sludge on the right of 3.

This area is about 75% of sludge content.

Sludge quantity coinciding with cement.

I measured the sludge area from 1 to 2 (look at the graphic above). The area of sludge coinciding with cement on the right of 2 is compensated with the area of sludge out of cement on the left of 2.

This area is about 20% of sludge content.

Sludge quantity with bigger than cement particle size

I measured the sludge area on the right of 2 (look at the graphic above). The area of cement on the right of 2 is compensated with the sludge area out of cement on the left of 2.

This area is about 80% of sludge content.

Sludge quantity with smaller than cement particle size

I cannot found sludge with smaller particle size than cement.





#### 6.2.3. - Matrix density

The matrix density of sewage sludge was got by means of helium pycnometer, which is an instrument invented in 1967 by Edward Y. H. Keng used to measure the matrix density of solids without damaging samples.

The principle of this method is based on putting a sample with known mass into a cell of known volume. Then helium is introduced into the cell, so helium occupies the entire volume of the cell that is not occupied by the sample, assuring maximum accuracy. The real volume of the sample (without pores) can be determined due to the volume of cell is known. Below we can see the instrument of the laboratory where were performed the measurements.



Figure 59: Helium pycnometer

The matrix density measured was **2.87gr/cm³**, it is a similar value (lightly lower) than matrix density of Portland cement, which is around 3 gr/cm³, even fly ash (one of the most extended cement replacement material over the world) in general has 2-2.5 gr/cm³, so we can say that our value is quite good.

#### 6.2.4. - Chemical composition

#### 6.2.4.1. - X-ray Fluorescence (XRF) analysis

X-ray Fluorescence can be defined as "The emission of characteristic fluorescent X-rays from a material that has been excited by bombarding with high-energy X-rays". This phenomenon is widely used for elemental analysis.

X-rays are an electromagnetic wave and X-ray Fluorescence (XRF) is a consequence of changes that take place within an atom. Orbiting electrons are organised into shells with the same energy per shell. When a high energy incident (primary) X-ray collides with an atom it disturbs this stability, so an electron is ejected from a low energy level. This leaves the atom in an excited state, with a vacancy in the shell. Then an electron with higher energy level falls into this space, emitting photons (secondary X-rays) with energy equal to the energy difference between the two states.





Each element has a unique set of energy levels, so each element emits a pattern of X-ray characteristic of the element. This process is called XRF.

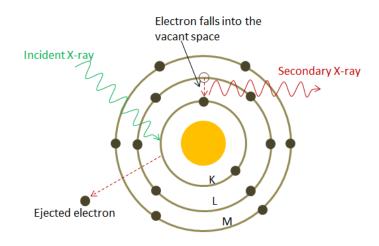


Figure 60: XRF performance scheme

As follows the results from XRF analysis are given, the complete results are in Appendix

<u>4</u>.

	XRF analysis
Substance	Amount [%]
SiO <sub>2</sub>	17.810 ± 0.19
Al <sub>2</sub> O <sub>3</sub>	13.200 ± 0.17
Fe <sub>2</sub> O <sub>3</sub>	6.130 ± 0.12
CaO	32.860 ± 0.23
MgO	3.490 ± 0.09
S	3.91 ± 0.10
ZnO	0.397 ± 0.031
Na <sub>2</sub> O	0.583 ± 0.038
K <sub>2</sub> O	1.660 ± 0.06
TiO <sub>2</sub>	1.340 ± 0.06
P <sub>2</sub> O <sub>5</sub>	17.400 ± 0.19
Cl	0.449 ± 0.033
Cr <sub>2</sub> O <sub>3</sub>	0.101 ± 0.016
NiO	0.0332 ± 0.0091
CuO	0.181 ± 0.021





SrO	0.073 ± 0.013
ZrO <sub>2</sub>	0.0287 ± 0.0085
Σ	99.64 ± 1.3796

Table 14: XRF analysis

Results of XRF analysis of heavy metals are given in the following table compared with the limit values current in Europe Directive 86/278 EEC and Spanish regulation.

XRF analysis (heavy metals)					
	Concentration	Limit values [mg/kg]			
Substance	[mg/kg]	Directive 86/278 EEC	Spanish regulation		
Cd	<	20-40	20-40		
Cu	3,050	1000-1750	1000-1750		
Ni	550	300-400	300-400		
Pb	1,150	750-1200	750-1200		
Zn	6,370	2500-4000	2500-4000		
Hg	<	16-25	16-25		
Cr	1,380	-	1000-1500		
Ag	<	Ø	Ø		
As	<	Ø	Ø		
Co	102	Ø	Ø		
Mn	1,820	Ø	Ø		
Мо	<	Ø	Ø		
Rb	<	Ø	Ø		
Se	<	Ø	Ø		
Sr	1,260	Ø	Ø		
Ti	15,900	Ø	Ø		
Ва	1,910	Ø	Ø		

Table 15: XRF heavy metals analysis

#### 6.2.4.2. - X-ray Diffraction (XRD) analysis

X-ray Diffraction is an analytical technique used for phase identification of a **crystalline** material.





X-ray Diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. The X-rays are generated and filtered to produce monochromatic radiation directed toward the sample. From the interaction of the rays with the samples generates constructive interference and a diffracted ray when conditions satisfy Bragg's Law. Finally the diffracted X-rays are then detected, processed and counted. Scanning the sample through a range of  $2\theta$  angles, the identification of the mineral is possible thanks to each mineral has a set of unique spacing between diffraction peaks.

Below we can see schematically how works this method:

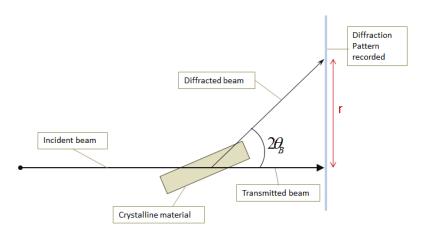
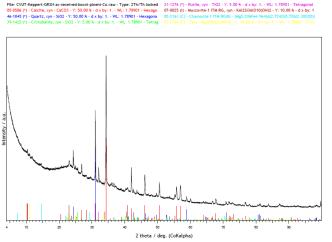


Figure 60: XRF performance scheme

The results of XRD analysis of the sludge used in the laboratory are shown as follows, we can see the typical graphic of X-ray Diffraction analysis and the amount of crystalline substances in the sludge (around 40% of the sludge). In <a href="Appendix 5">Appendix 5</a> is shown the graphic of XRD bigger than below.



Fiaure 61: XRD results





The following table presents the results from XRD analysis of dried sewage sludge, the complete results are in Appendix 2.

XRD analysis						
Element (Crystalline form)	Substance	Amount [%]				
Calcite	CaCO₃	22.4				
Quartz	SiO <sub>2</sub>	6.1				
Muscovite	$KAl_2(AlSi_3O_{10})(F,OH)_2$	3.1				
Chlorite	(Mg,Fe,Al) <sub>6</sub> (Si,Al) <sub>4</sub> O <sub>10</sub> (OH) <sub>8</sub>	4.8				
Rutile	TiO <sub>2</sub>	2.1				
Talc	Talc $Mg_3Si_4O_{10}(OH)_2$					
	Amorf					
	Σ					

Table 16: XRD analysis

#### 6.3. – Design and making cement samples

#### 6.3.1. - Design

The samples were designed to make 3 prismatic samples by each type (0, 10, 20, 30 and 40% of sludge about cement weight) while maintaining the ratio water/binder in all samples with the same value as we can verify in the following table:

CEMENT SAMPLES DESIGN							
Sewage sludge content about cement weight	Cement (gr)	Sludge(gr)	H20 (ml)	Water/binder			
REFERENCE: 0%	1800	0	720	0.4			
10%	1620	180	720	0.4			
20%	1440	360	720	0.4			
30%	1260	540	720	0.4			
40%	1080	720	720	0.4			

Table 17: Cement samples design





We can see easily in the following bar graph how the water amount is the same while el Portland cement content is substituted by sewage sludge (cement replacement material used in this research). All data about samples design such as volume, weight or density of each component is available in <a href="Appendix 6">Appendix 6</a>.

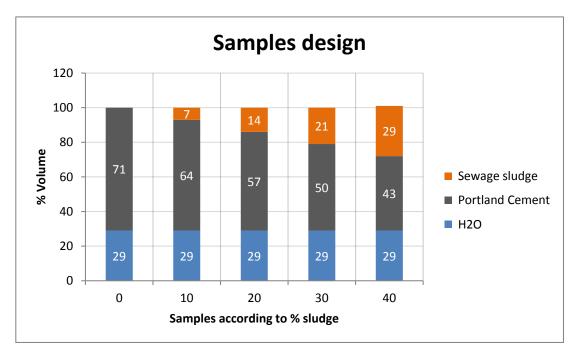


Figure 62: Samples design graphic

#### 6.3.2. - Making and curing

Once we designed the composition of the samples, we proceeded to make them. The process is described as follows. At first the moulds are impregnated with an oil substance to take out the samples easier from the moulds.



Figure 63: Prismatic cement moulds





After that, the components of samples are weighted and mixed correctly in the kneading machine.







Figure 65: Mixing machine

When the elements are completely mixed, the mix (cement paste) is poured into the moulds, which are placed in the cement jolting table in two times with 60 impacts by layer according to EN 196-1. In the picture below is shown the cement jolting table to compact moulded specimens.



Figure 66: Cement jolting table





After compaction, the samples are 24 hours at the laboratory with plastic covering the samples as we can see in the following picture.



Figure 67: Cement samples with plastic covering

24 hours elapsed, the samples are unmoulded by means of a spatula as the picture shows, not forgetting that the moulds had to be cleaned after the unmoulded to maintain the laboratory clean and tidy.



Figure 68: Unmoulding cement samples

Finally, the samples are named and conserved under water waiting their respective tests: compressive and bending strength, bulk density, elastic modulus, porosity, etc.



Figure 69: Cement samples in water





#### 6.4. - Testing cement samples

Once the samples has been designed, made and cured, I proceeded to testing them by analyzing its mechanical and physical properties like it is explained below.

#### 6.4.1. – Mechanical properties

The mechanical properties that we tested were compressive strength, flexural strength, and elastic modulus. All data from the testing is presented in Appendix 2.

#### 6.4.1.1. - Compression strength

The compressive strength was measured according to the ČSN EN 12390-3 of fragments of samples from bending strength testing. In the picture below (left) is shown how was made the test, while in the right picture we can see a bigger press because we needed a higher stress capacity to break the sample of reference without sludge.



Figure 70: Compressive strength test



Figure 71: Compressive strength test

The results of breakage at 28 and 90 days are summarized in the following graph. Laboratory testing gave us 2 results by sample (2 fragments each), the complete list of results are in the Appendix 2.





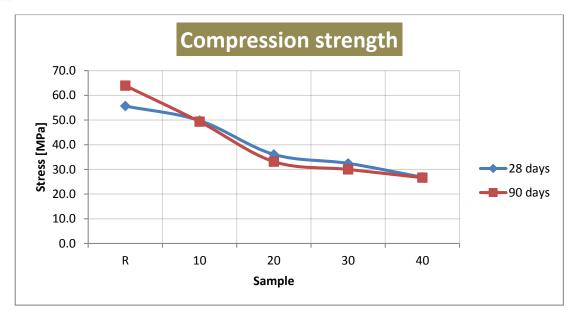


Figure 72: Compressive strength results

We can see in the graphic above how the compressive strength decreases with increasing the sludge content.

#### 6.4.1.2. - Bending strength

The bending strength of cured samples was measured according to the procedure described in ČSN EN 12390-5 of prismatic samples with 16 centimetres length, 4 of width and 4 of height as it can be observed in the picture below.



Figure 73: Bending strength test



The laboratory gave us one result of bending strength by sample tested and we can see them in the following graph. The table with the complete results can be found in Appendix 2.

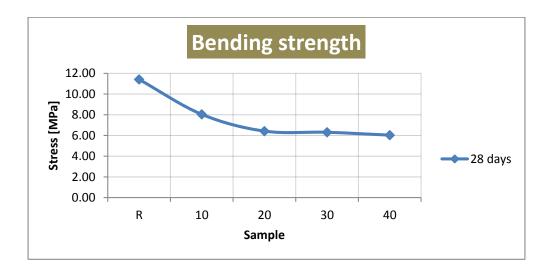


Figure 74: Bending strength results

#### 6.4.1.3. - Elastic modulus

Elastic modulus is a material property that describes its stiffness and is therefore one of the most important properties of solid materials. To determine the elastic modulus, we have used a known equation:

$$v_s = \sqrt{\frac{E}{\delta}} \Rightarrow v_s^2 = \frac{E}{\delta} \Rightarrow E = v_s^2 \cdot \delta$$

Where:

$$E\left[\frac{kg}{m \cdot s^2} = Pa\right] \rightarrow \text{Elastic Modulus/Young Modulus}$$

$$v_s\left[\frac{m}{s}\right] \rightarrow \text{Speed sound in the samples}$$

$$\delta\left[\frac{kg}{m^3}\right] \rightarrow \text{Bulk density of the samples}$$





Speed sound in the samples ( $v_s$ ) was determined by ultrasonic testing, this test consists of measuring the time required for the sound wave to travel completely through the sample. The wave travels faster and takes a shorter time to reach the other side of the sample if the cement is harder than other where the stiffness is lower. More stiffness, less time of the wave sound to travel through the sample.





Figure 75: Ultrasonic testing

Figure 76: Ultrasonic testing

It is interesting to mention the several applications which we can have with this method, we can estimate the strength of concrete, establishing homogeneity of concrete, studying on the hydration of cement, studying on durability of concrete or measurement of surface crack depth, between other.

Once we have the time ( $\mu$ s), to get the speed sound, the length of the sample should be divided by the time of the wave, as follows:

$$Vs\left[\frac{m}{s}\right] = \frac{\text{Length of the sample } [m]}{\text{Time of the wave} [\mu s] * 10^6}$$

Leslie and Cheesman (1949) established a classification of the quality concrete according to the speed sound to travel through the complete sample:

Speed sound (m/s)	Cement quality
More than 4570	Excelent
From 3650 to 4570	Good
From 3050 to 3650	Questionable
From 2130 to 3050	Poor
Lower than 2130	Very poor

Table 18: Quality concrete according to speed sound

On the other hand we measured the bulk density by means of a digital caliper which was used to measure the three dimensions (length, width and height) of the samples to get





the volume. We used too the weight to get the weight of the samples. In the pictures below we can see both instruments.





Figure 77: Measuring cement samples

Figure 78: weighting cement samples

Now we are capable of calculate the elastic modulus according to the equation above, the following table shows the calculation of the elastic modulus:

$$E = v_s^2 \cdot \delta$$

Sample	dim	ensions (m	1)	volume (m³)	Weight	Bulk density	time t [µs]	speed	v <sup>2</sup> [m <sup>2</sup> /s <sup>2</sup> ]	Modulus of
Sample	a	b	С	a*b*c	[kg]	[kg/m³]	time t [µs]	v[m/s]	v [III /S ]	Elasticity E [Gpa]
REF	0.15960	0.03965	0.04055	0.000256606	0.42784	1667.30	47.09	3389.25	11487046.871	19.15
10%	0.15980	0.04028	0.04090	0.000263263	0.41607	1580.44	54.12	2952.70	8718423.760	13.78
20%	0.15956	0.04004	0.04042	0.000258235	0.38556	1493.06	59.31	2690.27	7237560.502	10.81
30%	0.15888	0.03988	0.04013	0.000254269	0.37598	1478.67	62.91	2525.51	6378214.080	9.43
40%	0.15901	0.04032	0.04020	0.000257734	0.36245	1406.30	65.95	2411.07	5813253.683	8.18

We can see in the table above that the sound speed are not too good, according to Leslie and

Table 19: Elastic modulus calculation

Cheesman the classification all samples with sludge are "poor" but we must specify that the samples are cement paste, not concrete. The main factors which affects to elastic modulus in concrete are the followings;

- Moisture content
- Porosity
- Elastic modulus of ground and sand.
- Gravel and sand content

Our samples are free of moisture due to were in the oven 4 weeks before the tests, are very porous because of the sludge has a low density and it is free of gravel and sand, decreasing the elastic modulus significantly. Taking this as our starting point we have to conclude that the elastic modulus obtained is very good. We can see in the following graphic the decreasing of elastic modulus with increasing of sludge content.





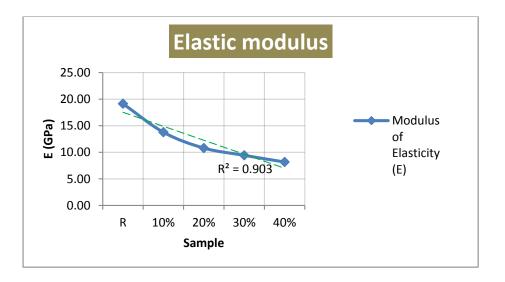


Figure 79: Elastic modulus results

#### 6.4.2. – Physical properties

#### 6.4.2.1. - Matrix density

Matrix density of samples was measured at 28 days with the same helium pycnometer used to measure matrix density of sludge (6.2.3)In the pictures below we can see the cell where are introduced the fragments of the samples and the helium bottle used by the machine to full the cell and measure the matrix density of the samples.



Figure 80: Helium pycnometer



Figure 81: Helium





The results measured are presented in the following table:

Sample	Matrix density samples[kg/m³]
Sample	17/04/2014 (28 days)
R	2056.13
10%	2016.70
20%	1951.26
30%	1910.75
40%	1866.95

Table 20: Matrix density results

Matrix density tends to decrease with an increase of sludge content, this is due to the sewage sludge has lower density than cement.

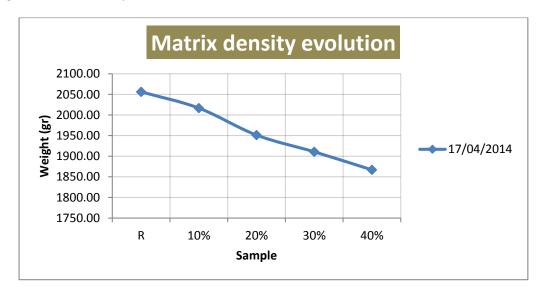


Figure 82: Matrix density according to sludge content

6.4.2.2. - Bulk density

Bulk density is the mass of many particles of the material divided by the volume they occupy.

$$\rho_d = \frac{m_{solids}}{V_{solids} + V_{pores}}$$





To calculate bulk density of samples must first be removed water from them, with this aim all samples are introduced in the oven at 105°. We know the samples have not water when weight between two times are the same as is shown in the following table. Once the samples are dried, bulk density is calculated according to the equation above.

Sample		Weigl	ht [gr]		Bulk den	sity [kg/m³]	Matrix density samples[kg/m³]	Open porosity
	17/04/2014	07/05/2014	15/05/2014	22/05/2014	17/04/2014	22/05/2014	17/04/2014	
R	519.2	433.03	427.91	427.84	1964	1667.3	2056.13	0.19
10%	501.4	418.69	416.07	416.56	1912	1580.44	2016.70	0.22
20%	481.6	387.22	385.56	386.26	1871	1493.06	1951.26	0.23
30%	481.8	377.25	375.98	376.73	1807	1478.67	1910.75	0.23
40%	453.2	363.5	362.45	363.35	1765	1406.3	1866.95	0.25

Table 21: Cement jolting table

The following graph shows how the density decreases in all samples because of water loss in the oven for 1 month, obtaining the real bulk density (without water in the samples).

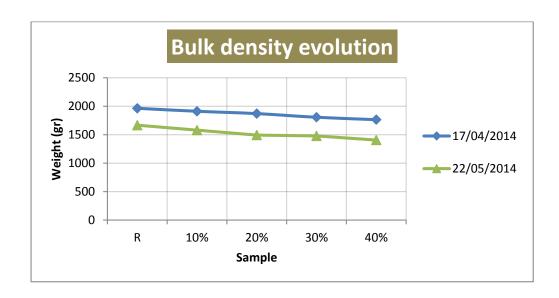


Figure 83: Bulk density evolution

6.4.2.3. - Porosity distribution

Porosity can be defined as void space in the material, where the void may contain air or water and it is calculated by means of this equation:

$$\Phi = 1 - \frac{\rho_{bulk}}{\rho_{particle}}$$





In the following table are presented the open porosity calculated in our samples; the porosity rise with an increasing sludge content.

Sample	Bulk density [kg/m3]	Matrix density[kg/m3]	Porosity(%)
Sample	22/05/2014	17/04/2014	22/05/2014
R	1667.30	2277.36	0.27
10.00	1580.44	2253.55	0.30
20.00	1493.06	2250.01	0.34
30.00	1478.67	2249.07	0.34
40.00	1406.30	2247.04	0.37

Table 22: Open porosity

An example of these results are found in the picture below where we can see at a glance the pore size in the sample with sludge is bigger than the sample without sludge.

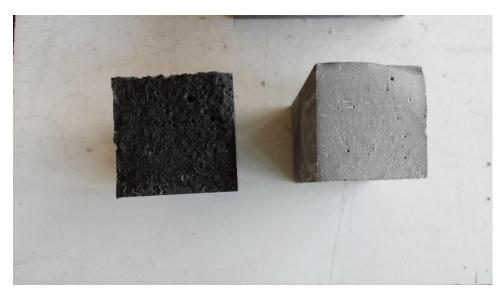


Figure 84: Aspect of samples with/without sludge

#### 6.4.3. - Pozzolanic activity (Fratini study)

This test was carried out according to the procedure described by ČSN EN 196-5. Test samples were prepared as 20g of blended cement (10, 20, 30, 40, 50, 70 and 100% of sludge about cement weight) and mixed with 100 mil of boiled distilled water. Then samples were left in a sealed plastic bottle in an oven at 40°C.





After 8 days, samples were vacuum filtered by Buchner funnel (the picture below). The filtrate was analyzed for [OH-] by titration against HCl with methylorange indicator and for [Ca2+] by pH adjustment to 12,5 by NaOH, followed by titration with EDTA solution using Murexide indicator.

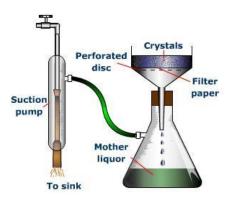


Figure 85: Buchner funnel

This test compares the [Ca2+] and [OH] contained in an aqueous solution by means of a graph. The graph shows on the y-axis the CaO (mmol/l) as equivalent of [Ca2+] versus [Oh-] (mmol/l) on the x-axis. If the results are situated below the solubility isotherm curve of Ca(OH)2, Ca2+ has been removed from the solution, so there is pozzolanic activity.

As follows we can observe the dates of the testing and the graphic generated, where only 2 out of 7 samples present pozzolanic activity (below the curve).

Pozzolanic activity results								
Poměr	V HCl (ml) Průměr	OH <sup>-</sup> [mmol/l]	V EDTA [ml] Průměr	CaO [mmol/l]	Pozzolanic activity			
10%	5.6	56.056	6.55	12.710275	-			
20%	5.35	53.5535	7.25	14.068625	-			
30%	5.3	53.053	7.65	14.844825	-			
40%	4.85	48.5485	8.15	15.815075	-			
50%	4.35	43.5435	7.7	14.94185	-			
70%	1.55	15.5155	1.9	3.68695	Show pozzolanic activity			
100%	0.4	4.004	8.85	17.173425	Show pozzolanic activity			

Table 23: Pozzolanic activity results





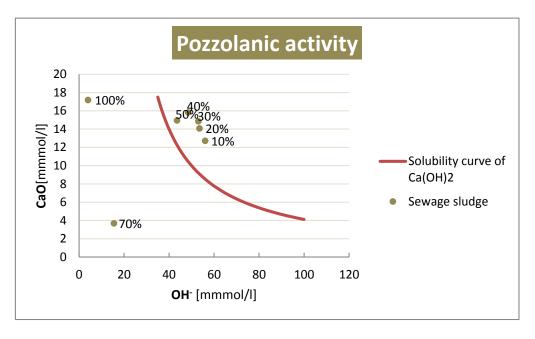


Figure 86: Pozzolanic activity results

#### 6.5. - Abstract scheme



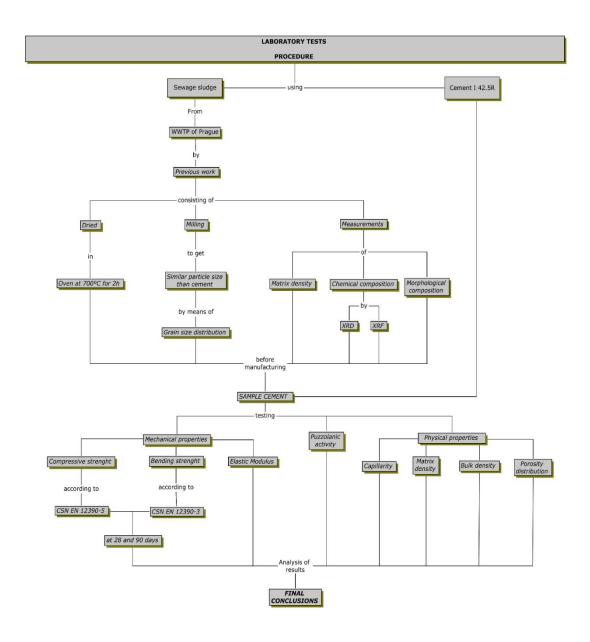


Figure 87: Laboratory tests procedure results





## 7.- The role of sewage sludge on Sustainable Development.

<<People 'over-produce' pollution because they are not paying for the costs of dealing with it>>

(Ha-Joon Chang, 23 Things They Don't Tell You About Capitalism, 2011)

#### 7.1. – Introduction

30 years ago, in 1984, the United Nations established an independent group of 22 people from member states of the developing and developed worlds who aim the identification of the long-term environmental strategies for the international community. This group of people introduced the known term "Sustainable Development", used today, which it is defined and generally explained on the next paragraph.

There is a need to reflect on what is trying to be achieved, some question need a response. Do development and environmental concerns contradict each other? How can sustainable development be achieved?

#### 7.2. - What is Sustainable Development?

Sustainable Development has been defined in many ways, but the most common definition was given from the United Nations World Commission on Environment and Development (WCED) in 1987 when was published "Our Common Future", also known as the Brundtland Report. This report defines Sustainable Development as:

<< Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs >>

United Nations World Commission on Environment and Development, "Our Common Future", 1987)



It contains within it two key concepts;

- The concept of **needs**, in particular the essential needs of the world's poor, to which overriding priority should be given.
- The idea of **limitations** imposed by the state of technology and social organization on the environment's ability to meet present and future needs.

The Commission identified too the critical objectives for sustainable development in the future, which are the followings;

- o Reviving growth
- o Changing the quality of growth
- o Meeting essential needs for jobs, food, energy, water and sanitation
- o Ensuring a sustainable level of population
- Conserving and enhancing the resource base
- Reorienting technology and managing risk

However, to get this objectives it is necessary establish the sustainable development requires, and the Commission described these ones;

- A political system that secures effective citizen participation in decisionmaking.
- A production system that respects the obligation to preserve the ecological base for development
- o A production system that fosters sustainable patterns of trade and finance.
- o A technological system that fosters sustainable patterns of trade and finance
- An administrative system that is flexible and has the capacity for selfcorrection

Sustainability is more than environmental impact. It has three essential pillars introduced by John Elkington in his in his 1998 book "Cannibals with Forks: the Triple Bottom Line of 21st Century Busines".

- Economic: A sustainable economic model that ensure an equal distribution and efficient use of our resources, maintaining our economic growth resulting a healthy balance with our ecosystem.
- Environmental: Not all natural resources all unlimited. We must to protect our planet developing initiatives such as renewable energy, sustainable agriculture and fishing, recycling and better waste management.





 Social: We have the responsibility to do something about human rights, such as human inequality or social injustices. To achieve this initiatives like peace, social justice, reducing poverty are essential.

The following picture explains these 3 concepts as only one: SUSTAINABLE DEVELOPMENT.



Figure 88: Sustainable Development scheme

## 7.3. – Sewage sludge and other SCM related to Sustainable Development.

Concrete is one the most used construction materials in the world and its main component is Portland cement, which generates a significant amount of  $CO_2$  and other Greenhouse gases (GHGs). One ton of Portland cement clinker production creates more or less another ton of  $CO_2$ .

It is known that sustainable development of the cement and construction industries can be achieved by means of the use of pozzolanic and industrial by-products. However, we must know the effects not only in structural properties, but the durability also has to be taken into account.

The most important environmental advantages of the use of supplementary cementing materials are the followings;





- Reduced cement usage (Lowering CO<sub>2</sub> emissions)
- Conserving natural resources (limestone)
- Reduced landfill (industrial by-products are not disposed to landfills)
- Use of recycled materials (industrial by-products)
- Saving money (less energy)
- Saving energy (less clinker on the kiln)

It can be verified on the table below the big differences on the environmental impact of a typical Portland cement and one cement- replacement material as granulated ground blast furnace slag (4.2.3).

Fusing a month lines	Measured	Impact		
Environmental issue	ivieasured	One tonne of GGBS <sup>1</sup>	One tonne of PC	
Climate change	CO2	0.07 tonnes	0.95 tonnes	
Energy use	Primary energy <sup>2</sup>	1300 MJ	5000MJ	
Mineral extraction	Weight quarried	0 tonnes	1.5 tonnes	
Waste disposal	Weight to tip	1 tonne saved <sup>3</sup>	0.02 tonnes	

#### Notes:

- The profile for GGBS is the impacts involved in processing granulated blast furnace slag to produce GGBS. No
  account has been taken of the impacts of iron-making because the slag evolves irrespective of whether or not it can
  be used.
- 2. Includes energy involved in the generation and distribution of electricity.
- 3. The use of slag for the manufacture of GGBS potentially saves it from having to be disposed of to tip.

Source: Higgins D D, Sustainable concrete: How can additions contribute?

Institute of Concrete Technology Annual Technical Symposium, 2006

Table 24: Environmental impact of GGBS and PC manufacture





### 8.- Final conclusions

Once analysed the possible use of dried sewage sludge from wastewater treatment plant in Prague, Czech Republic, in cement-based composites mix design, we can conclude that sewage sludge can be used as cement replacement material, but the research confirms that it must be used under certain conditions.

- Chemical composition is good for cement, although some heavy metals are higher than required limits, the pollutant elements are fixed in cement matrix generating a good disposal route for recycling. In addition, it presents the main elements for produce the pozzolanic reaction, by means of a good thermal treatment and correct milling can be obtained a good pozzolanic activity like more extended cement replacement materials such as fly ash or silica fume.
- 2. Mechanical properties are decreasing with an increasing of sewage sludge content, these results have a clear connexion with the open porosity, with more sludge content, the open porosity is higher. Assessing the results we can conclude that the sludge content recommended depends on the final use of the concrete (structural or non-structural).
- 3. Related to durability, with higher sludge content we have verified that the open porosity and capillarity absorption increases. It means that cements with sludge can present lower durability for structures in aggressive environments.
- 4. According to its possible uses in construction, they must be categorized on structural and non-structural uses. For structural uses, concrete must not present a sludge content higher than 10%, while if we want manufacture some bricks, blocks or mass-concrete, it is recommended using a higher content but not up to 30% due to durability reasons, the open porosity would be really high for any building element.
- 5. As it is described in the last spot about Sustainable Development, large quantities of sewage sludge are generated all over the world, so the purposed solution would create a proper disposal route for removing this industrial byproduct without any disadvantage for the environmental.

Finally, I trust that following researches about this topic will boost the use of sewage sludge in other new routes, not only in cement design, can be used too as fuel in the kilns to produce clinker, for example.





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## **Appendices**

### Appendix 1: CEN/TC 308 Characterization of sludge

	CEN/TC 308 Characterization of sludge
SFS-EN ISO 5667-13:2011	Water quality. Sampling. Part 13: Guidance on sampling of sludges (ISO 566713:2011)
SFS-EN ISO 5667-15:2009	Water quality. Sampling. Part 15: Guidance on the preservation and handling of sludge and sediment samples (ISO 5667-15:2009)
SFS-EN 12176:1998	Characterization of sludge - Determination of pH-value
SFS-EN 12879:2000	Characterization of sludges - Determination of the loss on ignition of dry mass
SFS-EN 12880:2000	Characterization of sludges - Determination of dry residue and water content
SFS-EN 13342:2000	Characterization of sludges - Determination of Kjeldahl nitrogen
SFS-EN 13346:2000	Characterization of sludges - Determination of trace elements and phosphorus - Aqua regia extraction methods
CEN/TR 13714:2010	Characterisation of sludges - Sludge management in relation to use or disposal
CEN/TR 13767:2004	Characterisation of sludges - Good practice for sludges incineration with and without grease and screenings
CEN/TR 13768:2004	Characterisation of sludges - Good practice for combined incineration of sludges and household wastes
CEN/CR 13846:2000	Characterisation of sludges -Recommendations to preserve and extend sludge utilization and disposal routes
SFS-EN 14672:2005	Characterization of sludges - Determination of total phosphorus
CEN/TR 14742:2006	Characterization of sludges - Laboratory chemical conditioning procedure
SFS-EN 14701-1:2006	Characterization of sludges - Filtration properties - Part 1: Capillary suction time (CST)
SFS-EN 14701-2:2006	Characterization of sludges - Filtration properties - Part 2: Determination of the specific resistance to filtration
SFS-EN 14701-3:2006	Characterization of sludges - Filtration properties - Part 3: Determination of the compressibility
SFS-EN 14701-4	Characterization of sludges. Filtration properties. Part 4: Determination of the drainability of flocculated sludges
SFS-EN 14702-2:2006	Characterization of sludges - Settling properties - Part 2: Determination of thickenability
SFS-EN 15170:2008	Characterization of sludges – Determination of calorific values





CEN/TR 15175:2006	Characterization of sludges - Protocol for organizing and conducting interlaboratory tests of methods for chemical and microbiological analysis of sludges
CEN/TR 15214-1:2006	Characterization of sludges - Detection and enumeration of Escherichia coli in sludges, soils, soil improvers, growing media and biowastes - Part 1: Membrane filtration method for quantification
CEN/TR 15214-2:2006	Characterization of sludges - Detection and enumeration of Escherichia coli in sludges, soils, soil improvers, growing media and biowastes - Part 2: Miniaturised method (Most Probable Number) by inoculation in liquid medium
CEN/TR 15214-2006	Characterization of sludges - Detection and enumeration of Escherichia coli in sludges, soils, soil improvers, growing media and biowastes - Part 3:  Macromethod (Most Probable Number) in liquid medium
CEN/TR 15215-1:2006	Characterization of sludges - Detection and enumeration of Salmonella spp. in sludges, soils, soil improvers, growing media and biowastes - Part 1: Membrane filtration method for quantitative resuscitation of sub-lethally stressed bacteria (to confirm efficacy of log drop treatment procedures)
CEN/TR 15215-2:2006	Characterization of sludges - Detection and enumeration of Salmonella spp. in sludges, soils, soil improvers, growing media and biowastes - Part 2: Liquid enrichment method in selenite-cystine medium followed by Rapport-Vassiliadis for semi-quantitative Most Probable Number (MPN) determination
CEN/TR 15215-3:2006	Characterization of sludges - Detection and enumeration of Salmonella spp. in sludges, soils, soil improvers, growing media and biowastes - Part 3:  Presence/absence method by liquid enrichment in peptone-novobiocin medium followed by Rapport-Vassiliadis
CEN/TR 15252:2006	Characterization of sludges - Protocol for validating methods for physical properties of sludges
CEN/TR 15463:2007	Characterization of sludges – Physical consistency – Thixotropic behaviour and piling behaviour
CEN/TR 15809:2009	Characterization of sludges - Hygienic aspects - Treatments
SFS-EN ISO 16720:2007	Soil quality. Pretreatment of samples by freeze drying for subsequent analysis





WG 2 Guidelines for good practise in the production, and for disposal of sludges					
SFS-EN 12832:2000 Guide 1	Characterization of sludges – Utilisation and disposal of sludges - Vocabulary				
CEN/TR 13097:2010 Guide 4	Characterization of sludges – Good practice for sludges utilisation in agriculture				
CEN/TR 13983:2003 Guide 5	Characterization of sludges – Good practice for sludge utilization in land reclamation				
CEN/TR 15126:2005 Guide 8	Characterization of sludges- Good practice for landfilling of sludges and sludge treatment residues				
CEN/TR 15473:2007	Characterization of sludges - Good practice for sludges drying				

WG 3 Measures to preserve, to improve and to extend utilization and disposal routes					
CEN/CR 13846:2000	Characterization of sludges-Recommendations to preserve and extend sludge utilization and disposal routes				
CEN/TR 15584:2007	Characterization of sludges - Guide to risk assessment especially in relation to use and disposal of sludges				





### Appendix 2: Mechanical properties

				Compress	ive stren	gth	
	Sample	width	height	strength	Stress	Ø pevnost	%Decreasing stress relating
		[mm]	[mm]	[kN]	[MPa]	[MPa]	with sludge content
	R1	40.0	40.0	98.7	61.7	55.7	
	R2	40.0	40.0	79.5	49.7	33.7	
	10,1	40.0	40.0	77.0	48.1	49.8	89.4
v	10,2	40.0	40.0	82.4	51.5	49.8	65.4
28 days	20,1	40.0	40.0	60.4	37.8	36.1	64.8
28	20,2	40.0	40.0	55.0	34.4	30.1	04.8
	30,1	40.0	40.0	53.1	33.2	32.4	58.3
	30,2	40.0	40.0	50.8	31.7	32.4	30.3
	40,1	40.0	40.0	38.9	24.3	26.8	48.2
	40,2	40.0	40.0	47.0	29.4		40.2
	R,1	40.0	40.0	92.8	58.0	63.94	
	R,2	40.0	40.0	111.8	69.9	03.94	-
	10,1	40.0	40.0	73.9	46.2	40.24	77.2
	10,2	40.0	40.0	84.0	52.5	49.34	77.2
ays	20,1	40.0	40.0	61.2	38.3	22.46	F1.0
90 days	20,2	40.0	40.0	44.9	28.1	33.16	51.9
	30,1	40.0	40.0	47.3	29.6	20.00	46.0
	30,2	40.0	40.0	48.7	30.4	30.00	46.9
	40,1	40.0	40.0	43.8	27.4	25.55	44 =
	40,2	40.0	40.0	41.5	25.9	26.66	41.7





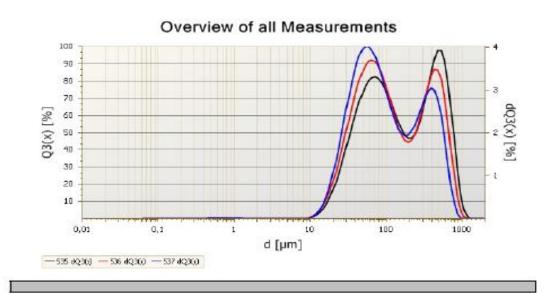
	Bending strength									
	Sample	length [mm]	width [mm]	height [mm]	Weight [g]	bulk density [kgm-3]	Strenght [kN]	Stress [MPa]	%Decreasing stress relating with sludge content	
	R	160.0	40.9	40.4	519.20	1964	5.080	11.41	-	
۸s	10	159.9	40.8	40.2	501.40	1912	3.530	8.04	70.5	
days	20	160.5	40.2	39.9	481.60	1871	2.310	5.42	47.5	
28	30	160.2	41.1	40.5	481.80	1807	2.840	6.31	55.3	
	40	160.1	40.0	40.1	453.20	1765	2.580	6.03	52.9	





### Appendix 3: Size distribution



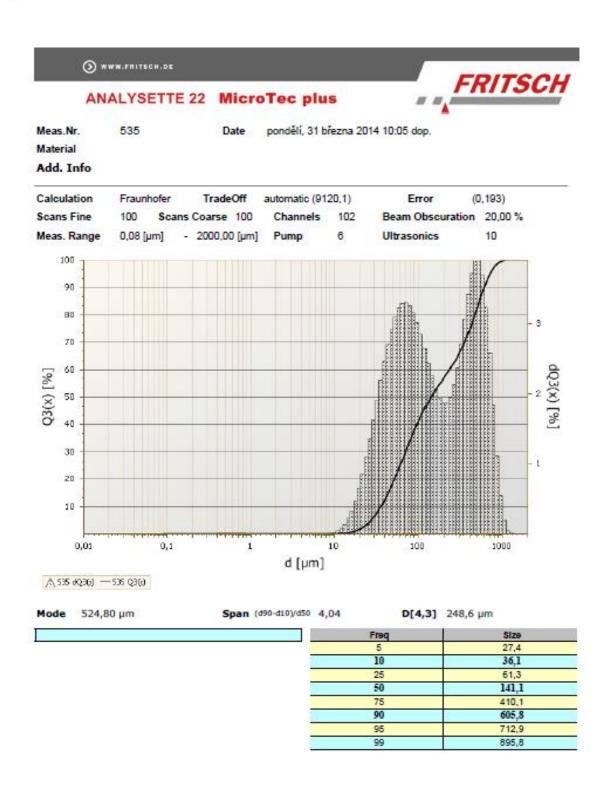


Freq	Size	VarCoeff	M535	M536	M537
1	16,4	4,1	17,4	16,1	15,8
5	25,3	6,2	27,4	25	23,6
10	32,9	7,6	36,1	32,5	30
30	61,9	12	71,4	61	53,3
50	113,6	18,4	141,1	109,2	90,4
90	528,3	12,1	605,8	529,6	449,5

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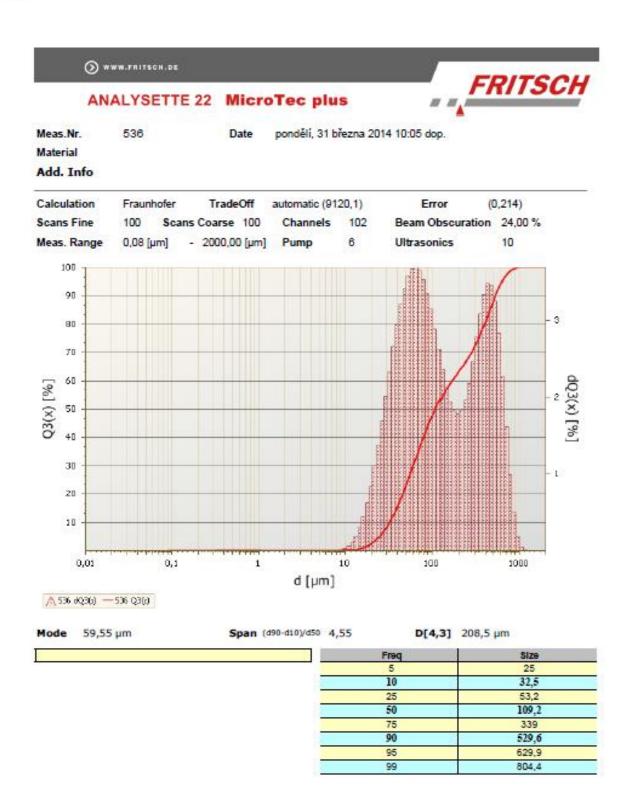




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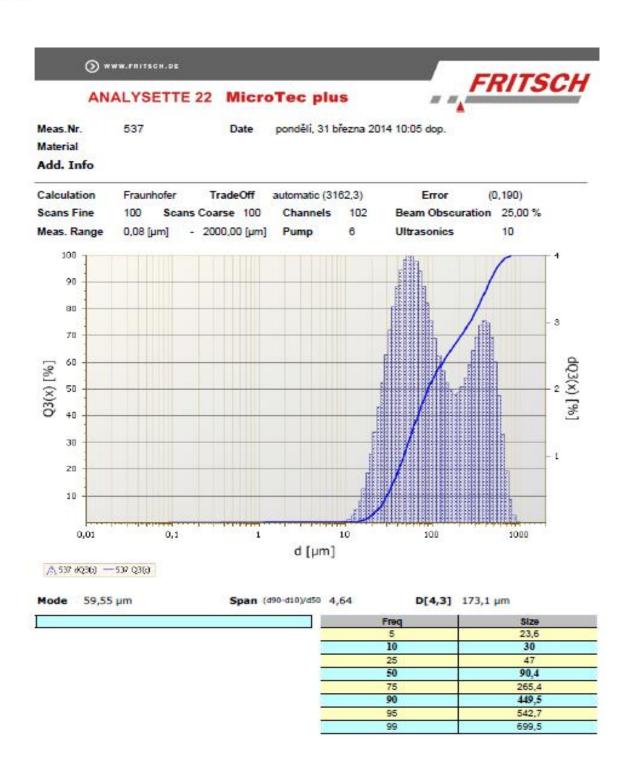




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0.00 0.02 2,020.00 0.00 1,252.00 0.00 0.00 1,252.00 0.00 0.00 1,1654.00 0.00 1,1654.00 0.01 0.01 1,054.00 0.01 1,054.00 0.01 1,054.00 0.01 1,054.00 0.01 1,054.00 0.01 1,054.00 0.01 1,054.00 0.01 1,054.00 0.01 1,054.00 0.01 1,054.00 0.01 1,054.00 0.01 1,054.00 0.01 1,054.00 0.01 1,054.00 0.01 1,054.00 0.02 1,228.00 0.20 1,228.00 0.20 1,228.00 0.00 0.55 1,356.00 0.14 0.02 1,112.00 0.55 1,112.00 0.16 0.01 1,112.00 0.55 1,112.00 0.16 0.01 1,112.00 0.55 1,112.00 0.16 0.01 1,006.00 1.12 1,006.00 1.12 1,006.00 1.12 1,006.00 1.01 0.01 0.01 0.01 0.01 0.01 0.0	2 dQ3(x) [%] dQ3(x) [%] 0.00 0.00 0.00 0.00 0.00 0.01 0.05 0.19 0.50 0.99 1.62 2.27 2.84 3.25 3.48 3.34 3.34 3.34 3.39 2.78 2.46 2.18 1.96 1.82 1.78 1.82 1.96 1.82 1.78 1.82 1.96 1.82 1.78 1.82 1.96 1.82 1.78 1.82 1.96 1.82 1.96 1.82 1.96 1.82 1.96 1.82 1.98 1.96 1.82 1.96 1.83 1.10 1.00 1.00 1.00 1.00 1.00 1.00 1.0	Size Low [µm] 2,020.00 1,826.00 1,826.00 1,458.00 1,458.00 1,356.00 1,112.00 1,006.00 910.00 824.00 746.00 612.00 554.00 412.00 372.00 338.00 372.00 338.00 276.00 256.00 256.00 185.80 113.780 113.00 124.80 113.00 68.80 62.20 68.80 62.20 68.80 62.20 41.80 37.80	SS3	Avera; Size Low [µm] 2,020.00 1,826.00 1,988.00 1,198.00 1,198.00 1,198.00 1,198.00 1,112.00 1,112.00 1,112.00 1,112.00 1,112.00 1,112.00 676.00 612.00 554.00 454.00 454.00 454.00 276.	ce 4PSS
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0.09	0.00 0.00 0.00 0.00 0.00 0.01 0.05 0.19 0.50 0.99 1.62 2.27 3.46 3.25 3.48 3.34 3.34 3.34 2.78 1.82 1.96 1.82 1.78 1.82 1.96 1.82 1.93 3.15 3.36 3.53 3.65 3.67 3.67 3.69 3.67 3.169 3.169 3.67 3.17 3.18 3.19 3.19 3.19 3.19 3.19 3.19 3.19 3.19	1,826.00 1,654.00 1,498.00 1,356.00 1,228.00 1,112.00 1,006.00 910.00 824.00 746.00 612.00 554.00 454.00 412.00 372.00 338.00 276.00 226.00 226.00 226.00 226.00 226.00 226.00 226.00 256.00 185.80 113.00 26.00 168.20 152.40 137.80 113.00 68.80 62.20 684.00 68.80 62.20 41.80 37.80 31.00 28.20 41.80 37.80 31.00 28.20 41.80 37.80 31.00 28.20 41.80 37.80 31.00 28.20 41.80 37.80 31.00 28.20 41.80 37.80 31.00 28.20 41.80 37.80 31.00 28.20 41.80 37.80 31.00 28.20 25.40 21.00 25.40 25.40 21.00 25.40 25.50 25.50 25.50 25.50 25.50 25.50 25.50 25.50 25.50 25.50 25.50 25.50 25.50 25.50 25.50	0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.0	1,826.00 1,654.00 1,498.00 1,498.00 1,356.00 1,112.00 1,112.00 1,112.00 1,112.00 824.00 746.00 676.00 612.00 554.00 454.00 412.00 372.00 338.00 276.0	0.00 0.00 0.00 0.00 0.00 0.02 0.08 0.25 0.58 1.06 1.66 2.28 3.19 3.39 3.40 3.27 3.04 2.76 2.47 2.23 2.03 1.91 1.87 1.90 2.00 2.16 2.36 2.59 2.83 3.07 3.27 3.45 3.57 3.63 3.63 3.63 3.56 3.43 3.23 2.98 2.70 2.38 2.05 1.72 1.40 0.84 0.62 0.43
0.10	0.00 0.00 0.00 0.00 0.01 0.05 0.19 0.50 0.99 1.62 2.27 2.84 3.25 3.46 3.48 3.34 3.09 2.78 2.18 1.96 1.82 1.78 1.82 1.78 1.82 1.78 1.82 1.78 1.82 1.78 1.82 1.78 1.82 1.94 2.13 2.63 2.89 3.15 3.36 3.53 3.65 3.69 3.67 3.58 3.42 3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01	1,654.00 1,498.00 1,498.00 1,1356.00 1,128.00 1,128.00 1,100.00 910.00 824.00 676.00 612.00 502.00 454.00 412.00 372.00 338.00 306.00 276.00 205.00 226.00 205.00 185.80 168.20 152.40 137.80 124.80 113.00 68.80 168.20 56.40 51.00 76.00 68.80 76.00 68.80 376.00 76.00 68.80 378.00 378	0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.0	1,654.00 1,498.00 1,1356.00 1,1356.00 1,128.00 1,106.00 910.00 824.00 676.00 612.00 554.00 502.00 454.00 412.00 372.00 338.00 276.00 206.00 226.00 226.00 2152.40 137.80 124.80 113.00 102.40 92.60 88.00 76.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 33.00 34.40 31.00 28.20 25.40 31.00 28.20 26.20	0.00 0.00 0.00 0.00 0.00 0.02 0.08 0.25 0.58 1.06 1.66 2.28 2.81 3.19 3.39 3.40 2.76 2.47 2.23 2.03 1.91 1.87 1.90 2.16 2.36 2.59 2.83 3.07 3.27 3.45 3.63 3.63 3.63 3.63 3.63 3.27 3.23 2.08 2.70 2.38 2.09
0.11	0.00 0.01 0.05 0.19 0.50 0.99 1.62 2.27 2.84 3.25 3.46 3.48 3.34 3.34 3.39 2.78 2.46 2.18 1.96 1.82 1.78 1.82 1.78 1.82 1.94 2.13 2.37 2.63 2.89 3.15 3.36 3.67 3.53 3.69 3.67 3.58 3.42 3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01	1,498.00 1,356.00 1,228.00 1,1228.00 1,112.00 1,006.00 910.00 824.00 676.00 612.00 554.00 502.00 454.00 372.00 338.00 276.00 226.00 226.00 226.00 185.80 168.20 152.40 137.80 124.80 137.80 62.20 56.40 51.00 46.20 41.80 37.80	0.00 0.00 0.00 0.00 0.00 0.02 0.11 0.35 0.77 1.32 1.90 2.41 2.79 2.99 3.04 2.96 2.79 2.58 2.37 2.18 2.04 1.95 1.93 1.98 2.10 2.28 2.50 2.76 3.03 3.55 3.77 3.92 4.01 4.01 4.01 3.94 3.78 3.54 2.89 2.51 2.11 1.73 1.36 1.03 0.75 0.51 0.33	1,498.00 1,356.00 1,228.00 1,1228.00 1,112.00 1,006.00 910.00 824.00 676.00 612.00 554.00 502.00 454.00 372.00 338.00 276.00 226.00 226.00 226.00 185.80 168.20 152.40 137.80 102.40 92.60 84.00 76.00 68.80 102.40 92.60 46.20 46.20 41.80 37.80 34.40 31.00 28.20 25.40 31.00 28.20 29.30	0.00 0.02 0.08 0.02 0.08 0.25 0.58 1.06 1.66 2.28 2.81 3.19 3.39 3.40 3.27 3.04 2.76 2.47 2.23 2.03 1.91 1.87 1.90 2.16 2.36 2.48 3.3.7 3.45 3.57 3.63 3.63 3.57 3.63 3.56 3.43 3.22 2.98 2.70 2.38 2.09 2.140 2.38 2.09
0.13	0.05 0.19 0.19 0.50 0.19 0.50 0.99 1.62 2.27 2.84 3.25 3.46 3.48 3.34 3.09 2.78 2.18 1.96 1.82 1.78 1.82 1.78 1.82 1.94 2.13 2.37 2.63 2.89 3.15 3.36 3.65 3.69 3.67 3.58 3.42 3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	1,228.00 1,112.00 1,1006.00 910.00 824.00 676.00 612.00 554.00 552.00 454.00 372.00 255.00 226.00 206.00 185.80 168.20 152.40 137.80 124.80 113.00 66.20 46.20 46.20 41.80 37.80 37.80 37.80 37.80 31.00 28.20 25.40 31.00 28.20 56.40 51.00 28.20 56.40 51.00 56.88 56.40 51.00 56.88 57.80 58.80 58.80 58.80 59.	0.00 0.02 0.11 0.35 0.77 1.32 1.90 2.41 2.79 2.99 3.04 2.96 2.79 2.58 2.37 2.18 2.04 1.95 2.10 2.28 2.10 3.03 3.50 3.77 3.92 4.01 4.01 3.78 3.54 3.24 2.89 2.51 1.73 1.36 1.03 0.75 0.51 0.33	1,228.00 1,1006.00 1,006.00 910.00 824.00 676.00 612.00 554.00 552.00 454.00 412.00 372.00 338.00 306.00 276.00 226.00 206.00 185.80 168.20 152.40 137.80 124.80 124.80 152.40 92.60 68.80 662.20 56.40 51.00 68.20 46.20 41.80 37.80 31.00 28.20 25.40 31.00 28.20	0.08 0.25 0.58 1.06 1.66 1.66 2.28 2.81 3.19 3.39 3.40 2.76 2.47 2.23 2.03 1.91 1.87 1.90 2.16 2.36 2.59 2.83 3.07 3.27 3.45 3.63 3.57 3.63 3.56 3.43 3.23 2.98 2.70 2.38 2.05 1.72 1.40 1.11 0.84 0.62 0.43
0.14	0.19 0.50 0.99 1.62 2.27 2.84 3.25 3.46 3.48 3.34 3.39 2.78 2.46 1.82 1.96 1.82 1.78 1.82 1.94 2.13 2.37 2.63 2.89 3.15 3.36 3.67 3.53 3.65 3.69 3.67 3.58 3.42 3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	1,112.00 1,006.00 910.00 824.00 746.00 612.00 554.00 552.00 454.00 372.00 338.00 276.00 226.00 226.00 226.00 185.80 168.20 152.40 113.00 68.80 62.20 68.80 62.20 56.40 51.00 37.80 37.80 37.80 37.80 37.80 37.80 37.80 37.80 37.80 37.80 37.80 38.80 62.20 55.40 51.00 56.40 51.00 56.40 51.00 56.40 57.00 58.80 67.00 68.80 67.00 68.80 67.00 68.80 67.00 68.80 67.00 68.80 67.00 68.80 67.00 68.80 67.00 68.80 67.00 68.80 67.00 68.80 67.00 68.80 67.00 68.80 67.00 68.80 67.00 68.80 67.00	0.02 0.11 0.35 0.77 1.32 1.90 2.41 2.79 2.99 3.04 2.96 2.79 2.58 2.37 2.18 2.04 1.95 1.93 1.98 2.10 2.28 2.50 3.03 3.55 3.77 3.92 4.01 4.01 4.01 3.94 3.78 3.54 2.89 2.51 1.73 1.36 1.03 0.75 0.51 0.33	1,112.00 1,006.00 1,006.00 910.00 824.00 746.00 612.00 612.00 454.00 554.00 552.00 454.00 338.00 276.00 226.00 226.00 226.00 185.80 168.20 152.40 113.780 124.80 113.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 31.00 28.20 25.40 31.00 28.20	0.25 0.58 1.06 1.66 2.28 2.81 3.19 3.40 3.27 3.04 2.76 2.47 2.23 2.03 1.91 1.87 1.90 2.16 2.36 2.59 2.83 3.07 3.27 3.45 3.57 3.63 3.56 3.43 3.23 2.98 2.70 2.38 2.05 1.72 1.40 0.84 0.62 0.43
0.16	0.50 0.99 1.62 2.27 2.84 3.25 3.46 3.34 3.34 3.39 2.78 2.46 2.18 1.96 1.82 1.78 1.82 1.94 2.13 2.37 2.63 3.15 3.36 3.53 3.65 3.67 3.58 3.42 3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	1,006.00 910.00 910.00 924.00 746.00 676.00 612.00 554.00 412.00 372.00 338.00 372.00 250.00 226.00 206.00 185.80 168.20 152.40 137.80 113.00 102.40 92.60 84.00 76.00 68.80 62.20 41.80 37.80 34.40 31.00 28.20 25.40 21.90 25.40 21.90 26.20 26.20 26.20 26.20 276.00 276.00 284.00 284.00 285.20	0.11 0.35 0.77 1.32 1.90 2.41 2.79 3.04 2.96 2.79 2.58 2.37 2.18 2.04 1.95 1.93 1.98 2.10 2.28 2.50 3.03 3.30 3.30 3.30 3.30 3.30 3.30 3	1,006.00 910.00 910.00 824.00 746.00 612.00 554.00 412.00 372.00 338.00 372.00 250.00 276.00 250.00 26.00 185.80 168.20 152.40 113.00 102.40 92.60 84.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 28.20 20.80	0.58 1.06 1.66 2.28 2.81 3.19 3.39 3.40 3.27 3.04 2.76 2.47 2.23 2.03 1.91 1.87 1.90 2.00 2.16 2.36 2.59 2.83 3.07 3.27 3.45 3.57 3.63 3.63 3.56 3.43 3.23 2.98 2.70 2.38 2.05 1.72 1.40 0.84 0.62 0.43
0.17	0.99 1.62 2.27 2.84 3.25 3.46 3.48 3.34 3.09 2.78 2.18 1.96 1.82 1.78 1.82 1.78 1.82 1.94 2.13 2.37 2.63 2.89 3.15 3.36 3.65 3.69 3.67 3.58 3.42 3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	910.00 824.00 746.00 676.00 612.00 554.00 502.00 454.00 372.00 338.00 306.00 276.00 226.00 206.00 185.80 168.20 152.40 137.80 124.80 113.00 68.80 76.00 68.80 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 25.40 21.550	0.35 0.77 1.32 1.90 2.41 2.79 2.99 3.04 2.96 2.79 2.58 2.37 2.18 2.04 1.95 2.10 2.28 2.10 3.03 3.55 3.77 3.92 4.01 4.01 3.94 3.78 3.54 3.24 2.89 2.51 1.73 1.36 1.03 0.75 0.51 0.33	910.00 824.00 746.00 676.00 612.00 554.00 502.00 454.00 372.00 338.00 306.00 276.00 226.00 206.00 185.80 168.20 152.40 137.80 124.80 113.00 68.80 76.00 68.80 51.00 76.00 68.80 31.00 76.00 68.80 31.00 76.00 76.00	1.06 1.66 2.28 2.81 3.19 3.39 3.40 2.76 2.47 2.23 2.03 1.91 1.87 1.90 2.16 2.36 2.59 2.83 3.07 3.27 3.45 3.63 3.63 3.63 3.63 3.57 3.63 3.70 3.27 3.19 1.91 1.87 1.90 2.10 2.16 2.36 2.59 2.83 3.07 3.27 3.45 3.63 3.63 3.63 3.63 3.63 3.63 3.63 3.6
0.19	1.62 2.27 2.84 3.25 3.48 3.34 3.34 3.39 2.78 2.46 2.18 1.96 1.82 1.78 1.82 1.78 1.82 1.94 2.13 2.37 2.63 2.89 3.15 3.36 3.53 3.65 3.67 3.58 3.42 3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	824.00 746.00 676.00 612.00 554.00 454.00 372.00 338.00 276.00 250.00 226.00 206.00 185.80 168.20 152.40 137.80 124.80 113.00 68.80 62.20 56.40 51.00 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90 18.90 17.12	0.77 1.32 1.90 2.41 2.79 2.99 3.04 2.96 2.79 2.58 2.37 2.18 2.04 1.95 1.93 1.98 2.10 2.28 2.50 2.76 3.03 3.30 3.30 3.30 3.355 3.77 3.92 4.01 4.01 4.01 3.94 3.78 3.54 2.89 2.51 2.11 1.73 1.36 1.03 0.75 0.51	824.00 746.00 676.00 612.00 554.00 454.00 372.00 338.00 276.00 226.00 226.00 226.00 226.00 168.20 152.40 113.780 1124.80 113.00 68.80 62.20 66.40 51.00 46.20 41.80 37.80 31.00 28.20 25.40 31.00 28.20 25.40 21.00	1.66 2.28 2.81 3.19 3.39 3.40 3.27 3.04 2.76 2.47 2.23 2.03 1.91 1.87 1.90 2.16 2.36 2.59 2.83 3.07 3.27 3.45 3.57 3.63 3.63 3.56 3.43 3.23 2.98 2.70 2.38 2.05 1.72 1.40 0.84 0.62 0.43
0.21	2.27 2.84 3.25 3.46 3.48 3.34 3.09 2.78 2.46 2.18 1.96 1.82 1.78 2.13 2.37 2.63 2.89 3.15 3.36 3.53 3.65 3.69 3.65 3.69 3.15 3.16 3.58 3.42 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	746.00 676.00 676.00 612.00 554.00 554.00 412.00 372.00 338.00 306.00 250.00 226.00 226.00 185.80 113.00 102.40 92.60 84.00 68.80 62.20 46.20 46.20 41.80 37.80 31.00 28.20 25.40 31.00 28.20 26.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 20.80 21.90 20.80 21.90 21	1.32 1.90 2.41 2.79 2.99 3.04 2.96 2.79 2.58 2.37 2.18 2.04 1.95 1.93 1.98 2.10 2.28 2.50 3.03 3.30 3.30 3.30 3.30 3.35 3.77 3.92 4.01 4.01 4.01 3.78 3.54 2.89 2.51 1.73 1.36 1.03 0.75 0.51 0.33	746.00 676.00 676.00 554.00 552.00 454.00 412.00 372.00 338.00 306.00 276.00 226.00 226.00 185.80 168.20 152.40 137.80 124.80 113.00 102.40 92.60 88.40 51.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80	2.28 2.81 3.19 3.39 3.40 2.76 2.47 2.23 2.03 1.91 1.87 1.90 2.00 2.16 2.36 2.59 2.83 3.07 3.27 3.45 3.63 3.63 3.63 3.63 3.23 2.98 2.70 2.38 2.05 1.72 1.40 1.11 0.84 0.62
0.23	2.84 3.25 3.46 3.48 3.34 3.09 2.78 2.18 1.96 1.82 1.78 1.82 1.78 1.82 1.94 2.13 2.37 2.63 2.89 3.15 3.36 3.53 3.65 3.69 3.67 3.58 3.42 3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	676.00 612.00 554.00 552.00 454.00 372.00 454.00 372.00 338.00 306.00 276.00 226.00 206.00 185.80 168.20 152.40 113.780 1124.80 113.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 31.00 28.20 25.40 21.90 25.40 21.50 25.40 21.50 25.40 21.50 25.40 21.50 25.40 21.50 25.40 21.50 25.40 21.50 25.40 21.50 21.50	1.90 2.41 2.79 2.99 3.04 2.96 2.79 2.58 2.37 2.18 2.04 1.95 1.93 1.98 2.10 2.28 2.50 2.76 3.03 3.55 3.77 3.92 4.01 4.01 4.01 3.94 3.78 3.54 3.24 2.89 2.51 2.11 1.73 1.36 1.03 0.75 0.51	676.00 612.00 612.00 554.00 5554.00 552.00 454.00 372.00 338.00 306.00 276.00 226.00 226.00 206.00 185.80 168.20 152.40 137.80 124.80 113.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 31.00 28.20 25.40 31.00 28.20 25.40 23.00 20.80	2.81 3.19 3.39 3.40 3.27 3.04 2.76 2.47 2.23 2.03 1.91 1.87 1.90 2.00 2.16 2.36 2.59 2.83 3.07 3.27 3.45 3.63 3.63 3.57 3.63 3.56 3.43 3.23 2.98 2.70 2.38 2.05 1.72 1.40 1.11 0.84 0.62 0.43
0.25	3.25 3.46 3.48 3.34 3.34 3.09 2.78 2.46 2.18 1.96 1.82 1.78 1.82 1.94 2.13 2.37 2.63 2.89 3.15 3.36 3.53 3.65 3.69 3.67 3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.001 0.000	612.00 554.00 554.00 454.00 412.00 338.00 338.00 226.00 226.00 226.00 226.00 185.80 168.20 152.40 137.80 113.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 21.80 37.80 28.20 21.50 20.80 20.80 21.90	2.41 2.79 2.99 3.04 2.96 2.79 2.58 2.37 2.18 2.04 1.95 1.93 1.98 2.10 2.28 2.50 3.03 3.30 3.30 3.30 3.37 4.01 4.01 4.01 3.94 3.78 3.54 2.89 2.51 2.11 1.73 1.36 1.03 0.75 0.51	612.00 554.00 554.00 454.00 412.00 372.00 338.00 276.00 250.00 26.00 26.00 185.80 168.20 152.40 137.80 124.80 113.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 22.80	3.19 3.39 3.40 3.27 3.04 2.76 2.47 2.23 2.03 1.91 1.87 1.90 2.00 2.16 2.36 2.59 2.83 3.07 3.27 3.45 3.57 3.63 3.63 3.56 3.43 3.23 2.98 2.70 2.38 2.05 1.72 1.40 0.84 0.62 0.43
0.37	3.46 3.48 3.34 3.09 2.78 2.46 2.18 1.96 1.82 1.78 2.19 1.82 1.94 2.13 2.63 2.89 3.15 3.36 3.53 3.65 3.69 3.67 3.58 3.42 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	554,00 502,00 454,00 412,00 372,00 338,00 306,00 226,00 226,00 226,00 185,80 168,20 152,40 137,80 124,80 113,00 102,40 92,60 88,00 76,00 68,80 51,00 46,20 41,80 37,80 31,00 28,20 56,40 51,00 56,20 56,40 51,00 68,80 37,80 31,00 28,20 56,40 51,00 68,80 37,80 31,10 31,00	2.79 2.99 3.04 2.96 2.79 2.58 2.37 2.18 2.04 1.95 1.93 1.98 2.10 2.28 2.50 3.03 3.30 3.30 3.35 3.77 3.92 4.01 4.01 3.94 3.78 3.54 2.89 2.51 1.73 1.36 1.03 0.75 0.51	554.00 502.00 412.00 372.00 372.00 338.00 306.00 276.00 226.00 226.00 185.80 168.20 152.40 137.80 124.80 113.00 102.40 92.60 884.00 76.00 68.80 56.40 51.00 46.20 41.80 37.80 31.00 28.20 25.40 31.00 28.20	3.39 3.40 3.27 3.04 2.76 2.47 2.23 2.03 1.91 1.87 1.90 2.00 2.16 2.36 2.59 2.83 3.07 3.27 3.45 3.63 3.63 3.63 3.63 3.23 2.98 2.70 2.38 2.05 1.72 1.40 1.11 0.84 0.62 0.43
0.30	3.48 3.34 3.39 2.78 2.46 2.18 1.96 1.82 1.78 1.82 1.94 2.13 2.37 2.63 2.89 3.15 3.36 3.53 3.65 3.69 3.67 3.58 3.42 3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	502.00 454.00 412.00 372.00 338.00 306.00 276.00 226.00 206.00 185.80 168.20 152.40 137.80 124.80 113.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 31.00 28.20 25.40 23.00 20.80 18.90 17.12	2.99 3.04 2.96 2.79 2.58 2.37 2.18 2.04 1.95 1.93 1.98 2.10 2.28 2.50 2.76 3.03 3.55 3.77 3.92 4.01 4.01 4.01 3.94 3.78 3.54 3.24 2.89 2.51 2.11 1.73 1.36 1.03 0.75 0.51	502.00 454.00 412.00 372.00 338.00 276.00 226.00 226.00 206.00 185.80 168.20 152.40 137.80 102.40 92.60 84.00 76.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 31.00 28.20 25.40 31.00 28.20	3.40 3.27 3.04 2.76 2.47 2.23 2.03 1.91 1.87 1.90 2.00 2.16 2.36 2.59 2.83 3.07 3.27 3.45 3.57 3.63 3.63 3.56 3.43 3.23 2.98 2.70 2.38 2.05 1.72 1.40 1.11 0.84 0.62 0.43
0.37	3.09 2.78 2.46 2.18 1.96 1.82 1.78 1.92 1.94 2.13 2.63 2.89 3.15 3.36 3.53 3.65 3.69 3.67 3.58 3.42 3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	412.00 372.00 378.00 338.00 306.00 276.00 226.00 226.00 2185.80 168.20 152.40 137.80 124.80 113.00 102.40 92.60 88.40 76.00 68.80 62.20 56.40 51.00 37.80 31.00 28.20 41.80 37.80 31.00 28.20 56.40 51.00 68.80 76.00	2.96 2.79 2.58 2.37 2.18 2.04 1.95 1.93 1.98 2.10 2.28 2.50 3.03 3.30 3.55 3.77 3.92 4.01 4.01 4.01 3.78 3.54 2.89 2.51 1.73 1.36 1.03 0.75 0.51 0.33	412.00 372.00 378.00 306.00 276.00 226.00 226.00 2185.80 168.20 152.40 137.80 124.80 102.40 92.60 88.40 76.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 31.00 28.20 25.40 23.00 20.80	3.04 2.76 2.47 2.23 2.03 1.91 1.87 1.90 2.00 2.16 2.36 2.59 2.83 3.07 3.27 3.45 3.63 3.63 3.63 3.63 3.23 2.98 2.70 2.38 2.05 1.72 1.40 1.11 0.84 0.62 0.43
0.40 0.10 372.00 2.71 372.00 0.40 0.44 0.10 138.00 2.38 338.00 0.00 0.49 0.11 336.00 2.13 336.00 0.53 0.11 276.00 1.96 276.00 0.59 0.12 250.00 1.87 250.00 0.65 0.12 226.00 1.87 226.00 0.65 0.12 226.00 1.87 226.00 0.65 0.12 226.00 1.87 226.00 0.65 0.12 260.00 1.94 260.00 0.71 0.12 260.00 1.94 260.00 0.71 0.12 260.00 1.94 260.00 0.78 0.11 185.80 2.07 185.80 2.07 185.80 0.00 0.94 0.11 185.80 2.05 185.80 2.07 185.80 1.04 0.11 137.80 2.65 137.80 1.14 0.11 137.80 2.65 137.80 1.14 0.11 137.80 2.65 137.80 1.15 0.11 137.80 2.65 137.80 1.16 0.11 133.00 3.02 113.00 1.38 0.12 102.40 3.16 102.40 3.16 102.40 1.55 0.13 92.60 3.26 92.60 1.67 0.15 84.00 3.30 84.00 3.20 2.65 137.80 1.84 0.18 76.00 3.29 76.00 2.22 0.22 68.80 3.28 68.80 3.28 68.80	2.78 2.46 2.18 1.96 1.82 1.78 1.82 1.94 2.13 2.37 2.63 2.89 3.15 3.36 3.53 3.65 3.69 3.67 3.58 3.42 3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	372.00 338.00 336.00 276.00 250.00 226.00 206.00 185.80 168.20 152.40 137.80 124.80 113.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 31.00 28.20 25.40 23.00 20.80 18.90 17.12	2.79 2.58 2.37 2.18 2.04 1.95 1.93 1.98 2.10 2.28 2.50 2.76 3.03 3.55 3.77 3.92 4.01 4.01 4.01 3.94 3.78 3.54 2.89 2.51 2.11 1.73 1.36 1.03 0.75 0.51 0.33	372.00 338.00 336.00 276.00 226.00 226.00 206.00 185.80 168.20 152.40 137.80 1124.80 113.00 68.80 662.20 56.40 51.00 46.20 41.80 37.80 31.00 28.20 25.40 23.00 20.80	2.76 2.47 2.23 2.03 1.91 1.87 1.90 2.00 2.16 2.36 2.59 2.83 3.07 3.45 3.57 3.63 3.56 3.43 3.23 2.98 2.70 2.38 2.05 1.72 1.40 1.11 0.84 0.62 0.43
0.49	2.46 2.18 1.96 1.82 1.78 1.82 1.94 2.13 2.37 2.63 2.89 3.15 3.36 3.65 3.69 3.58 3.42 2.95 2.66 2.34 2.01 1.69 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	338.00 306.00 276.00 250.00 250.00 26.00 185.80 168.20 152.40 137.80 113.00 102.40 92.60 84.00 68.80 62.20 41.80 37.80 31.00 28.20 25.40 31.00 28.20 20.80 21.20 20.80 21.20 21.50 21.50 21.50 21.50 21.50 21.50 21.50	2.58 2.37 2.18 2.04 1.95 1.93 1.98 2.10 2.28 2.50 3.03 3.30 3.35 3.77 3.92 4.01 4.01 3.94 3.78 3.54 2.89 2.51 1.73 1.36 1.03 0.75 0.51	338.00 306.00 276.00 250.00 26.00 185.80 168.20 152.40 137.80 113.00 102.40 92.60 84.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 28.30	2.47 2.23 2.03 1.91 1.87 1.90 2.00 2.16 2.36 2.59 2.83 3.07 3.27 3.45 3.57 3.63 3.56 3.43 3.23 2.98 2.70 2.38 2.05 1.72 1.40 1.11 0.84 0.62 0.43
0.49	2.18 1.96 1.82 1.78 1.82 1.94 2.13 2.37 2.63 2.89 3.15 3.36 3.53 3.65 3.69 3.67 3.58 3.42 3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	306.00 276.00 276.00 250.00 26.00 26.00 26.00 185.80 168.20 152.40 137.80 124.80 102.40 92.60 84.00 76.00 68.80 51.00 46.20 41.80 37.80 31.00 28.20 25.40 23.00 20.80 18.90 17.12	2.37 2.18 2.04 1.95 1.93 1.98 2.10 2.28 2.50 2.76 3.03 3.30 3.55 3.77 3.92 4.01 4.01 3.94 3.78 3.54 3.24 2.89 2.51 2.11 1.73 1.36 1.03 0.75 0.51 0.33	306.00 276.00 276.00 250.00 26.00 26.00 185.80 168.20 152.40 137.80 124.80 113.00 102.40 92.60 84.00 76.00 68.80 51.00 46.20 41.80 37.80 31.00 28.20 25.40 23.00 20.80	2.23 2.03 1.91 1.87 1.90 2.00 2.16 2.36 2.59 2.83 3.07 3.27 3.45 3.63 3.63 3.63 3.63 3.23 2.98 2.70 2.38 2.05 1.72 1.40 1.11 0.84 0.62 0.43
0.53	1.96 1.82 1.78 1.82 1.94 2.13 2.37 2.63 2.89 3.15 3.36 3.53 3.65 3.69 3.67 3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	276.00 250.00 260.00 185.80 168.20 152.40 137.80 1124.80 113.00 102.40 92.60 84.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90 17.12	2.18 2.04 1.95 1.93 1.98 2.10 2.28 2.50 2.76 3.03 3.30 3.55 3.77 3.92 4.01 4.01 4.01 3.94 3.78 3.54 2.89 2.51 2.11 1.73 1.36 1.03 0.75 0.51 0.33	276.00 250.00 250.00 226.00 206.00 185.80 168.20 152.40 1137.80 1124.80 113.00 92.60 84.00 76.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80	2.03 1.91 1.87 1.90 2.00 2.16 2.36 2.59 2.83 3.07 3.45 3.57 3.63 3.63 3.63 3.56 3.43 3.23 2.98 2.70 2.38 2.05 1.72 1.40 0.84 0.62 0.43
0.69	1.82 1.78 1.82 1.94 2.13 2.37 2.63 2.89 3.15 3.36 3.53 3.65 3.69 3.58 3.42 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	250.00 226.00 226.00 185.80 168.20 152.40 137.80 124.80 113.00 102.40 92.60 84.00 76.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90 17.12 15.50	2.04 1.95 1.93 1.98 2.10 2.28 2.50 3.03 3.30 3.35 3.77 3.92 4.01 4.01 3.78 3.54 2.89 2.51 1.73 1.36 1.03 0.75 0.51 0.33	250.00 226.00 226.00 185.80 168.20 152.40 137.80 124.80 113.00 102.40 92.60 84.00 76.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90	1.91 1.87 1.90 2.00 2.16 2.36 2.59 2.83 3.07 3.27 3.45 3.57 3.63 3.63 3.56 3.43 3.23 2.98 2.70 2.38 2.05 1.72 1.40 1.11 0.84 0.62 0.43
0.65	1.78 1.82 1.94 2.13 2.37 2.63 2.89 3.15 3.36 3.53 3.65 3.69 3.67 3.58 3.42 3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	226.00 206.00 185.80 168.20 152.40 137.80 124.80 113.00 92.60 84.00 76.00 68.80 51.00 46.20 41.80 37.80 31.00 28.20 25.40 23.00 28.20 25.40 21.55 14.02	1.95 1.93 1.98 2.10 2.28 2.50 2.76 3.03 3.30 3.55 3.77 3.92 4.01 4.01 4.01 3.94 3.78 3.54 3.24 2.89 2.51 2.11 1.73 1.36 1.03 0.75 0.51	226.00 206.00 185.80 168.20 152.40 137.80 124.80 113.00 102.40 92.60 84.00 76.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 31.00 28.20 25.40 23.00 20.80	1.87 1.90 2.00 2.16 2.36 2.59 2.83 3.07 3.27 3.45 3.63 3.63 3.63 3.23 2.98 2.70 2.38 2.05 1.72 1.40 1.11 0.84 0.62 0.43
0.71	1.82 1.94 2.13 2.37 2.63 2.89 3.15 3.36 3.53 3.65 3.69 3.67 3.58 3.42 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	206.00 185.80 168.20 152.40 137.80 1124.80 113.00 92.60 84.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90 17.12	1.93 1.98 2.10 2.28 2.50 2.76 3.03 3.30 3.55 3.77 3.92 4.01 4.01 3.94 3.78 3.54 2.89 2.51 1.73 1.36 1.03 0.75 0.51 0.33	206.00 185.80 168.20 152.40 137.80 1124.80 112.40 92.60 84.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 20.80	1.90 2.00 2.16 2.36 2.59 2.83 3.07 3.27 3.45 3.57 3.63 3.63 3.56 3.43 3.23 2.98 2.70 2.38 2.05 1.72 1.40 0.84 0.62 0.43
0.78	1.94 2.13 2.37 2.63 2.89 3.15 3.36 3.53 3.65 3.69 3.58 3.42 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	185.80 168.20 152.40 137.80 124.80 113.00 102.40 92.60 84.00 76.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90 17.12	1.98 2.10 2.28 2.50 2.76 3.03 3.30 3.55 3.77 3.92 4.01 4.01 3.78 3.54 3.24 2.89 2.51 1.73 1.36 1.03 0.75 0.51	185.80 168.20 152.40 137.80 124.80 113.00 102.40 92.60 84.00 76.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90	2.00 2.16 2.36 2.36 2.59 2.83 3.07 3.27 3.45 3.57 3.63 3.63 3.63 3.23 2.98 2.70 2.38 2.05 1.72 1.40 1.11 0.84 0.62 0.43
0.86	2.13 2.37 2.63 2.89 3.15 3.36 3.53 3.65 3.69 3.67 3.58 3.42 3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	168.20 152.40 152.40 137.80 124.80 113.00 102.40 92.60 84.00 76.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 31.40 31.00 28.20 25.40 23.00 20.80 18.90 17.12	2.10 2.28 2.50 2.76 3.03 3.30 3.55 3.77 3.92 4.01 4.01 4.01 3.94 3.78 3.54 2.89 2.51 2.11 1.73 1.36 1.03 0.75 0.51	168.20 152.40 137.80 124.80 113.00 102.40 92.60 84.00 76.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80	2.16 2.36 2.59 2.83 3.07 3.27 3.45 3.63 3.63 3.56 3.43 3.23 2.98 2.70 2.38 2.05 1.72 1.40 0.84 0.62 0.43
0.94	2.37 2.63 2.89 3.15 3.36 3.53 3.65 3.69 3.67 3.58 3.42 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00 0.00	152.40 137.80 124.80 113.00 102.40 92.60 84.00 76.00 68.80 62.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90 17.12	2.28 2.50 2.76 3.03 3.30 3.55 3.77 3.92 4.01 4.01 3.94 3.78 3.54 2.89 2.51 1.73 1.36 1.03 0.75 0.51	152.40 137.80 124.80 113.00 102.40 92.60 84.00 76.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90	2.36 2.59 2.83 3.07 3.27 3.45 3.57 3.63 3.63 3.56 3.43 3.23 2.98 2.70 2.38 2.05 1.72 1.40 0.84 0.62 0.43
1.04	2.63 2.89 3.15 3.36 3.53 3.65 3.69 3.67 3.58 3.42 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	137.80 124.80 113.00 102.40 92.60 84.00 76.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90 17.12 15.50 14.02	2.50 2.76 3.03 3.30 3.55 3.77 3.92 4.01 4.01 3.94 3.78 3.54 2.89 2.51 1.73 1.36 1.03 0.75 0.51 0.33	137.80 124.80 113.00 102.40 92.60 84.00 76.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90	2.59 2.83 3.07 3.27 3.45 3.57 3.63 3.63 3.56 3.43 3.23 2.98 2.70 2.38 2.05 1.72 1.40 1.11 0.84 0.62 0.43
1.26	3.15 3.36 3.53 3.65 3.69 3.67 3.58 3.42 3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	113.00 102.40 92.60 84.00 76.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90 17.12 15.50	3.03 3.30 3.55 3.77 3.92 4.01 4.01 3.94 3.78 3.54 2.89 2.51 1.73 1.36 1.03 0.75 0.51	113.00 102.40 92.60 84.00 76.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90	3.07 3.27 3.45 3.57 3.63 3.63 3.56 3.43 2.98 2.70 2.38 2.05 1.72 1.40 1.11 0.84 0.62 0.43
1.38	3.36 3.53 3.69 3.69 3.67 3.58 3.42 3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	102.40 92.60 84.00 76.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 18.90 17.12 15.50 14.02	3.30 3.55 3.77 3.92 4.01 3.94 3.78 3.54 3.24 2.89 2.51 2.11 1.73 1.36 1.03 0.75 0.51 0.33	102.40 92.60 84.00 76.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90	3.27 3.45 3.57 3.63 3.63 3.56 3.43 3.23 2.98 2.70 2.38 2.05 1.72 1.40 1.11 0.84 0.62 0.43
1.52         0.13         92.60         3.26         92.60           1.67         0.15         84.00         3.30         84.00           1.84         0.18         76.00         3.29         76.00           2.02         0.22         68.80         3.22         68.80           2.22         0.28         62.20         3.09         62.20           2.44         0.34         56.40         2.92         56.40           2.96         0.52         46.20         2.46         46.20           3.24         0.62         41.80         2.20         41.80           3.56         0.74         37.80         1.91         37.80           3.92         0.87         34.40         1.63         34.40           4.32         1.00         31.00         1.36         31.00           4.74         1.14         28.20         1.10         28.20           5.72         1.29         25.40         0.86         25.40           5.74         1.44         23.00         0.65         23.00           6.94         1.76         18.90         0.33         18.90           7.62         1.93         17.12	3.53 3.65 3.69 3.67 3.58 3.42 3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	92.60 84.00 76.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90 17.12	3.55 3.77 3.92 4.01 4.01 3.94 3.78 3.54 2.89 2.51 2.11 1.73 1.36 1.03 0.75 0.51 0.33	92.60 84.00 76.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80	3.45 3.57 3.63 3.63 3.56 3.43 3.23 2.98 2.70 2.38 2.05 1.72 1.40 0.84 0.62
1.67         0.15         84.00         3.30         84.00           1.84         0.18         76.00         3.29         76.00           2.02         0.22         68.80         3.22         68.80           2.22         0.28         62.20         3.09         62.20           2.44         0.34         56.40         2.92         56.40           2.68         0.42         51.00         2.71         51.00           2.96         0.52         46.20         2.46         46.20           3.24         0.62         41.80         2.20         41.80           3.56         0.74         37.80         1.91         37.80           3.92         0.87         34.40         1.63         34.40           4.32         1.00         31.00         1.36         31.00           4.74         1.14         28.20         1.10         28.20           5.72         1.29         25.40         0.86         25.40           5.74         1.44         23.00         0.65         23.00           6.30         1.60         20.80         0.48         20.80           6.94         1.76         18.90	3.65 3.69 3.67 3.58 3.42 3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	84.00 76.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90 17.12 15.50 14.02	3.77 3.92 4.01 4.01 3.94 3.78 3.54 2.89 2.51 1.73 1.36 1.03 0.75 0.51 0.33	84.00 76.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90	3.57 3.63 3.63 3.56 3.43 2.98 2.70 2.38 2.05 1.72 1.40 1.11 0.84 0.62 0.43
1.84	3.69 3.67 3.58 3.42 3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	76.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90 17.12 15.50	3.92 4.01 4.01 3.94 3.78 3.54 2.89 2.51 2.11 1.73 1.36 1.03 0.75 0.51	76.00 68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90	3.63 3.56 3.43 3.23 2.98 2.70 2.38 2.05 1.72 1.40 1.11 0.84 0.62 0.43
2.02         0.22         68.80         3.22         68.80           2.22         0.28         62.20         3.09         62.20           2.44         0.34         56.40         2.92         56.40           2.68         0.42         51.00         2.71         51.00           2.96         0.52         46.20         2.46         46.20           3.24         0.62         41.80         2.20         41.80           3.56         0.74         37.80         1.91         37.80           3.92         0.87         34.40         1.63         31.00           4.32         1.00         31.00         1.36         31.00           4.74         1.14         28.20         1.10         28.20           5.22         1.29         25.40         0.86         25.40           5.74         1.44         23.00         0.65         23.00           6.30         1.60         20.80         0.48         20.80           6.94         1.76         18.90         0.33         18.90           7.62         1.93         17.12         0.22         17.12           8.38         2.12         15.50	3.67 3.58 3.42 3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	68.80 62.20 56.40 51.00 46.20 41.80 37.80 31.40 31.00 28.20 25.40 23.00 20.80 18.90 17.12 15.50	4.01 4.01 3.94 3.78 3.54 2.89 2.51 2.11 1.73 1.36 1.03 0.75 0.51	68.80 62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80	3.63 3.56 3.43 3.23 2.98 2.70 2.38 2.05 1.72 1.40 0.84 0.62 0.43
2.22         0.28         62.20         3.09         62.20           2.44         0.34         56.40         2.92         56.40           2.68         0.42         51.00         2.71         51.00           2.96         0.52         46.20         2.46         46.20           3.24         0.62         41.80         2.20         41.80           3.56         0.74         37.80         1.91         37.80           3.92         0.87         34.40         1.63         34.40           4.32         1.00         31.00         1.36         31.00           4.74         1.14         28.20         1.10         28.20           5.22         1.29         25.40         0.86         25.40           5.74         1.44         23.00         0.65         23.00           6.94         1.76         18.90         0.33         18.90           7.62         1.93         17.12         0.22         17.12           8.38         2.12         15.50         0.14         15.50           9.22         2.33         14.02         0.08         14.22           10.14         2.57         12.70	3.58 3.42 3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90 17.12 15.50 14.02	4.01 3.94 3.78 3.54 2.89 2.51 1.73 1.36 1.03 0.75 0.51	62.20 56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90	3.56 3.43 3.23 2.98 2.70 2.38 2.05 1.72 1.40 1.11 0.84 0.62 0.43
2.44         0.34         56.40         2.92         56.40           2.68         0.42         51.00         2.71         51.00           2.96         0.52         46.20         2.46         46.20           3.24         0.62         41.80         2.20         41.80           3.56         0.74         37.80         1.91         37.80           3.92         0.87         34.40         1.63         34.40           4.32         1.00         31.00         1.36         31.00           4.74         1.14         28.20         1.10         28.20           5.74         1.44         23.00         0.65         23.00           6.30         1.60         20.80         0.48         20.80           6.94         1.76         18.90         0.33         18.90           7.62         1.93         17.12         0.22         17.12           8.38         2.12         15.50         0.14         15.50           9.22         2.33         14.02         0.08         14.02           10.14         2.57         12.70         0.04         12.70           11.16         2.85         11.50	3.42 3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90 17.12 15.50 14.02	3.94 3.78 3.54 3.24 2.89 2.51 2.11 1.73 1.36 1.03 0.75 0.51	56.40 51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90	3.43 3.23 2.98 2.70 2.38 2.05 1.72 1.40 1.11 0.84 0.62 0.43
2.68         0.42         51.00         2.71         51.00         46.20           2.96         0.52         46.20         2.46         46.20         46.20           3.24         0.62         41.80         2.20         41.80           3.56         0.74         37.80         1.91         37.80           3.92         0.87         34.40         1.63         34.40           4.32         1.00         31.00         1.36         31.00           4.74         1.14         28.20         1.10         28.20           5.22         1.29         25.40         0.86         25.40           5.74         1.44         23.00         0.65         23.00           6.30         1.60         20.80         0.48         20.80           6.94         1.76         18.90         0.33         18.90           7.62         1.93         17.12         0.22         17.12           8.38         2.12         15.50         0.14         15.50           10.14         2.57         12.70         0.04         12.70           11.16         2.85         11.50         0.02         11.50           12.26	3.21 2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03	51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90 17.12 15.50	3.78 3.54 3.24 2.89 2.51 1.73 1.36 1.03 0.75 0.51	51.00 46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90	3.23 2.98 2.70 2.38 2.05 1.72 1.40 1.11 0.84 0.62 0.43
2.96         0.52         46.20         2.46         46.20         41.80           3.24         0.62         41.80         2.20         41.80         37.80         1.91         37.80         1.91         37.80         33.40         33.92         0.87         34.40         1.63         34.40         33.40         34.40         1.36         31.00         34.40         1.36         31.00         34.40         1.36         31.00         34.40         1.36         31.00         1.36         31.00         1.36         31.00         1.36         31.00         1.36         31.00         1.36         31.00         1.36         31.00         1.36         31.00         1.36         31.00         1.36         31.00         1.36         31.00         1.36         31.00         1.36         31.00         1.36         31.40         1.63         3.44         1.41         1.72         2.20         1.71         1.12         0.22         17.12         1.26         3.18         31.00         1.36         1.12         1.55         0.14         15.50         0.14         15.50         0.14         15.50         0.14         15.50         0.14         15.50         0.14         15.50         11.10         12.	2.95 2.66 2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90 17.12 15.50	3.54 3.24 2.89 2.51 2.11 1.73 1.36 1.03 0.75 0.51	46.20 41.80 37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90	2.98 2.70 2.38 2.05 1.72 1.40 1.11 0.84 0.62
3.56         0.74         37.80         1.91         37.80           3.92         0.87         34.40         1.63         34.40           4.32         1.00         31.00         1.36         31.00           4.74         1.14         28.20         1.10         28.20           5.22         1.29         25.40         0.86         25.40           5.74         1.44         23.00         0.65         23.00           6.30         1.60         20.80         0.48         20.80           6.94         1.76         18.90         0.33         18.90           7.62         1.93         17.12         0.22         17.12           8.38         2.12         15.50         0.14         15.50           9.22         2.33         14.02         0.08         14.02           10.14         2.57         12.70         0.04         12.70           11.16         2.85         11.50         0.02         11.50           12.26         3.18         10.42         0.01         10.42           13.48         3.55         9.42         0.00         9.42           14.82         3.97         8.54	2.34 2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01	37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90 17.12 15.50 14.02	2.89 2.51 2.11 1.73 1.36 1.03 0.75 0.51	37.80 34.40 31.00 28.20 25.40 23.00 20.80 18.90	2.38 2.05 1.72 1.40 1.11 0.84 0.62 0.43
3.92         0.87         34.40         1.63         34.40           4.32         1.00         31.00         1.36         31.00           4.74         1.14         28.20         1.10         28.20           5.22         1.29         25.40         0.86         25.40           5.74         1.44         23.00         0.65         23.00           6.30         1.60         20.80         0.48         20.80           6.94         1.76         18.90         0.33         18.90           7.62         1.93         17.12         0.22         17.12           8.38         2.12         15.50         0.14         15.50           9.22         2.33         14.02         0.08         14.02           10.14         2.57         12.70         0.04         12.70           11.16         2.85         11.50         0.02         11.50           12.26         3.18         10.42         0.01         10.42           13.48         3.55         9.42         0.00         9.42           14.82         3.97         8.54         0.00         7.72           17.92         4.87         7.00	2.01 1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	34.40 31.00 28.20 25.40 23.00 20.80 18.90 17.12 15.50 14.02	2.51 2.11 1.73 1.36 1.03 0.75 0.51	34.40 31.00 28.20 25.40 23.00 20.80 18.90	2.05 1.72 1.40 1.11 0.84 0.62 0.43
4.32         1.00         31.00         1.36         31.00           4.74         1.14         28.20         1.10         28.20           5.22         1.29         25.40         0.86         25.40           5.74         1.44         23.00         0.65         23.00           6.30         1.60         20.80         0.48         20.80           6.94         1.76         18.90         0.33         18.90           7.62         1.93         17.12         0.22         17.12           8.38         2.12         15.50         0.14         15.50           9.22         2.33         14.02         0.08         14.02           10.14         2.57         12.70         0.04         12.70           11.16         2.85         11.50         0.02         11.50           12.26         3.18         10.42         0.01         10.42           13.48         3.55         9.42         0.00         9.42           14.82         3.97         8.54         0.00         9.42           17.92         4.87         7.00         0.00         7.72           17.92         4.87         7.00	1.69 1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	31.00 28.20 25.40 23.00 20.80 18.90 17.12 15.50	2.11 1.73 1.36 1.03 0.75 0.51	31.00 28.20 25.40 23.00 20.80 18.90	1.72 1.40 1.11 0.84 0.62 0.43
4.74         1.14         28.20         1.10         28.20           5.22         1.29         25.40         0.86         25.40           5.74         1.44         23.00         0.65         25.40           6.30         1.60         20.80         0.48         20.80           6.94         1.76         18.90         0.33         18.90           7.62         1.93         17.12         0.22         17.12           8.38         2.12         15.50         0.14         15.50           9.22         2.33         14.02         0.08         14.02           10.14         2.57         12.70         0.04         12.70           11.16         2.85         11.50         0.02         11.50           12.26         3.18         10.42         0.01         10.42           13.48         3.55         9.42         0.00         9.42           14.82         3.97         8.54         0.00         8.54           16.30         4.41         7.72         0.00         7.72           17.92         4.87         7.00         0.00         7.00           19.72         5.29         6.34	1.38 1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	28.20 25.40 23.00 20.80 18.90 17.12 15.50	1.73 1.36 1.03 0.75 0.51	28.20 25.40 23.00 20.80 18.90	1.40 1.11 0.84 0.62 0.43
5.22         1.29         25.40         0.86         25.40           5.74         1.44         23.00         0.65         23.00           6.30         1.60         20.80         0.48         20.80           6.94         1.76         18.90         0.33         18.90           7.62         1.93         17.12         0.22         17.12           8.38         2.12         15.50         0.14         15.50           9.22         2.33         14.02         0.08         14.02           10.14         2.57         12.70         0.04         12.70           11.16         2.85         11.50         0.02         11.50           12.26         3.18         10.42         0.01         10.42           13.48         3.55         9.42         0.00         9.42           14.82         3.97         8.54         0.00         8.54           16.30         4.41         7.72         0.00         7.72           17.92         4.87         7.00         0.00         7.72           21.60         5.65         5.74         0.00         5.74           23.80         5.89         5.20	1.10 0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00 0.00	25.40 23.00 20.80 18.90 17.12 15.50 14.02	1.36 1.03 0.75 0.51 0.33	25.40 23.00 20.80 18.90	1.11 0.84 0.62 0.43
5.74         1.44         23.00         0.65         23.00           6.30         1.60         20.80         0.48         20.80           6.94         1.76         18.90         0.33         18.90           7.62         1.93         17.12         0.22         17.12           8.38         2.12         15.50         0.14         15.50           9.22         2.33         14.02         0.08         14.02           10.14         2.57         12.70         0.04         12.70           11.16         2.85         11.50         0.02         11.50           12.26         3.18         10.42         0.01         10.42           13.48         3.55         9.42         0.00         9.42           14.82         3.97         8.54         0.00         9.42           14.82         3.97         8.54         0.00         7.72           17.92         4.87         7.700         0.00         7.72           17.92         4.87         7.700         0.00         7.74           21.60         5.65         5.74         0.00         5.74           23.80         5.89         5.20	0.84 0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	23.00 20.80 18.90 17.12 15.50 14.02	1.03 0.75 0.51 0.33	23.00 20.80 18.90	0.84 0.62 0.43
6.30         1.60         20.80         0.48         20.80           6.94         1.76         18.90         0.33         18.90           7.62         1.93         17.12         0.22         17.12           8.38         2.12         15.50         0.14         15.50           9.22         2.33         14.02         0.08         14.02           10.14         2.57         12.70         0.04         12.70           11.16         2.85         11.50         0.02         11.50           12.26         3.18         10.42         0.01         10.42           13.48         3.55         9.42         0.00         9.42           14.82         3.97         8.54         0.00         8.54           16.30         4.41         7.72         0.00         7.72           17.92         4.87         7.00         0.00         7.02           19.72         5.29         6.34         0.00         6.34           21.60         5.65         5.74         0.00         5.74           23.80         5.89         5.20         0.00         5.74           28.80         5.87         4.70	0.63 0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00	20.80 18.90 17.12 15.50 14.02	0.75 0.51 0.33	20.80 18.90	0.62 0.43
6.94         1.76         18.90         0.33         18.90           7.62         1.93         17.12         0.22         17.12           8.38         2.12         15.50         0.14         15.50           9.22         2.33         14.02         0.08         14.02           10.14         2.57         12.70         0.04         12.70           11.16         2.85         11.50         0.02         11.50           12.26         3.18         10.42         0.01         10.42           13.48         3.55         9.42         0.00         9.42           14.82         3.97         8.54         0.00         8.54           16.30         4.41         7.72         0.00         7.72           17.92         4.87         7.00         0.00         7.00           19.72         5.29         6.34         0.00         5.74           21.60         5.65         5.74         0.00         5.74           23.80         5.89         5.20         0.00         5.74           23.80         5.87         4.70         0.00         4.70           28.80         5.87         4.26	0.45 0.30 0.19 0.11 0.06 0.03 0.01 0.00 0.00	18.90 17.12 15.50 14.02	0.51 0.33	18.90	0.43
7.62         1.93         17.12         0.22         17.12           8.38         2.12         15.50         0.14         15.50           9.22         2.233         14.02         0.08         14.02           10.14         2.57         12.70         0.04         12.70           11.16         2.85         11.50         0.02         11.50           12.26         3.18         10.42         0.01         10.42           13.48         3.55         9.42         0.00         9.42           14.82         3.97         8.54         0.00         9.42           16.30         4.41         7.72         0.00         7.72           17.92         4.87         7.00         0.00         7.00           19.72         5.29         6.34         0.00         6.34           21.60         5.65         5.74         0.00         5.74           23.80         5.89         5.20         0.00         4.70           28.80         5.87         4.26         0.00         4.70           28.80         5.87         4.26         0.00         3.50           34.80         5.02         3.50	0.30 0.19 0.11 0.06 0.03 0.01 0.00 0.00	17.12 15.50 14.02	0.33		
8.38         2.12         15.50         0.14         15.50           9.22         2.33         14.02         0.08         14.02           10.14         2.57         12.70         0.04         12.70           11.16         2.85         11.50         0.02         11.50           12.26         3.18         10.42         0.01         10.42           13.48         3.55         9.42         0.00         9.42           14.82         3.97         8.54         0.00         8.54           16.30         4.41         7.72         0.00         7.02           17.92         4.87         7.00         0.00         7.00           19.72         5.29         6.34         0.00         6.34           21.60         5.65         5.74         0.00         5.74           23.80         5.89         5.20         0.00         5.74           26.20         5.97         4.70         0.00         4.70           28.80         5.87         4.26         0.00         3.86           31.60         5.55         3.86         0.00         3.50           34.80         5.02         3.50 <t< td=""><td>0.19 0.11 0.06 0.03 0.01 0.00 0.00</td><td>15.50 14.02</td><td></td><td></td><td></td></t<>	0.19 0.11 0.06 0.03 0.01 0.00 0.00	15.50 14.02			
10.14         2.57         12.70         0.04         12.70           11.16         2.85         11.50         0.02         11.50           12.26         3.18         10.42         0.01         10.42           13.48         3.55         9.42         0.00         9.42           14.82         3.97         8.54         0.00         8.54           16.30         4.41         7.72         0.00         7.02           17.92         4.87         7.00         0.00         7.00           19.72         5.29         6.34         0.00         6.34           21.60         5.65         5.74         0.00         5.74           23.80         5.89         5.20         0.00         5.20           26.20         5.97         4.70         0.00         4.70           28.80         5.87         4.26         0.00         4.26           31.60         5.55         3.86         0.00         3.86           34.80         5.02         3.50         0.00         3.50           38.40         4.32         3.16         0.00         3.16           42.20         3.49         2.86	0.06 0.03 0.01 0.00		0.20	15.50	0.18
11.16         2.85         11.50         0.02         11.50           12.26         3.18         10.42         0.01         10.42           13.48         3.55         9.42         0.00         9.42           14.82         3.97         8.54         0.00         8.54           16.30         4.41         7.72         0.00         7.72           17.92         4.87         7.00         0.00         7.00           19.72         5.29         6.34         0.00         6.34           21.60         5.65         5.74         0.00         5.74           23.80         5.89         5.20         0.00         5.74           26.20         5.97         4.70         0.00         4.70           28.80         5.87         4.26         0.00         4.26           31.60         5.55         3.86         0.00         3.86           34.80         5.02         3.50         0.00         3.50           38.40         4.32         3.16         0.00         3.50           38.40         2.61         2.60         0.00         2.60           46.40         2.61         2.60         0.	0.03 0.01 0.00 0.00	12.70	0.11	14.02	0.10
12.26         3.18         10.42         0.01         10.42           13.48         3.55         9.42         0.00         9.42           14.82         3.97         8.54         0.00         8.54           16.30         4.41         7.72         0.00         7.72           17.92         4.87         7.00         0.00         7.00           19.72         5.29         6.34         0.00         6.34           21.60         5.65         5.74         0.00         5.74           23.80         5.89         5.20         0.00         5.20           26.20         5.97         4.70         0.00         4.70           28.80         5.87         4.26         0.00         4.26           31.60         5.55         3.86         0.00         3.86           34.80         5.02         3.50         0.00         3.50           38.40         4.32         3.16         0.00         3.16           42.20         3.49         2.86         0.00         2.86           46.40         2.61         2.60         0.00         2.34           46.40         2.61         2.60         0.00	0.01 0.00 0.00	12.70	0.05	12.70	0.05
13.48         3.55         9.42         0.00         9.42           14.82         3.97         8.54         0.00         8.54           16.30         4.41         7.72         0.00         7.72           17.92         4.87         7.00         0.00         7.00           19.72         5.29         6.34         0.00         6.34           21.60         5.65         5.74         0.00         5.74           23.80         5.89         5.20         0.00         5.20           26.20         5.97         4.70         0.00         4.76           28.80         5.87         4.26         0.00         4.26           31.60         5.55         3.86         0.00         3.86           34.80         5.02         3.50         0.00         3.50           38.40         4.32         3.16         0.00         3.16           42.20         3.49         2.86         0.00         2.86           46.40         2.61         2.60         0.00         2.34           56.00         1.06         2.12         0.00         2.12           67.80         0.21         1.74         0.00 </td <td>0.00</td> <td>11.50</td> <td>0.02</td> <td>11.50</td> <td>0.02</td>	0.00	11.50	0.02	11.50	0.02
14.82         3.97         8.54         0.00         8.54           16.30         4.41         7.72         0.00         7.72           17.92         4.87         7.00         0.00         7.00           19.72         5.29         6.34         0.00         6.34           21.60         5.65         5.74         0.00         5.74           23.80         5.89         5.20         0.00         5.20           26.20         5.97         4.70         0.00         4.70           28.80         5.87         4.26         0.00         4.26           31.60         5.55         3.86         0.00         3.86           34.80         5.02         3.50         0.00         3.50           38.40         4.32         3.16         0.00         3.50           46.40         2.61         2.60         0.00         2.60           46.40         2.61         2.60         0.00         2.60           51.00         1.07         2.34         0.00         2.12           61.60         0.53         1.92         0.00         1.92           67.80         0.21         1.74         0.00 </td <td>0.00</td> <td>10.42</td> <td>0.01</td> <td>10.42</td> <td>0.01</td>	0.00	10.42	0.01	10.42	0.01
16.30         4.41         7.72         0.00         7.72           17.92         4.87         7.00         0.00         7.00           19.72         5.29         6.34         0.00         6.34           21.60         5.65         5.74         0.00         5.74           23.80         5.89         5.20         0.00         5.20           26.20         5.97         4.70         0.00         4.70           28.80         5.87         4.26         0.00         4.26           31.60         5.55         3.86         0.00         3.50           34.80         5.02         3.50         0.00         3.16           42.20         3.49         2.86         0.00         3.16           42.20         3.49         2.86         0.00         2.66           46.40         2.61         2.60         0.00         2.34           56.00         1.06         2.12         0.00         2.34           56.00         1.06         2.12         0.00         2.12           67.80         0.21         1.74         0.00         1.58           74.40         0.06         1.58         0.00 </td <td></td> <td>9.42</td> <td>0.00</td> <td>9.42</td> <td>0.00</td>		9.42	0.00	9.42	0.00
17.92         4.87         7.00         0.00         7.00           19.72         5.29         6.34         0.00         6.34           21.60         5.65         5.74         0.00         5.74           23.80         5.89         5.20         0.00         5.20           26.20         5.97         4.70         0.00         4.70           28.80         5.87         4.26         0.00         4.26           31.60         5.55         3.86         0.00         3.86           34.80         5.02         3.50         0.00         3.16           42.20         3.49         2.86         0.00         2.86           46.40         2.61         2.60         0.00         2.60           51.00         1.77         2.34         0.00         2.12           56.00         1.06         2.12         0.00         2.12           67.80         0.21         1.74         0.00         1.74           74.40         0.06         1.58         0.00         1.58           82.00         0.01         1.43         0.00         1.43           99.00         0.00         1.17         0.00 </td <td>0.00</td> <td>8.54</td> <td>0.00</td> <td>8.54</td> <td>0.00</td>	0.00	8.54	0.00	8.54	0.00
19.72         5.29         6.34         0.00         6.34           21.60         5.65         5.74         0.00         5.74           23.80         5.89         5.20         0.00         5.20           26.20         5.97         4.70         0.00         4.70           28.80         5.87         4.26         0.00         4.26           31.60         5.55         3.86         0.00         3.86           34.80         5.02         3.50         0.00         3.50           38.40         4.32         3.16         0.00         3.16           42.20         3.49         2.86         0.00         2.86           46.40         2.61         2.60         0.00         2.60           51.00         1.77         2.34         0.00         2.34           56.00         1.06         2.12         0.00         1.92           67.80         0.21         1.74         0.00         1.74           74.40         0.06         1.58         0.00         1.58           82.00         0.01         1.43         0.00         1.43           99.00         0.00         1.17         0.00 </td <td></td> <td>7.72 7.00</td> <td>0.00</td> <td>7.72</td> <td>0.00</td>		7.72 7.00	0.00	7.72	0.00
21.60         5.65         5.74         0.00         5.74           23.80         5.89         5.20         0.00         5.20           26.20         5.97         4.70         0.00         4.70           28.80         5.87         4.26         0.00         4.26           31.60         5.55         3.86         0.00         3.86           34.80         5.02         3.50         0.00         3.16           42.20         3.49         2.86         0.00         2.86           46.40         2.61         2.60         0.00         2.34           56.00         1.06         2.12         0.00         2.12           61.60         0.53         1.92         0.00         1.92           67.80         0.21         1.74         0.00         1.58           82.00         0.01         1.43         0.00         1.43           99.00         0.00         1.17         0.00         1.29           99.00         0.00         1.17         0.00         1.29           119.80         0.00         0.87         0.01         0.87           144.80         0.00         0.71         0.01	0.00	6.34	0.00	7.00 6.34	0.00
23.80         5.89         5.20         0.00         5.20           26.20         5.97         4.70         0.00         4.70           28.80         5.87         4.26         0.00         4.26           31.60         5.55         3.86         0.00         3.86           34.80         5.02         3.50         0.00         3.50           38.40         4.32         3.16         0.00         2.86           46.40         2.61         2.60         0.00         2.60           51.00         1.77         2.34         0.00         2.34           556.00         1.06         2.12         0.00         2.12           67.80         0.21         1.74         0.00         1.74           74.40         0.06         1.58         0.00         1.58           82.00         0.01         1.43         0.00         1.43           99.00         0.00         1.17         0.00         1.79           109.00         0.00         1.17         0.00         1.79           119.80         0.00         0.96         0.01         0.96           131.60         0.00         0.79         0.	0.00	5.74	0.00	5.74	0.00
26.20         5.97         4.70         0.00         4.70           28.80         5.87         4.26         0.00         4.26           31.60         5.55         3.86         0.00         3.86           34.80         5.02         3.50         0.00         3.50           38.40         4.32         3.16         0.00         3.16           42.20         3.49         2.86         0.00         2.86           46.40         2.61         2.60         0.00         2.60           51.00         1.77         2.34         0.00         2.12           66.00         1.06         2.12         0.00         1.92           67.80         0.21         1.74         0.00         1.74           74.40         0.06         1.58         0.00         1.58           82.00         0.01         1.43         0.00         1.43           99.00         0.00         1.17         0.00         1.17           109.00         0.00         1.17         0.00         1.17           109.00         0.00         1.17         0.00         1.29           99.01         0.00         1.17         0.00	0.00	5.20	0.00	5.20	0.00
28.80         5.87         4.26         0.00         4.26           31.60         5.55         3.86         0.00         3.86           34.80         5.02         3.50         0.00         3.50           38.40         4.32         3.16         0.00         3.16           42.20         3.49         2.86         0.00         2.86           46.40         2.61         2.60         0.00         2.34           56.00         1.77         2.34         0.00         2.34           56.00         1.06         2.12         0.00         2.12           61.60         0.53         1.92         0.00         1.92           67.80         0.21         1.74         0.00         1.74           74.40         0.06         1.58         0.00         1.58           82.00         0.01         1.43         0.00         1.58           82.00         0.00         1.29         0.00         1.29           99.00         0.00         1.17         0.00         1.17           109.00         0.00         1.17         0.00         1.17           109.00         0.00         0.87         0.01	0.00	4.70	0.00	4.70	0.00
34.80         5.02         3.50         0.00         3.50           38.40         4.32         3.16         0.00         3.16           42.20         3.49         2.86         0.00         2.86           46.40         2.61         2.60         0.00         2.60           51.00         1.77         2.34         0.00         2.34           56.00         1.06         2.12         0.00         1.92           61.60         0.53         1.92         0.00         1.92           67.80         0.21         1.74         0.00         1.74           74.40         0.06         1.58         0.00         1.58           82.00         0.01         1.43         0.00         1.43           90.00         0.00         1.29         0.00         1.29           99.00         0.00         1.17         0.00         1.17           109.00         0.00         1.06         0.01         1.06           119.80         0.00         0.96         0.01         0.96           131.60         0.00         0.79         0.01         0.79           144.80         0.00         0.71         0.	0.00	4.26	0.00	4.26	0.00
38.40         4.32         3.16         0.00         3.16           42.20         3.49         2.86         0.00         2.86           46.40         2.61         2.60         0.00         2.60           51.00         1.77         2.34         0.00         2.34           56.00         1.06         2.12         0.00         2.12           61.60         0.53         1.92         0.00         1.92           67.80         0.21         1.74         0.00         1.74           74.40         0.06         1.58         0.00         1.58           82.00         0.01         1.43         0.00         1.43           90.00         0.00         1.29         0.00         1.29           99.00         0.00         1.17         0.00         1.17           109.00         0.00         1.06         0.01         1.06           119.80         0.00         0.87         0.01         0.96           131.60         0.00         0.87         0.01         0.87           144.80         0.00         0.79         0.01         0.71	0.00	3.86	0.00	3.86	0.00
42.20         3.49         2.86         0.00         2.86           46.40         2.61         2.60         0.00         2.60           51.00         1.77         2.34         0.00         2.34           55.00         1.06         2.12         0.00         2.12           61.60         0.53         1.92         0.00         1.92           67.80         0.21         1.74         0.00         1.74           74.40         0.06         1.58         0.00         1.58           82.00         0.01         1.43         0.00         1.43           99.00         0.00         1.17         0.00         1.17           109.00         0.00         1.17         0.00         1.17           109.00         0.00         0.01         1.06         0.01         1.06           119.80         0.00         0.96         0.01         0.96         0.13         0.87           131.60         0.00         0.79         0.01         0.79         144.80         0.00         0.71         0.01         0.71	0.00	3.50	0.00	3.50	0.00
46.40         2.61         2.60         0.00         2.60           51.00         1.77         2.34         0.00         2.34           56.00         1.06         2.12         0.00         2.12           61.60         0.53         1.92         0.00         1.92           67.80         0.21         1.74         0.00         1.74           74.40         0.06         1.58         0.00         1.58           82.00         0.01         1.43         0.00         1.43           90.00         0.00         1.29         0.00         1.29           99.00         0.00         1.17         0.00         1.17           109.00         0.00         1.06         0.01         1.06           119.80         0.00         0.96         0.01         0.96           131.60         0.00         0.87         0.01         0.87           144.80         0.00         0.71         0.01         0.71	0.00	3.16	0.00	3.16	0.00
51.00         1.77         2.34         0.00         2.34           56.00         1.06         2.12         0.00         2.12           61.60         0.53         1.92         0.00         1.92           67.80         0.21         1.74         0.00         1.74           74.40         0.06         1.58         0.00         1.58           82.00         0.01         1.43         0.00         1.43           90.00         0.00         1.29         0.00         1.29           99.00         0.00         1.17         0.00         1.17           109.00         0.00         1.06         0.01         1.06           119.80         0.00         0.96         0.01         0.96           131.60         0.00         0.87         0.01         0.87           144.80         0.00         0.71         0.01         0.71	0.00	2.86	0.00	2.86	0.00
56.00         1.06         2.12         0.00         2.12           61.60         0.53         1.92         0.00         1.92           67.80         0.21         1.74         0.00         1.74           74.40         0.06         1.58         0.00         1.58           82.00         0.01         1.43         0.00         1.43           90.00         0.00         1.29         0.00         1.29           99.00         0.00         1.17         0.00         1.17           109.00         0.00         1.06         0.01         1.06           119.80         0.00         0.96         0.01         0.96           131.60         0.00         0.87         0.01         0.87           144.80         0.00         0.79         0.01         0.79           155.20         0.00         0.71         0.01         0.71	0.00	2.60	0.00	2.60	0.00
61.60         0.53         1.92         0.00         1.92           67.80         0.21         1.74         0.00         1.74           74.40         0.06         1.58         0.00         1.58           82.00         0.01         1.43         0.00         1.43           90.00         0.00         1.29         0.00         1.29           99.00         0.00         1.17         0.00         1.17           109.00         0.00         1.06         0.01         1.06           119.80         0.00         0.96         0.01         0.96           131.60         0.00         0.87         0.01         0.87           144.80         0.00         0.79         0.01         0.79           159.20         0.00         0.71         0.01         0.71	0.00	2.34	0.00	2.34	0.00
67.80         0.21         1.74         0.00         1.74           74.40         0.06         1.58         0.00         1.58           82.00         0.01         1.43         0.00         1.43           90.00         0.00         1.29         0.00         1.29           99.00         0.00         1.17         0.00         1.17           109.00         0.00         1.06         0.01         1.06           119.80         0.00         0.96         0.01         0.96           131.60         0.00         0.87         0.01         0.87           144.80         0.00         0.79         0.01         0.79           159.20         0.00         0.71         0.01         0.71	0.00	1.92	0.00	1.92	0.00
74.40         0.06         1.58         0.00         1.58           82.00         0.01         1.43         0.00         1.43           90.00         0.00         1.29         0.00         1.29           99.00         0.00         1.17         0.00         1.17           109.00         0.00         1.06         0.01         1.06           119.80         0.00         0.96         0.01         0.96           131.60         0.00         0.87         0.01         0.87           144.80         0.00         0.79         0.01         0.79           159.20         0.00         0.71         0.01         0.71	0.00	1.74	0.00	1.74	0.00
90.00         0.00         1.29         0.00         1.29           99.00         0.00         1.17         0.00         1.17           109.00         0.00         1.06         0.01         1.06           119.80         0.00         0.96         0.01         0.96           131.60         0.00         0.87         0.01         0.87           144.80         0.00         0.79         0.01         0.79           159.20         0.00         0.71         0.01         0.71	0.00	1.58	0.01	1.58	0.00
99.00         0.00         1.17         0.00         1.17           109.00         0.00         1.06         0.01         1.06           119.80         0.00         0.96         0.01         0.96           131.60         0.00         0.87         0.01         0.87           144.80         0.00         0.79         0.01         0.79           159.20         0.00         0.71         0.01         0.71	0.00	1.43	0.01	1.43	0.00
109.00     0.00     1.06     0.01     1.06       119.80     0.00     0.96     0.01     0.96       131.60     0.00     0.87     0.01     0.87       144.80     0.00     0.79     0.01     0.79       159.20     0.00     0.71     0.01     0.71	0.00	1.29	0.01	1.29	0.01
119.80     0.00     0.96     0.01     0.96       131.60     0.00     0.87     0.01     0.87       144.80     0.00     0.79     0.01     0.79       159.20     0.00     0.71     0.01     0.71	0.01	1.17	0.01	1.17	0.01
131.60     0.00     0.87     0.01     0.87       144.80     0.00     0.79     0.01     0.79       159.20     0.00     0.71     0.01     0.71	0.01	1.06	0.01	1.06	0.01
144.80     0.00     0.79     0.01     0.79       159.20     0.00     0.71     0.01     0.71	0.01	0.96	0.01	0.96	0.01
159.20 0.00 0.71 0.01 0.71	0.01	0.87	0.01	0.87	0.01
	0.01	0.71	0.01	0.79	0.01
175.00 0.00 0.64 0.01 0.64	0.01	0.64	0.01	0.64	0.01
192.60 0.00 0.58 0.01 0.58	0.01	0.58	0.01	0.58	0.01
212.00 0.00 0.53 0.01 0.53	0.01	0.53	0.01	0.53	0.01
232.00 0.00 0.48 0.01 0.48	0.01	0.48	0.01	0.48	0.01
256.00 0.00 0.43 0.00 0.43	0.01	0.43	0.01	0.43	0.01
282.00 0.00 0.39 0.00 0.39	0.01	0.39	0.00	0.39	0.00
310.00 0.00 0.36 0.00 0.36	0.00	0.36	0.00	0.36	0.00
340.00 0.00 0.32 0.00 0.32 374.00 0.00 0.39 0.00 0.39	0.00	0.32	0.00	0.32	0.00
374.00 0.00 0.29 0.00 0.29	0.00	0.29	0.00	0.29	0.00
412.00     0.00     0.26     0.00     0.26       452.00     0.00     0.24     0.00     0.24	0.00	0.26	0.00	0.26 0.24	0.00
452.00 0.00 0.24 0.00 0.24 498.00 0.00 0.22 0.00 0.22		0.24	0.00	0.24	0.00
548.00 0.00 0.20 0.00 0.20 0.20	(7,116)		0.00	0.22	0.00
602.00 0.00 0.18 0.00 0.18	0.00	0.20	0.00	0.18	0.00
662.00 0.00 0.16 0.00 0.16	0.00	0.20		0.16	0.00
728.00 0.00 0.15 0.00 0.15		0.20 0.18 0.16	0.00	0.15	0.00
800.00 0.00 0.13 0.00 0.13	0.00	0.18	0.00		0.00
880.00 0.00 0.12 0.00 0.12	0.00 0.00 0.00	0.18 0.16		0.13	0.00
968.00 0.00 0.11 0.00 0.11	0.00 0.00 0.00 0.00 0.00	0.18 0.16 0.15 0.13 0.12	0.00 0.00 0.00	0.12	
99.98 0.10 0.00 0.10	0.00 0.00 0.00 0.00	0.18 0.16 0.15 0.13	0.00		0.00





#### Appendix 4: X-Ray Fluorescence

VSCHT PRAHA

INSTITUTE OF CHEMICAL TECHNOLOGY

TECHNICKA 5

CZ-16628-PRAHA Fax:0042-2-3116109

2013-09-18 \uq4\Job\JOB.598 Keppert GR2/N 0.8g,f

ARL 9400 Rh 60kV LiF200 LiF220 Ge111 TlAP

\uq4\ASC\Kdata.asc 2001-05-15 ..\ChData.asc 2010-02-01

Calculated as : Elements Matrix (Shape & ImpFc) : 4 Ca..
X-ray path = Vacuum Film type = 2 PP 4mikr

Case number = 0 Known Mass, Area, Rest, Dilution Eff.Diam. = 25.0 mm Eff.Area = 490.6 mm2

KnownConc = 0 용

90 Rest = 0 Viewed Mass = 432.526

Dil/Sample = 0Sample Height = 0.80 mm

•			the concent < 2 StdErr.				0 %
sum	<ze ille<="" th=""><th>alls wto</th><th>&lt; 2 Stuerr.</th><th>A + OI</th><th>&amp; means:</th><th>Part OI 10</th><th>U To</th></ze>	alls wto	< 2 Stuerr.	A + OI	& means:	Part OI 10	U To
Z	wt%	StdErr	Z	wt%	StdErr	Z	wt%
StdErr	0 0	230211	_		200211	_	
			========		======		
======							
			29+Cu	0.305	0.028	52 Te	<
11+Na	0.550	0.037	30+Zn	0.673	0.041	53 I	<
12+Mg	2.81	0.08	31 Ga	<2e	0.0018	55 Cs	<
13+Al	9.61	0.15	32 Ge	<		56+Ba	
0.191	0.025						
14+Si	12.07	0.16	33 As	<		SumLaLu	0
0.11							
15 P			34 Se	<		72 Hf	<
15+Px	11.63	0.16	35+Br	0.0341	0.0092	73 Ta	<
16 Sx			37 Rb	<		74 W	<
16+S	6.27	0.12	38+Sr	0.126	0.018	75 Re	<
17+Cl	0.742	0.043	39 Y	<		76 Os	<
18+Ar	<		40+Zr	0.041	0.010	77 Ir	<
19+K	2.34	0.08	41+Nb	0.0243	0.0078	78+Pt	<
20+Ca	41.75	0.25	42 Mo	<		79 Au	<
21 Sc	<		44 Ru	<		80 Hg	<2e
0.0037							
22+Ti	1.59	0.06	45 Rh	<		81+Tl	<
23+V	0.0291	0.0085	46+Pd	<		82+Pb	
0.115	0.017						
24+Cr	0.138	0.019	47 Ag	<		83 Bi	<
25+Mn	0.182	0.021	48 Cd	<		90 Th	<
26+Fe	8.71	0.14	49 In	<		92 U	<
27+Co	0.0102	0.0051	50 Sn	<		94 Pu	<
28+Ni	0.055	0.012	51 Sb	<		95 Am	<
==== T.i	ght Element	9 =====	==== Noble	Element	ts =====	====	
	ides =====		NODIC	птешен			
SumBe		0	44 Ru	<		57 La	<
4 Be		O	45 Rh	<		58 Ce	<
5 B			46+Pd	<		59 Pr	<
6 C			47 Ag	<		60 Nd	<
7 N			75 Re	<		62 Sm	<
8 0			76 Os	<		63 Eu	<
9 F			70 05 77 Ir	<		64 Gd	<
<i>→</i> ±			, ,	•		01 00	`

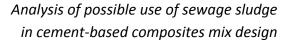




# Analysis of possible use of sewage sludge in cement-based composites mix design

78+Pt	<	65 Tb <
79 Au	<	66 Dy <
		67 Ho <
		68+Er <
		69 Tm <
		70 Yb <
		71 Lu <

Sum Conc's before normalisation to 100%: 45.3 %







VSCHT PRAHA INSTITUTE OF CHEMICAL TECHNOLOGY TECHNICKA 5

Fax:0042-2-3116109

\uq4\Job\JOB.598 2013-09-18 GR2/N 0.8g,f Keppert

ARL 9400 Rh 60kV LiF200 LiF220 Ge111 TlAP

CZ-16628-PRAHA

\uq4\ASC\Kdata.asc 2001-05-15 ..\ChData.asc 2010-02-01

Calculated as : Oxides Matrix (Shape & ImpFc) : 4 Ca.. X-ray path = Vacuum Film type = 2 PP 4mikr

Case number = 0 Known Mass, Area, Rest, Dilution Eff.Diam. = 25.0 mm

KnownConc = 0 % Eff.Area = 490.6 mm2

= 0 양 Viewed Mass = 432.526Rest

Dil/Sample Sample Height = 0.80 mm

Dil/Sample	= 0			S	Sample He	ight = 0.80	mm
			the concent				
	<2e mea	ans wt% <	<pre>&lt; 2 StdErr.</pre>	A + or	& means:	Part of 10	0%
sum							
Z	wt% S	StdErr	Z	wt%	StdErr	Z	wt
StdErr							
=======	=======	======	========	======	======		
=======	=======	======					
			29+CuO	0.181	0.021	52 TeO2	<
11+Na2O	0.583	0.038	30+ZnO	0.397	0.031	53 I	<
12+MgO	3.49	0.09	31 Ga203	<2e	0.0011	55 Cs20	<
	13.20	0.17	32 GeO2	<		56+BaO	
0.107 0.							
14+SiO2	17.81	0.19	33 As203	<		SumLaLu	0
0.065							
15 P			34 SeO2	<		72 HfO2	<
15+P2O5	17.40	0.19	35+Br	0.0161	0.0063	73 Ta205	<
16 SO3			37 Rb20	<		74 WO3	<
16+S	3.91	0.10	38+SrO	0.073	0.013	75 Re207	<
17+Cl	0.449	0.033	39 Y2O3	<		76 OsO4	<
18+Ar	<		40+ZrO2	0.0287	0.0085	77 IrO2	<
19+K2O	1.66	0.06	41+Nb2O5	0.0201	0.0071	78 PtO2	<
20+CaO	32.86	0.23	42 MoO3	<		79 Au	<
21 Sc203	<		44 RuO4	<		80 HgO	<
22+TiO2	1.34	0.06	45 Rh2O3	<		81+T12O3	<
23+V2O5	0.0262	0.0081	46+PdO	<		82+Pb0	
0.059 0.	012						
24+Cr2O3	0.101	0.016	47 Ag20	<		83 Bi2O3	<
25+MnO	0.116	0.017	48 CdO	<		90 ThO2	<
26+Fe2O3	6.13		49 In2O3	<		92 U308	<
	0.0071			<		94 PuO2	<
	0.0332		51 Sb203	<		95 Am2O3	<
2011120	0.0002	0.0031	01 00200	•		30 IMIL 00	`
==== Light	Elements	s =====	==== Noble	Element	s =====	=====	
Lanthanide			1.0220				
SumBeF	0	0	44 RuO4	<		57 La203	<
4 BeO	Ü	Ü	45 Rh203	<		58 CeO2	<
5 B2O3			46+PdO	<		59 Pr6011	<
6 CO2			47 Ag20	<		60 Nd2O3	<
7 N			75 Re207	<		62 Sm2O3	<
7 N 8 O			76 OsO4	<		63 Eu203	<
9 F			70 OSO4 77 IrO2	<		64 Gd203	<
Э E			78 PtO2	<		65 Tb407	<
			78 PtO2 79 Au	<			<
			19 Au			66 Dy2O3	

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# Analysis of possible use of sewage sludge in cement-based composites mix design

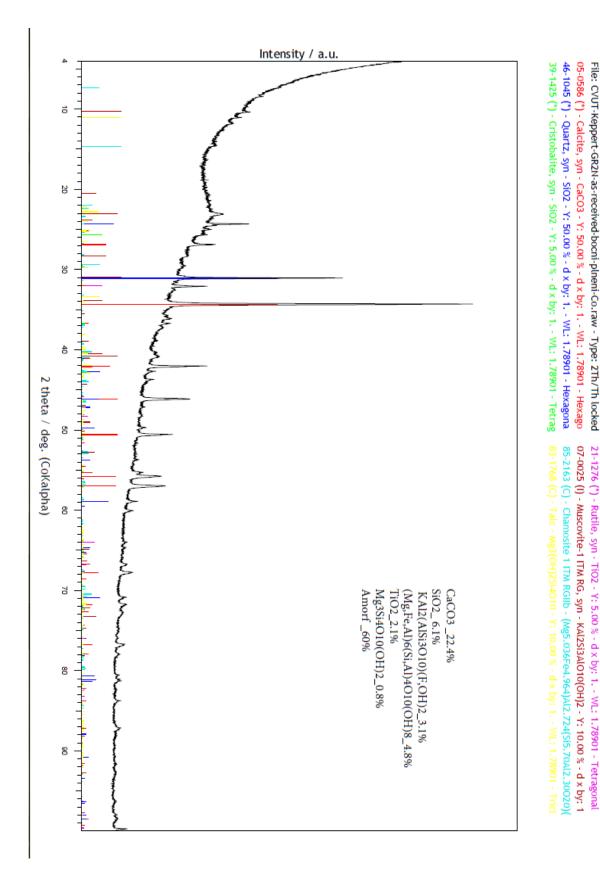
67 Ho2O3 < 68+Er2O3 < 69 Tm2O3 < 70 Yb2O3 < 71 Lu2O3 <

Sum Conc's before normalisation to 100% :  $\,$  57.4 %





#### Appendix 5: X-Ray Diffraction







## Appendix 6: Design and making cement samples

CEMENT SAMPLES DESIGN								
Sewage sludge content about cement weight	Cement (gr)	Sludge(gr)	H20 (ml)	Water/binder				
REFERENCE: 0%	1800	0	720	0.4				
10%	1620	180	720	0.4				
20%	1440	360	720	0.4				
30%	1260	540	720	0.4				
40%	1080	720	720	0.4				
30%	1008	432	576	0.4				
40%	864	576	576	0.4				

CEMENT SAMPLES DESIGN						
Component	Sample	Volume (cm³)	Matrix Density (gr/cm³)	Weight (gr)	% weight total	%volume total
Cement	Reference	600	3	1800	71%	45%
	10%	540		1620	64%	41%
	20%	480		1440	57%	36%
	30%	336		1008	50%	32%
	40%	288		864	43%	27%
Sewage sludge	Reference	0	2.87	0	0%	0%
	10%	62.72		180	7%	5%
	20%	125.44		360	14%	9%
	30%	150.52		432	21%	14%
	40%	200.70		576	29%	19%
H2O	Reference	720	1	720	29%	55%
	10%	720		720	29%	54%
	20%	720		720	29%	54%
	30%	576		576	29%	54%
	40%	576		576	29%	54%