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Recovery of metals from MSW fly ash by leaching and liquid-liquid extraction

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To you, Mamã

Abstract

One way to treat the garbage produced in households and enterprises is to incinerate it. However, even though giving a significant reduction of waste volume to be landfilled, this procedure leads to the production of residues which can contain heavy metals. Those metals, if leached, can be harmful to the environment and it is necessary to prevent their release from the ash. One way to do that is to extract the metals from the ash before it is land filled.

In the thesis, leaching and liquid-liquid extraction was used to recover Cu from the ash. Two different leaching methods were analysed and compared. The difference in the methods was the leaching agent. In one method, ammonium nitrate was used, while in the other, the leaching liquid was nitric acid.

The results in the leaching step showed that the acid leaching method recovered more Cu than the ammonium nitrate leaching method, but it is possible to say that both methods can remove Cu from the fly ashes with a substantial yield.

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1. Introduction

1.1. History of the garbage

Since the beginning of mankind, garbage is produced, and it has always been necessary to find a destination for that garbage.

In the Prehistoric era, people usually lived in small groups and never stayed in the same place for very long. Because of that, they had no problem with the garbage, so they dumped it directly on the land. Since it was mainly biodegradable food residues, bones and shells, it had no adverse effects on the environment.

By the time civilizations were beginning to form, there was no special concern about the garbage. It was normal that people left garbage on the floor of the house. Other ways to get rid of the garbage were to let it rot on the roads or even throw it in the rivers.

The situation was like that till the year of 500 BC, when the Greek people built the first limited area only for garbage. The Greek law said that the garbage had to be thrown at least one mile away from the city walls. Whoever did throw garbage in the streets would be accused of illegal practice and suffer the consequences [2].

As the time was passing, the population was increasing, so the garbage situation was becoming more dramatic. In the Middle Ages, the garbage was thrown on every single street becoming available to any kind of animal to eat the garbage. The food and other types of garbage were rotting in the streets, making a pleasant place for infestations of rats, insects and other types of animals. The Bubonic plague and typhoid fever were examples of diseases responsible for the killing of thousands of people in that age, resulting from the lack of hygiene that the garbage on the street and in rivers provided [1].

In the end of the XVIII century, came a time when there was a change in the concern of the population about the garbage. People started to bury it in the soil and also the first garbage collection system was created.

In the beginning of the XX century, the people of the United States of America were still throwing their garbage into the ocean. The situation was changed in the middle of that

same century, when they started to put the garbage in landfills, in order to implement a more environment friendly practice.

History tells that the garbage incineration was first applied in a regular way during the XIX century in England.

In late XIX century the first garbage incinerator was built, in the United States of America. The Americans were also the first ones to create facilities for recycling of waste [1].

Nowadays, the garbage is incinerated in modern facilities, where it is possible to produce electricity with the help of those operations. When the waste is incinerated, ashes are going to be produced, and they have to be properly managed in a land fill or elsewhere.

1.2. MSW Incineration

The term MSW means “Municipal Solid Waste”, which is all the waste that is produced in family houses, all kinds of commercial shops and also some industries. This type of waste is constituted by all sort of common things, like for instance organic rubbish like food, glass, all types of paper and carton, lots of metal in distinct appliances, plastic and wooden residues. MSW should include neither medical waste nor hazardous garbage, since those types of garbage are treated in other ways. The way MSW is treated is by a combination of three processes, which are recycling, incineration, also called thermal treatment, and landfilling.

When garbage is burned in incinerators, its inherent energy content is transformed into heat. That heat can be used in district heating systems or to generate electric power. Since incineration is a technology that allows treating garbage and after that enables the recovery of energy, it can be called a “waste to energy” system [3].

The largest benefit of MSW incineration is a reduction of the waste weight by 75% and volume by 90%, which is positive considering that landfilling takes up very much space and that the soil is valuable and needed for other uses [4].

There are some factors that make incineration difficult to implement in some countries, most of all, in the developing countries. The most relevant of those are the high

capital and operating costs involved, in comparison to the insignificant cost of landfilling. It is easy to understand, that countries with financial difficulties, are much more attracted by landfilling the waste, which is cheaper for them, than to invest in modern and expensive facilities capable of burning a wide range of waste types. In addition, it is necessary to have in those facilities trained workers, which of course has some adjacent costs. Plus, the high technical infrastructures, needed to provide the incineration, and in a posterior phase, control and cleaning of the resulting material streams, are very expensive [4].

In the incinerators, when garbage is burned, three products results from the operations. Those products have to be treated in different ways the make sure they do not harm the environment, and of course to ensure that the benefits of incineration are bigger than the damages. Those three products are:

1. Bottom ash;
2. Fly ash;
3. Flue gas.

These three products will be discussed later in this work.

In the EU and USA, 270 and 254 million tons per year of MSW are generated respectively. From those quantities, 33 million tons are incinerated in the United States of America (IN 2005). In Europe, 52.6 million tons of MSW are incinerated (IN 2003) [5]. A much larger quantity of waste could be burnt in incinerators, but there are some hindering issues. The amount of incineration facilities is not so big. Some countries stop constructing them, other are promoting it. The financial matter is also something very important to have in consideration and also the governmental position about incineration can influence the help or support to companies interested in incineration. Another issue is the concern of the population. Nowadays, people are still afraid of MSW incineration and the possible threat to the environment by flue gas emissions and contamination from the ashes. Lots of people still think incineration is the opposite of recycling. Recycling and incineration are not opposites but complements to each other.

1.3. Incineration techniques

For the combustion of municipal solid waste (MSW), many different techniques exist, each one with its special characteristics. The most common way to burn garbage is “mass burn” incineration. As it is easy to understand by the name, the waste is disposed in the incinerators without pre-treatment. This type of incineration is carried out in a variety of incinerators as will be described below.

1.3.1. Water-Wall Incineration

This technique is most common of the “mass burn” incineration technologies. The process is somehow simple. A crane has the task of distributing the waste in a hopper. From there, the garbage is conducted to a grate that moves the waste into the combustion chamber. In that place and with air coming from above and below the grate, the waste is burned. The air that comes from different places has different functions. The air coming from below is needed to initiate the combustion and to cool the grate, while the air coming from above has the purpose of standardizing the distribution of the gases created. In the end, ash and flue gas are produced. The ashes go to treatment equipments while the flue gas can be used in the production of electricity [6].

1.3.2. Controlled Air Modular Furnaces

This technology started to be used in the middle of the XX century. The characteristic of this furnace is burning garbage by controlling the amount of combustion air. With this ability, it is very easy to control the temperature of the chamber, and consequently the

combustion rate. These furnaces can also be named “starved air” combustors due to their burning characteristics referred above.

This furnace was a very big improvement when it was created. When compared to other types of furnaces, the Controlled Air Modular Furnace is much more beneficial. Because this system allows more control over the combustion than other incinerators, it confers it the possibility of achieving a significant reduction in gases that may become air pollutants [6].

1.3.3. Multiple Hearth Incinerators

This incinerator has a special way to work. It presents a system with a variety of grates. The waste is going to pass throw each grate at different temperatures, traveling through consecutive hotter zones until the waste is decomposed. This technique has the inconvenience of having a high operation cost and like others technologies, it is very sensitive to variations in the fuel heat values [6].

1.3.4. Rotary Kilns

The combustion in rotary kilns is a very versatile technique, which can burn waste in every kind of solution, solid, liquid or solid/liquid. Rotary Kilns are composed of a big cylinder, and they can be divided into Stationary Rotary Kilns, or land based, and Mobile Rotary Kilns, or transportable.

As it was said before, it is a very versatile technology, but despite of that, this incinerator has a lot of inconvenient draw backs. Like the Multiple Hearth Incinerator, it is very sensitive to heat differences, which implicates that those who work with this kind of incinerator have to be specialized and well trained. Also because of that, it has high maintenance costs, due to its sensibility [6].

1.3.5. Fluidized Bed Incinerators

As the name indicates, this incinerator has a bed of sand, which is transferring heat from the burning garbage to the walls which are acting as heat exchanger surfaces. The sand bed is supported by a perforated plate, through which heated air is passing in order to incinerate the waste. It has this name, because the air when passing through the sand makes the bed of particulates act like a fluid, which is why it is called “fluidized” bed incinerator [6].

The design of this technology is very simple and is also energetically efficient. It has the ability to burn solid, liquid and gaseous garbage and also allows minimum values of NO_x production. Economically it needs low capital and maintenance costs, which is a very important thing to consider when acquiring an incinerator. However, the particle size of the waste derived fuel has to be in a certain range not to disturb the fluidization. Thus, a size reduction device may be needed.

This incinerator, when compared with others, has the advantage to block some pollutants that can be released to the atmosphere by other incinerators. This is an advantage because it allows saving capital in emissions treatment [6].

With the increasing of the superficial velocity, the fluidization can behave in two ways: it can be a homogeneous fluidization (smoothly) or heterogeneous fluidization (bubbling).

In the homogeneous fluidization, the bed maintains a balance between fluidization velocity and the force that drags the particles by enlarging bed volume. On the opposite side, if the balance is achieved by the increasing of gas bubbles, the fluidization is heterogeneous [7].

Considering characteristics like operation and design, it is possible to divide a fluidized bed incinerator in two types: bubbling fluidized bed incinerator (BFB) or circulating fluidized bed incinerator (CFB). The most important differences between these incinerators are the requirement of higher superficial velocity by the CFB and a cyclone to treat some type of particles [7]. The CFB high velocity gives it such a hydrodynamic behavior that makes it superior over common combustion techniques, including the bubbling fluidized bed incinerator. These velocities in the combustion chamber, from 3 m/s to 10 m/s, lead to a fast

mixing between the solids and the gas phase, what will allow the process to reach high combustion efficiency [8].

Industrially, they are considered safe, effective and viable.

1.4. Residues from MSW incineration

During the process of burning the waste, water vapor and carbon dioxide are produced and they are going to be released in the flue gas.

However, water vapor and carbon dioxide are not the only flue gas constituents. Other flue gas components that must be removed as efficient as possible before emitting the flue gas to the atmosphere are SO_2, HCl, NO_x, dioxins, furans, other hydro carbons and vapor phase species of mercury and other metals.

During the incineration, the incombustible part of the waste is not going to be burned but will form a solid mixture, named slag. That residue can either be utilized or even recycled.

The slag, also named by bottom ash is the product that comes out in bigger amount from the incineration. It represents about 20 % in weight of the garbage incinerated and it contains a lot of metals in various chemical forms [9].

Information says that the best way to get rid of the bottom ash is to landfill it. It can be treated before landfilling, like for instance by recovering the iron present, which will help to reduce the amount of space needed to landfill. That iron can then be sold, representing a profitable operation to be done [9].

When a slag or other type of MSW ash is to be landfilled, then it is extremely important to evaluate the dangers that leaching of compounds present in slag represents to the environment. It is always important to know how the ash is going to behave under leaching conditions, and avoid contributing to the pollution of the soil and underground water.

Another important residue from the incineration is the fly ash. This type of ash is formed by particles which were not combusted in the furnace, and followed the flue gas all the way to the flue gas treatment system. There, with the decreasing of temperature of the flue gas, some compounds condense and form the fly ash together with the entrained particulates.

This ash, after collected, represents about 2 to 3 % in weight of the initial garbage and it has in its constitution heavy metals, salts and minerals [9].

So far, the only way to handle this type of ash has been to landfill it. Because of the presence of potentially toxic metals, it is very important to have special care about the way the ash is landfilled, to ensure minimum risks of heavy metal leaching and posterior contamination of the environment. The discovery of a use for this type of ash would be an accomplishment allowing the decreasing of ash to be landfilled and the consequent risk of toxic compounds leaching.

Other products resulting from incineration of garbage and other fuels are the dioxins and furans. They can be produced in numerous anthropogenic processes, but also naturally, like for instance in natural fires. These types of compounds are very stable towards degradation in the environment and are therefore accumulated in the food chains in nature [6].

From the moment they are present inside the human body, they can cause cancer and other kinds of diseases.

These are the major products resulting from incineration, and companies that deal with garbage combustion, must have the necessary technology for the corresponding treatment. The boiler owning companies are responsible for not allowing that these products and residues pollute the environment.

1.5. Knowledge about the ash

Many variables can influence the properties of an MSW ash. There are a lot of incineration facilities in the world and each facility burns the garbage under their own conditions, so, in the end, each ash is going to have somewhat different properties than the others.

Of course the composition of the waste is mostly important to the characteristics of the ash, but other examples of variables can affect them, for instance, at what stage in the combustor the ash was collected and the conditions under which garbage is burned.

The most important physical ash properties are particle size, density, and moisture content. In addition, the chemical composition, the chemical stability, hardening characteristics and permeability when mixed with water as well as toxicity of course have to be considered [10]. It is important to stress that these properties were not analysed in this thesis. They were only listed in order to give the information about the main ash properties that are studied in other works.

The particle size is very important to take in consideration when the ash has to be packed. The specific surface is directly connected with particle size and influences chemical reactions that can occur in the ash. Ash particles with larger size have smaller specific area, so, they have a smaller area of contact and therefore limits the amount of reactions occur in the surface. The moisture content is very important when it is necessary to transport the ash. It will interfere with the weight of the ash and of course that influences the price to transport any amount of ash. The heavier it is, the more expensive is the transportation.

About the chemistry of the ashes, it is very important to know how the ashes are composed. As it was said before, these ashes contain various metal compounds, which can be more or less easily leached to the environment if the ash is handled in the wrong way.

So, it is important that the researching work continues, in order to provide the knowledge that is necessary to have when dealing with ashes. It is essential to know how the leaching works and what kind of properties influences it. It is mandatory to know properties of the ash, like chemical bonds and their strengths and of course what are the environment

properties that can lead to bigger leaching phenomena. Properties like the environmental pH or presence of compounds in the leaching agent that could increase leaching should be documented.

Given the example of pH, it is a very important factor to have in consideration. The pH in the neighborhood of the ash will affect the amount of metals that are released to the leachate. Information tells that heavy metals have a higher leaching rate at low and high pH than at pH levels around neutral [10]. Thus, if the ash is landfilled, and the rain water penetrating the land filled masses has that range of pH values, then the metals will leach and contaminate the environment. This risk can be overcome by adjustment of the pH of the ash by mixing it with cement or other alkaline materials. By cement addition, the land filled mass is also solidified and gives it very low water permeability.

The work presented in this thesis did not include studies of the differences in the leaching rate, through making a certain number of trials, changing the pH or L/S ratio values for instance. The aim of this work was to evaluate the amount of metal (in this case Cu) that can be recovered by leaching and liquid-liquid extraction from several kinds of ashes. The work comprised also the comparison of two types of leaching methods: with nitric acid and with ammonium nitrate solution.

1.6. Metals analyzed

In this thesis, Cu was chosen as the metal to be studied. It is present in rather high concentrations on the MSW ashes, and because in high levels it is harmful to humans, it would be beneficial if it could be removed from the ash. An efficient metal removal method could also make it possible to recover valuable metals for recycling to the metallurgical industry.

Below, some properties and information about this metal are briefly provided.

1.6.1. Copper (Cu)

The name Copper is derivate from *aes cyprium*, and then Cuprum, because it was first seen is Cyprus. It was one of the first metals discovered by man and is known as one of the "coin metals".

This is a red colored very soft metal, very ductile and malleable. It is very resistant to corrosion and it is used as thermal and electrical conductor. It has an important utilization in cables and wires [11].

Copper is well known for forming a high number of alloys with other metals. Copper and its alloys are divided in six groups: coppers, high-copper alloys, bronzes, brasses, nickel silvers and copper nickels [16].

This metal can be found like Cu^{+}, but it is very unstable, and like Cu^{2+}. In very unusual circumstances, it can be found as Cu^{3+}, Copper (III) and in even more unusual conditions, as the same as saying that is very rare, it can be found as Cu^{4+}, Copper (IV).

Copper is a very important nutrient not only for humans, but also for animals and plants. It is fundamental for normal growth. Despite of that, it can be toxic if present in an excessive amount [16].

Copper can be discharged into the nature by various ways. One of them is by the leaching of MSW fly ash.

Information tells that the total flow of Cu from municipal solid waste is something like 20 % of all flow of Cu in the society, and traffic is the biggest source of Cu emissions [12].

As it was said before, copper in a high level is very dangerous. In the United States of America, the concentration of Cu in the water is not allowed to be over 1.3 ppm, and in Europe the maximum is 2.0 ppm [16].

2. Methods

In this work, five different ashes were used. All the ashes are from Sweden and they are going to be identified as Ash A, B, C, D and E. Ashes D and E were both produced in a GFC, grate fired combustor while the remaining three were produced in a BFB, bubbling fluidized bed incinerator.

Information about the ashes will be provided later in this work.

2.1. Experimental Procedure

In this thesis two methods for recovery of copper from MSW fly ash were compared. Both methods included the same laboratory procedure, but in one of them, the leaching agent was a solution of ammonium nitrate, while in the other the leaching substance was nitric acid.

The first step in the metal recovery method is the leaching of metal compounds from the ash, the second step is a selective extraction of Cu using a complex forming agent to an organic phase and the third step is a transfer (stripping) of the Cu to a pure water solution of Cu.

In this part, the laboratorial procedure concerning to the leaching of the ashes is described.

2.1.1. Leaching

Two ash samples of 5 g were weighed accurately and then mixed with 25 mL of leaching agent, at an L/S rate of 5. It means that the rate between the liquid and the solid is equal to 5 and it is expressed as L/kg or mL/g. The solution of ammonium nitrate has a concentration of 3 M and were added a few drops of concentrated NH_3. The ashes were left

to leach for 24 hours at room temperature inside the fume hood, in covered beakers under agitation.

After a few minutes, the pH was measured, and it should be near 9±1, because it is the optimal pH that allows the formation of amine complexes. If the pH was not at the optimal level, it was adjusted using concentrated solutions of HNO_3 or NaOH. Concentrated solutions were used in order to minimize the dilution of the solution. After 24 hours, the leaching was stopped. After that, both samples were centrifuged. The water phase was recovered and the ash was washed with 25 mL of deionised water (MQ-water) letting the sample centrifuge again. This step was repeated two more times. In the end, there were 4 samples, the leachate and 3 washes.

2.1.2. Extraction

After the leaching, the second step, i.e. the extraction of Cu from the leachate was carried out. When it was needed, filtration was applied in order to remove ash particles that remained in the water phase. 10 mL were collected of the water phase to a new recipient properly identified. The pH was adjusted to 2,2 with concentrated HNO_3. If the pH became lower than 2,2 it was raised with NaOH.

The water phase was put together with 10 mL of a 15 % V/V solution of a complex forming agent LIX 860 N-I in an organic solvent, Solvent 70 (kerosene). The volume ratio O/A (organic phase/aqueous phase) was equal to 1. The sample was stirred to force copper to pass through the water phase into the organic phase. LIX 860 N-I is a well known extraction agent for Cu^{2+} with the active substance being a hydroxy oxime. Agitation was applied for approximately 5 min, and then the mixture was left for other 5 min, to allow the two phases to separate completely. In the end, both phases were separated and collected into separate and identified plastic containers.

2.1.3. Stripping

The third step in the Cu recovery process is the stripping part. 2 mL of the previously separated organic phase were collected and 2 mL of H_2SO_4 2 M were added to get Cu into the aqueous phase again. The plastic container was agitated for 5 min and it was left to separate for other 5 min. After perfectly separated, the organic phase was collected with the use of a pipette into a new sample tube.

This work was performed in duplicates, using two samples each time, and only the leachate and the first wash were analysed.

In addition to these experiments, other equipments were used, mostly with the purpose of identification of substances and materials and their consecutive amounts present in the ash and in the samples after the leaching of the ashes. It is the case of the XRD, X-Ray Powder Diffraction and AAS, Atomic Absorption Spectroscopy. Next in this work, these technologies will be briefly addressed.

2.2. Analytical Techniques

2.2.1. XRD

When chemical characterization of solid materials is needed, the technique that is mostly used is the X-Ray powder Diffraction.

In powder XRD, x-rays are used to identify, and get structural information about compounds present in the powder. With this method, only crystalline compounds can be identified since amorphous species do not give clear diffraction patterns. X-rays are

electromagnetic radiation with wavelengths in the same length scale as the distances between atom layers in crystalline compounds. Due to their high frequency, X-rays can cause serious damage to living tissue and they must be handled with caution. Therefore, the diffractometer, in this work a Siemens D5000, is enclosed in a lead containing cover.

The samples in question should be fine powder, and grinded if needed and the powder must be placed randomly and not arranged, to ensure that crystals are found in a natural orientation [13].

In crystalline forms, atoms are very well organized in layers. The X-ray interacts with the electrons in the atoms, a process that can be regarded as if the X-ray is reflected with a specific angle and intensity. The interference pattern created from all diffracted rays is recorded as a diffraction pattern with specific peaks. The position and intensity of the peaks in the diffraction pattern allow the identification of the crystalline specie [13].

This analysis is supported by the Bragg's law, which says that:

$$2\,d\,\sin\theta = n\,\lambda$$

Being θ the angle of diffraction, *d* the space between layers, λ is the wavelength of the x-ray and *n* the integer number.

When the X-ray diffraction pattern has been obtained, it is compared with data for known compounds collected in a database. Since there is a pattern that is characteristic for each substance, the crystal compound can be found with a high percentage of confidence. Sometimes identification of sample constituents can be difficult because the sample contain similar substances, with similar structures. Samples containing many compounds are also somewhat difficult to analyse. Generally, the detection limit is about 2 weight% of a crystalline compound in a solid matrix.

The equipment used was Siemens D5000 powder diffractometer equipped with an X-ray tube giving Cu characteristic wavelength (1.54 Å), and a scintillation detector.

The data base is the Joint Committee of Powder Diffraction Standards data base release PDF-4 [18].

2.2.2. AAS

Atoms absorb light in the visible spectrum. This can be utilised for quantification of a specific element in a sample in the analytical technique called Atomic Absorption Spectrometry (AAS).

In this work, AAS, atomic absorption spectroscopy, was used in order to determine the amount of copper present in each sample.

The fundamentals are that the atoms are in the ground state, when they absorb energy from a source with a specific wavelength making them entering in an excited state. The absorbed energy increases with the increasing of the number of atoms. With this technique, it is possible to measure that amount of energy, and then know the quantity of the atom in question, that is present in the sample [17].

Standard solutions are also analysed, and this will help to build a calibration curve that will help to obtain the concentration of the atom.

A lamp has to be used in order to provide the light necessary to be absorbed by atoms. That lamp must give a wavelength that matches the energy that the atoms of the analysed element can absorb.

The flame, which serves to create the high energy thermal environment, necessary to excite atoms in the atomic emission, will only be necessary to turn the sample into atomic vapor in this case of atomic absorption. After that, the vapor will absorb the light from the respective source.

The instrument used for atomic absorption spectroscopy in this work was a Perkin-Elmer AAnalyst 800 Atomic Absorption spectrometer. The lamp was a multielement lamp for Cu with 324.8 nm of wavelength and 0.7 of slit width. The flame used was an acetylene/air flame. The flame technique is the most common and is used to analyse more than 35 elements with detection limits in the ppm range [17]. However, its applicability depends on the concentration of the respective elements in the sample. Low concentration elements can be analysed by the graphite furnace AAS technique instead, which has detection limits in the ppb range.

Liquid samples can be analysed directly or after dilution, whereas solid samples have to be dissolved totally before analysis by AAS.

3. Results

3.1. Characterisation of the raw ash

In this topic, it is going to be given information about the ashes analysed in this thesis, but only information about the ashes in their raw state, before being used in any kind of experiment.

As it was said before, five different ashes were analysed, all samples of fly ashes from Sweden.

3.1.1. Ash A

This ash is from a south-west part of Sweden and it was produced in a BFB. The particle separation in this boiler consists of a cyclone and a textile filter. A dry flue gas cleaning system including injection of activated carbon and lime is placed between the cyclone and the filter.

The analysed sample from this boiler was filter ash produced in 2007 so this ash is relatively new. It is a beige coloured and very homogeneous ash and it is very fine grained. It did not need any grinding to be analysed by XRD.

Figure 1 – Picture of ash A.

A sample of this ash was sent to an external laboratory in order to be analysed by ICP-MS, inductively coupled plasma mass spectroscopy, to give the element concentrations present in the ash.

The results are presented next.

Table 1 – Total amount of elements present in ash A, given by external analysis.

Ash A			
	% TS		**mg/kg TS**
SiO_2	6,68	**As**	46,5
Al_2O_3	4,19	**Ba**	1250
CaO	44	**Be**	<0,6
Fe_2O_3	1,4	**Cd**	63,6
K_2O	1,62	**Co**	17,8
MgO	1,57	**Cr**	380
MnO	0,0886	**Cu**	**7820**
Na_2O	2,45	**Hg**	1,07
P_2O_5	0,718	**Mo**	11
TiO_2	0,137	**Nb**	<6
Cl	18,9	**Ni**	89,4
F	-	**Pb**	4000
LOI	14,4	**S**	29000
		Sb	460
		Sc	<1
		Se	2,33
		Sn	249
		Sr	281
		V	9,7
		W	87,4
		Y	6,92
		Zn	5540
		Zr	64,3

In parallel, this ash was analyzed by XRD, to understand which crystalline compounds are present in it. The ash A diffractogram is showed next.

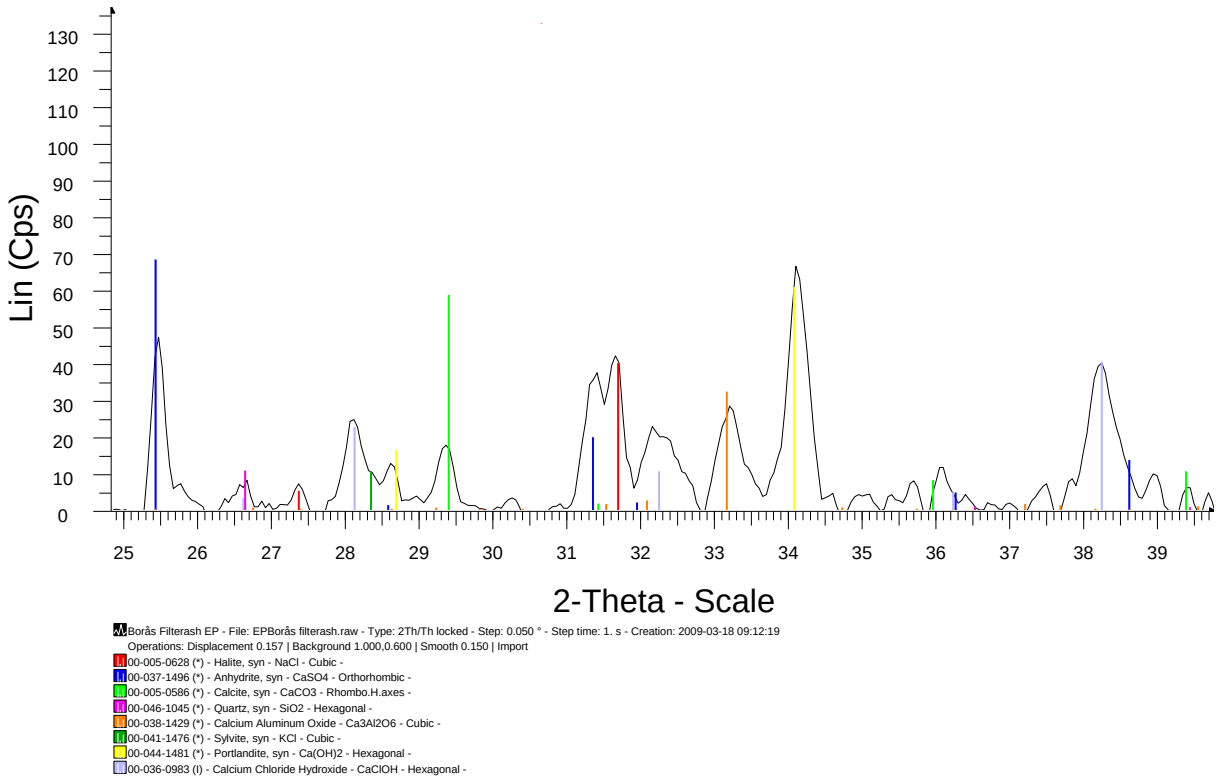

Figure 2 – Diffractogram of Ash A in raw state.

3.1.2. Ash B

This light grey coloured ash is very fine grained and it is also homogeneous. It was produced also in a south-western city of Sweden in 2007, and also in a BFB. At this boiler, the same type of flue gas cleaning system as in combustor A is used.

Figure 3 – Picture of ash B.

The results from the external analysis are presented as following.

Table 2 – Total amount of elements present in ash B, give by external analysis.

Ash B			
	% TS		**mg/kg TS**
SiO_2	5.55	**As**	33.5
Al_2O_3	3.1	**Ba**	443
CaO	57.5	**Cd**	28.4
Fe_2O_3	0.776	**Co**	8.28
K_2O	1.47	**Cr**	147
MgO	1.4	**Cu**	**3090**
MnO	0.0516	**Hg**	2.91
Na_2O	2.07	**Mo**	24.6
P_2O_5	0.61	**Ni**	26.3
TiO_2	0.296	**Pb**	2570
Cl	11.9	**S**	13000
F	0.04	**Sb**	162
LOI	21.1	**Se**	1.99
		Sn	145
		Sr	291
		V	17.1
		Zn	3260

This ash has the third largest amount of copper, only exceeded by ash A and ash C. When talking about lead and zinc, this ash is the one with the lowest concentrations in all the ashes studied.

This ash is more recent than ash C, and that can show a change in the products resulting from the incineration of garbage, since this ash is from the same place as ash C.

Figure 4 shows the diffractogram from the XRD of this ash.

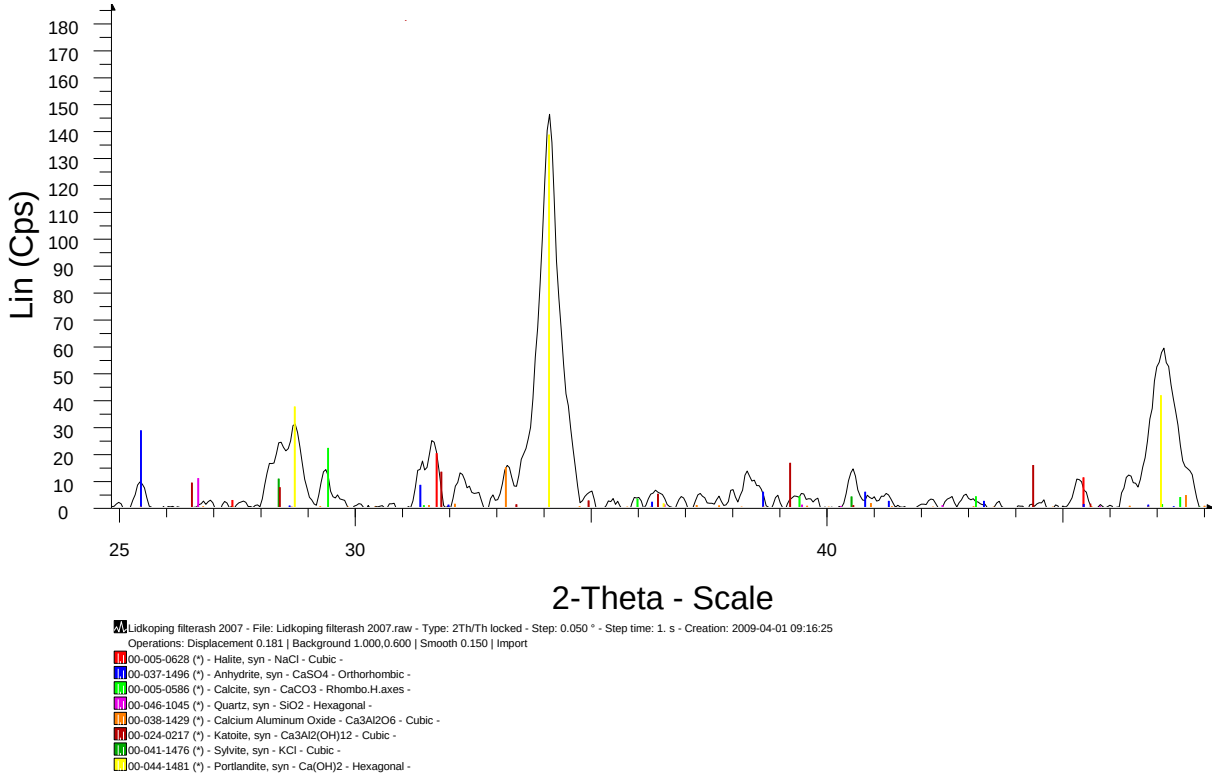

Figure 4 – Diffractogram of Ash B in raw state.

3.1.3. Ash C

This ash is very similar to ash B. It is the oldest of the examined ashes, being produced in the same combustor as ash B in the year of 2000. It presents very fine particles and it is a homogeneous ash. Like the previous one, it has a light grey colour.

Figure 5 – Picture of ash C.

Next are presented the results from the external analyses of this ash.

Table 3 – Total amount of elements present in ash C, give by external analysis.

Ash C			
	% TS		**mg/kg TS**
SiO_2	7.00	**As**	82.8
Al_2O_3	4.20	**Ba**	770
CaO	50.8	**Cd**	88.6
Fe_2O_3	1.60	**Co**	18.8
K_2O	2.74	**Cr**	194
MgO	1.68	**Cu**	**5400**
MnO	0.07	**Hg**	2.81
Na_2O	4.29	**Mo**	13.4
P_2O_5	0.92	**Ni**	31.9
TiO_2	0.31	**Pb**	5730
Cl	19.0	**S**	16000
F	-	**Sb**	-
LOI	0.02	**Se**	-
		Sn	23.8
		Sr	501
		V	14.0
		Zn	5780

This ash has the second highest copper concentration. However, copper is not the most abundant trace metal present. The amount of copper is exceeded by the quantity of Zinc and Lead. Analysing the table above, it is possible to see that these three elements are present in almost the same quantity in this ash. Just to stress out that this ash has no fluoride found in it.

The fact that this ash is from a different year than ash B, will make a difference in what concerns to its crystalline compounds. Not only because of the changing of human habits, which have consequences for the composition of garbage. That is just one of the reasons that will result in different amounts of compounds in the ash.

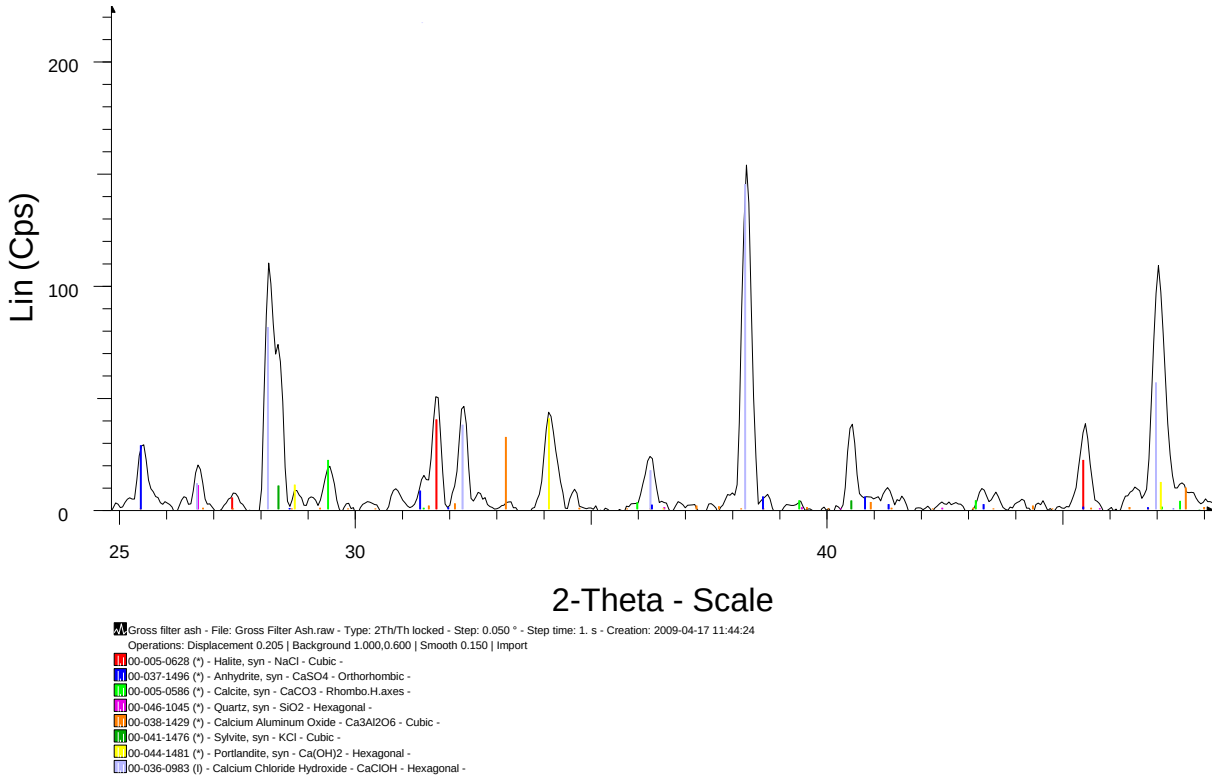

Figure 6 – Diffractogram of Ash C in raw state.

3.1.4. Ash D

This ash is from a city situated in the northeast, a different part of Sweden. It is an ash that presents physical differences when compared to the others. It is dark grey coloured and it has coarser particles than the other ashes.

This ash was produced in the beginning of 2009 in a grate fired combustor. The flue gas treatment system in this unit includes an injection of limestone powder to absorb acid gases, injection of activated carbon and a filter for particle separation.

Figure 7 – Picture of ash D.

After analysing the ash by ICP-MS, the external lab sent the following results for this ash composition.

Table 4 – Total amount of elements present in ash D, give by external analysis.

Ash D			
	% TS		**mg/kg TS**
SiO_2	9.52	**As**	107
Al_2O_3	4.58	**Ba**	1030
CaO	29.0	**Cd**	213
Fe_2O_3	1.29	**Co**	47.5
K_2O	6.01	**Cr**	469
MgO	1.58	**Cu**	**1460**
MnO	0.106	**Hg**	10.6
Na_2O	7.04	**Mo**	16.8
P_2O_5	1.03	**Ni**	43.1
TiO_2	1.03	**Pb**	4840
Cl	15.2	**S**	38100
F	-	**Sb**	1550
LOI	20.8	**Se**	11.6
		Sn	749
		Sr	304
		V	19.8
		Zn	25600

This is the ash with the lowest amount of copper. The compounds present in bigger amount are sulfur and zinc. It has also a considerable quantity of lead, but is not the ash with the biggest amount of it.

The XRD diffractogram is presented next. In it is possible to see the crystalline compounds presented in the ash.

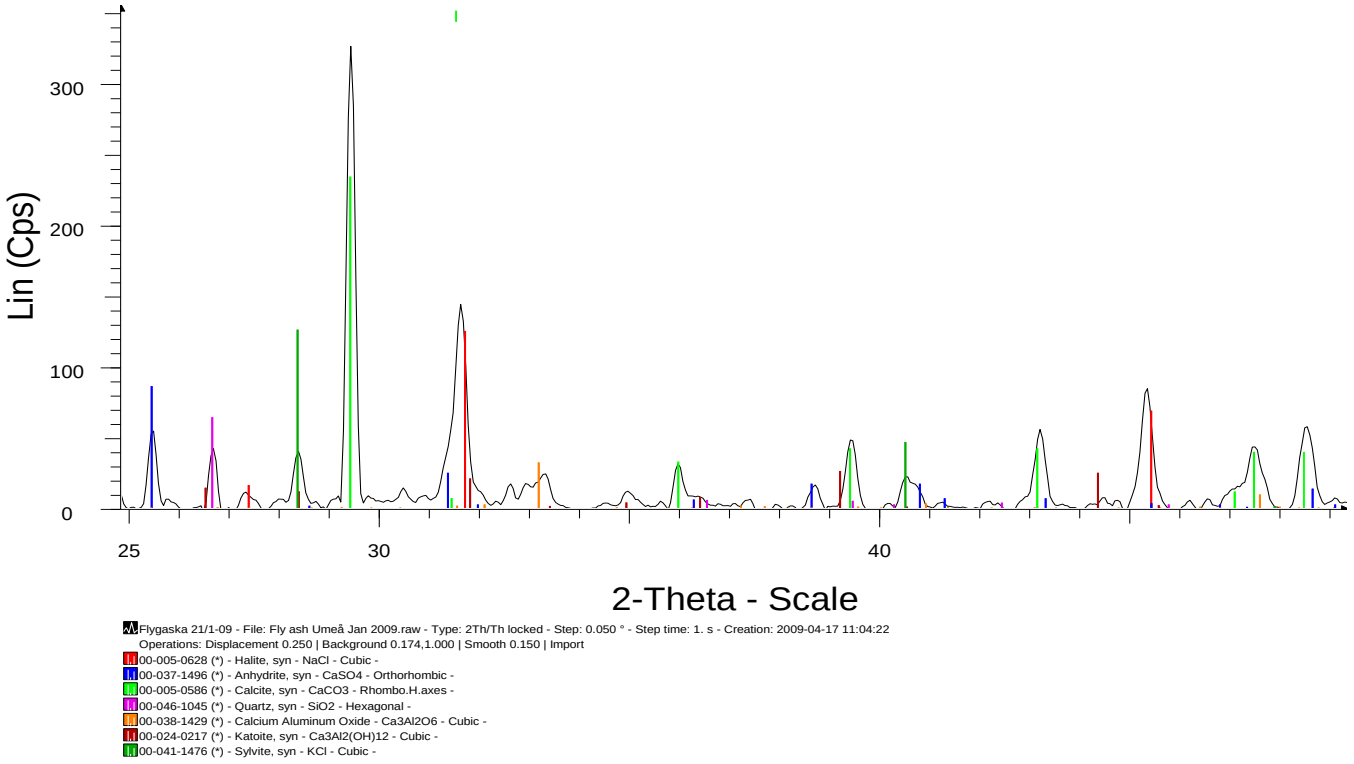

Figure 8 – Diffractogram of Ash D in raw state.

3.1.5. Ash E

This ash is from a different city, but also from the south-west part of Sweden. This is a light grey coloured ash produced in the middle of 2007 in a grate fired combustor. It is coarse grained and presents a slight heterogeneous appearance, since it contains coal particles.

A photo of the ash is showed next.

Figure 9 – Picture of ash E.

Like the other ashes, this one was also analysed by the external laboratory. The results are presented below.

Table 5 – Total amount of elements present in ash E, give by external analysis.

Ash E			
	% TS		**mg/kg TS**
SiO_2	14.4	**As**	1110
Al_2O_3	6.05	**Ba**	1090
CaO	16.7	**Cd**	373
Fe_2O_3	3.48	**Co**	21.5
K_2O	8.02	**Cr**	921
MgO	1.95	**Cu**	**2500**
MnO	0.11	**Hg**	0.698
Na_2O	10.5	**Mo**	36.3
P_2O_5	1.36	**Ni**	79.4
TiO_2	1.61	**Pb**	11000
Cl	11	**S**	75400
F	0.33	**Sb**	2270
LOI	16	**Se**	14.3
		Sn	2020
		Sr	292
		V	53.1
		Zn	55100

This ash has a considerable amount of copper, but again, it is not the biggest. In addition, this is the ash which is the most loaded with heavy metals. When comparing this one with the others, it is possible to see that this ash has the biggest quantity in almost every metal.

The reason for the high metal concentration in the fly ash from this combustor is a result of the composition of the waste including household waste from a very populated area in addition to all kinds of waste from enterprises in the area.

Then, analyses to this ash where made by XRD to evaluate which crystalline compounds are present in it. The result is showed next.

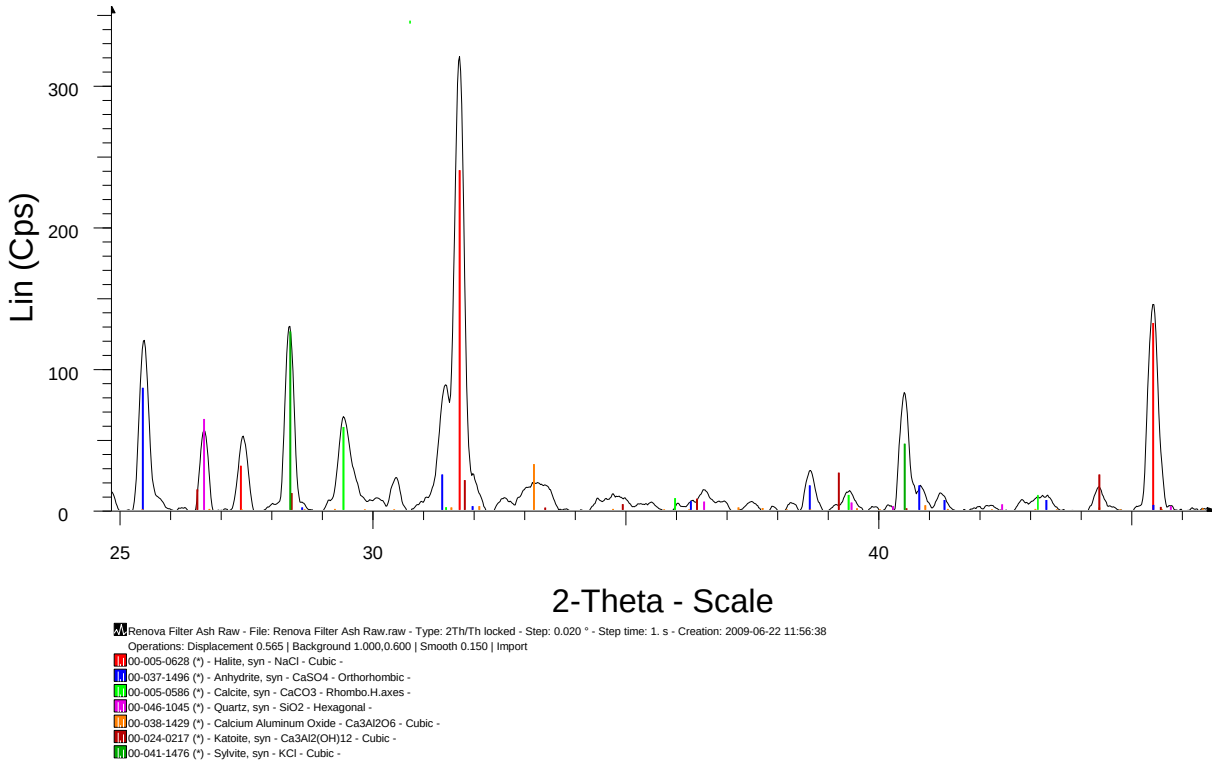

Figure 10 – Diffractogram of Ash E in raw state.

After some information about the ashes, the ICP-MS results are shown in order to elucidate in a more easy way the compounds present in the ashes, to simplify the comparison of the ash in the types of compounds present and the type of incinerator.

These tables are showed below.

Table 6 – Total amount of elements present in all ashes, give by external analysis. All amounts are given in % of dry matter.

Element (% TS)	Ash A BFB	Ash B BFB	Ash C BFB	Ash D GFC	Ash E GFC
SiO_2	6.68	5.55	7.00	9.52	14.4
Al_2O_3	4.19	3.10	4.20	4.58	6.05
CaO	44.0	57.5	50.8	29.0	16.7
Fe_2O_3	1.40	0.78	1.60	1.29	3.48
K_2O	1.62	1.47	2.74	6.01	8.02
MgO	1.57	1.40	1.68	1.58	1.95
MnO	0.09	0.05	0.07	0.11	0.11
Na_2O	2.45	2.07	4.29	7.04	10.5
P_2O_5	0.72	0.61	0.92	1.03	1.36
TiO_2	0.14	0.30	0.31	1.03	1.61
Cl	18.9	11.9	19.0	15.2	11.0
F	-	0.04	-	-	0.33
LOI	14.4	21.1	0.02	20.8	16.0

In this table is important to observe and compare the amount of CaO present in the ashes. From all the elements presented, CaO is the one that shows a big difference between ashes. All the first three ashes present high amount of CaO, while in the other two, that amount is considerably low. That can be explained by the type of incinerator that produced the ashes. While the first three where produced in a BFB, the others were obtained in a GFC.

Table 7 – Total amount of elements present in all ashes, give by external analysis. All amounts are given in mg metal/kg of dry ash.

Element (mg/kg)	Ash A BFB	Ash B BFB	Ash C BFB	Ash D GFC	Ash E GFC
As	46.5	33.5	82.8	107	1110
Ba	1250	443	770	1030	1090
Be	<0,6	-	-	-	-
Cd	63.6	28.4	88.6	213	373
Co	17.8	8.28	18.8	47.5	21.5
Cr	380	147	194	469	921
Cu	7820	3090	5400	1460	2500
Hg	1.07	2.91	2.81	10.6	0.70
Mo	11.0	24.6	13.4	16.8	36.3
Nb	<6	-	-	-	-
Ni	89.4	26.3	31.9	43.1	79.4
Pb	4000	2570	5730	4840	11000
S	29000	13000	16000	38100	75400
Sb	460	162	-	1550	2270
Sc	<1	-	-	-	-
Se	2.33	1.99	-	11.6	14.3
Sn	249	145	23.8	749	2020
Sr	281	291	501	304	292
V	9.70	17.1	14.0	19.8	53.1
W	87.4	-	-	-	-
Y	6.92	-	-	-	-
Zn	5540	3260	5780	25600	55100
Zr	64.3	-	-	-	-

With this table, it is easier to compare the amounts of elements present in the ashes, and also relate them to the incinerator responsible for the production of each ash.

As it is possible to notice, the ash A is the one that presents higher amount of Cu, while ash D presents lower amount of Cu.

3.2. Experimental Work

In this section, the results from the leaching method using Ammonium Nitrate are presented, followed by the results achieved with the leaching method using Nitric Acid.

Next, in the Table 8, gives the mass of each ash sample and the respective amount of Cu present in the quantity of ash for the leaching method using Ammonium Nitrate.

Table 8 – Mass of each sample of ash and the mass of copper present in each sample.

Ash	Sample	Mass of the sample (g)	Mass of Cu in sample (mg)
A	**1**	5,004	39,13
	2	5,001	39,11
B	**1**	5,002	15,46
	2	5,001	15,45
C	**1**	5,008	27,04
	2	5,007	27,04
D	**1**	5,004	7,31
	2	5,001	7,30
E	**1**	5,001	12,50
	2	5,000	12,50

In the Tables 9, 10 and 11 are present the results from the amount of Cu recovered in each of the three steps.

Table 9 – Percentage of copper recovered from the ash in the leaching step with Ammonium Nitrate and pH of the solutions.

Ash	Sample	% Cu Leachated	Initial pH	Final pH
A	**1**	90	8,9	8,8
	2	89	9,0	9,0
B	**1**	85	9,9	9,9
	2	89	10,0	10,0
C	**1**	114	9,6	9,5
	2	114	9,6	9,4
D	**1**	75	8,3	8,2
	2	73	8,5	8,4
E	**1**	56	8,4	8,2
	2	51	8,6	8,4

Table 10 – Percentage of copper taken from the leachate in the extraction step.

Ash	Sample	% Cu Extracted in Organic Phase	% Cu non Extracted in Water Phase
A	**1**	123	< 1
	2	128	< 1
B	**1**	108	< 1
	2	88	< 1
C	**1**	112	< 1
	2	104	< 1
D	**1**	92	< 1
	2	97	< 1
E	**1**	88	< 1
	2	92	< 1

In this table is possible to compare the percentage of copper that was possible to extract from the amount of leaching liquid referred in the Experimental Procedure section, with the percentage of copper that stayed in the water phase. The average extraction efficiency was about 100% in these experiments.

Table 11 – Percentage of copper taken from the organic phase in the stripping step.

Ash	Sample	% Cu Stripped to Water Phase	% Cu not Stripped, remaining in Organic Phase
A	**1**	78	4
	2	73	4
B	**1**	76	5
	2	88	10
C	**1**	77	4
	2	76	4
D	**1**	111	6
	2	109	12
E	**1**	111	10
	2	108	17

In this table, as the previous one, is also possible to compare the amount of copper recovered from the specific quantity of organic phase, in the stripping step, with the quantity of copper that remained in the organic phase, after the step.

In this method using ammonium nitrate, it is important to know that the leaching is mainly done by complexation phenomena between the copper and other compounds and the leaching agent.

When analysing the table 9, there are some results that seem not to be satisfactory. Some ashes present lower percentages of leached Cu than was expected. One answer can be that the missing copper is present in the three further wash liquids obtained from washing the filter cake remaining after leaching. These washing liquids were not analysed due to time limitations. But it is possible to see that the three washes, mostly the first one, present a light blue colour. That colour is due to the copper present there. If the washes were analysed by AAS, there is a probability that most of the missing copper would be there. As further work, it can be included the analyses of the three washes in order to see how much copper it is possible to find there.

Another reason for the different effects of leaching on the copper content in the ashes can be that copper has different speciation, i.e. occurs in different compounds, in the different ashes or that the Cu compounds are present as inclusions inside matrix compounds with low solubility and therefore are not easily accessible for the leaching solution.

The table 9 shows that from all the ashes, the samples from ash E are the ones that present the least efficient leaching of copper.

Comparing all the leaching results, it is possible to see that following the same procedure for the all the ashes, different results are obtained for different ashes. Clearly, the ashes vary in composition and leaching properties, since they are from different incinerators, or even produced in the same incinerator but in different years.

In the table 10, the results are closer to the expected 100 %. The organic extraction agent LIX 860 N-I used is highly selective for copper, and the results obtained show that the extraction method works very well and gives good results with all the ashes.

It is possible to say that the AAS is more accurate when measuring water phase samples than organic ones, so the results from water phase have fewer errors than the others from organic phase. The amount of copper that remained in the water phase is less than 1 % for every ash, what reinforces everything said before and shows that almost all copper from the amount in the leachate was extracted from to the organic phase.

The results obtained in the stripping step are interesting. The ashes D and E present the best results in this step, the ash E being the one which had the lower percentage of copper in its leachate. Anyhow, these results are not very satisfactory, because after this step, all the copper was supposed to be present in the water phase and the results do not show that, at least for the ashes A, B and C, which have stripping percentages lower than 80 %.

The organic phases from this step show also a bigger amount of copper than expected, despite of their analyses being less accurate than the water phases. This process needs further investigations and improvement.

This method was already developed and tested by Karin Karlfeldt, whereas the method using nitric acid as leaching agent has not been studied in detail before. During the experimental work using this method, no problem occurred and all the steps took place very well without any particular inconvenient or delay.

Now, the results from the acid leaching are going to be shown and analysed.

Table 12 – Mass of each ash sample and the correspondent mass of copper present for the acid leaching method.

Ash	Sample	Mass of the sample (g)	Mass of Cu in the sample (mg)
A	**1**	5,000	39,10
	2	5,000	39,10
B	**1**	5,000	15,45
	2	5,000	15,45
C	**1**	5,000	27,00
	2	5,000	27,00
D	**1**	5,000	7,30
	2	5,000	7,30
E	**1**	5,001	12,50
	2	5,000	12,50

After this table, are presented the results from the three steps of the method using nitric acid as leaching agent.

Table 13 – Percentage of copper recovered in the leaching step with nitric acid and pH of the solutions.

Ash	Sample	% Cu Leachated	Initial pH	Final pH
A	**1**	-	-	-
	2	-	-	-
B	**1**	93	2.3	2.3
	2	92	2.7	2.8
C	**1**	97	-	2.2
	2	110	-	2.0
D	**1**	90	3.8	3.9
	2	85	3.7	3.3
E	**1**	76	2.1	2.1
	2	81	2.4	2.4

Table 14 – Percentage of copper extracted from the leachate in the extraction step of the acid leaching method.

Ash	Sample	% Cu Extracted in Organic Phase	% Cu non Extracted in Water Phase
A	**1**	-	-
	2	-	-
B	**1**	78	1
	2	83	1
C	**1**	121	1
	2	112	1
D	**1**	77	2
	2	76	2
E	**1**	77	2
	2	79	< 1

In this table is compared the amount of copper that was possible to remove from the leachate to the organic phase in the extraction step with the quantity of copper that remained in the water phase.

Table 15 – Percentage of copper recovered from the organic phase in the stripping step of the acid leaching method.

Ash	Sample	% Cu Stripped in Water Phase	% Cu not Stripped, in Organic Phase
A	**1**	-	-
	2	-	-
B	**1**	111	13
	2	104	12
C	**1**	84	9
	2	83	9
D	**1**	92	22
	2	96	24
E	**1**	89	19
	2	84	18

In this table are presented the results from striping step, comparing the amount of copper that was possible to recover from the specific amount of organic phase formed in the extraction step, with the quantity of copper that remained non striped.

As it was referred previously, this acid leaching method is new, and there are little studies and information about it. So, comparing with the ammonium nitrate leaching method, this one offered much more problems, doubts and uncertainties.

The work was started with testing of a leaching with 3 M HNO_3. As it was expected, the pH was very low, lower than 1, but the leaching proceeded normally. It was necessary to filter the leachate and this presented some problems. The first samples to be filtrated in this method were from the ash A and D. The filtration was accomplished, but with difficulty, at least in the way it was being done, using a syringe and filters. The pH of the leachate had to be adjusted to 2.2 to suit the chemistry of the extraction agent. This was attempted by

addition of a NaOH solution, but that created problematic effects. The sample from ash A, when adding concentrated NaOH, started to precipitate and created some clots. After letting the sample rest for two days, the clots disappeared but the liquid acquired a jelly form.

In order to overcome that, weaker acids (2 M and 1.5 M) were used in the leaching step but that was not effective because the pH remained very low. After discussion, it was decided that the leaching had to start with a pH near 2.2, irrespective of the concentration of the used acid. All the samples leached normally, and the samples taken for extraction presented pH near 2.2. When the pH was higher than required value, it was decreased with 0.3 M HNO_3. When it was lower, nothing was done in order to avoid the occurrence of any kind of phenomena like the one described above.

Once again, there were huge problems with the filtration. Some ash particles were still present in the leachate, so filtration was required. There were samples which were filtrated with almost no difficulty, but others were very much difficult. In the case of the ash E, the sample nr 1 was easy to filtrate, but the nr 2 was very difficult. Those obstacles in the filtration gave the results that for some samples some leachate was lost. Because of that, the sample nr 2 from ash E lost very much liquid, and was not possible to take out the 10 mL needed for the extraction. To overcome this, only 5 mL of leachate were put to extract with 5 mL of organic agent.

In the case of the ash A, it was impossible to filtrate with the use of the syringe. Vacuum filtration was tried as well, but even that was impossible, because after a few minutes, some gel like substance appeared, which made it impossible to filter the liquid. The samples from the ash A were set aside and that is the reason for why there are no results from any analyses of ash A in the acid leaching method.

Another difficulty was encountered when both samples from ash E were put to extract. First, after shaking, the different phases took a very long time to separate. They had to be left resting during the night, in order to accomplish a better separation. However, it was even so very difficult to separate all the liquid which caused a loss of some volume of each phase.

Despite of all this problems, it was possible to achieve some results.

When analysing the table 13, it is possible to see that the percentages of leaching are high and very close to 100 %. The acid leaching method present better leaching results for the fly ashes from the grate fired combustors than the method using ammonium nitrate did. It is necessary to remember that in the first method, the copper was leached by complexation phenomena, while in this one the copper was leached by dissolution in the acid, due to the strong ability of the acid to break bonds. This characteristic, being good for recovering copper, will bring a disadvantage to the method.

At the same time as the acid is taking out the copper from the ash, it is dissolving compounds of other metals, like for instance zinc, lead and cadmium. This will influence the extraction step since it is possible that these metals will compete with Cu for the binding to the complexating agent LIX 860 N-I.

These results also show that the ash E presents the lowest leaching results, as it happened in the ammonium nitrate leaching. In opposition, the ash C presents the highest leaching results.

In the table 14 the results from extraction step are shown. The values were lower than expected. Since the organic extraction agent is Cu selective, it would be expected to have results near 100 %, but that does not happen. The results from water phase analyses are also a little bit higher, at least when compared with the same results from the ammonium nitrate leaching method. And as it was said before, the water phase data are more feasible and reliable than those from the organic phase.

It is very interesting to observe that almost all the results from ashes B, D and E are lower than 80 %, and once more, the sample's percentage for the ash C are not only the biggest but also bigger than 100 %.

The obtained result for the extraction of the sample nr 2 from ash E is strange. Even if only 5 mL of leachate was extracted, the important volume relation - organic phase volume/water phase volume equal to 1 was maintained, using 5 mL of LIX 860 N-I. The dilution factor was also the same used in the other sample from the same ash, so, there is no apparent reason for the difference between the results from ash E. Both samples should have the same concentration in the organic phase, but that does not happen.

About the stripping step, the results are acceptable, despite of being lower than 100 % as it would be expected. The organic phase percentages are bigger than the ones from the stripping step in the ammonium nitrate leaching method, which is not good, because it says that some copper remained in the organic phase and was not removed.

This time, the contrary happened with ash C. Until now, ash C had the biggest results in this acid leaching method, in the leaching and in the extraction, but in the stripping the opposite occurs.

Next are going to be presented two tables showing the Cu mass results after all the steps for the two methods. It is an easier way to evaluate how much Cu was present after each step and to compare, from the initial amount of Cu, how much was recovered in the end. It is a more practical way to see how the methods worked, and to know the quantity of extracted Cu.

Table 16 – Amount of copper recovered after each step of the ammonium nitrate leaching method.

Ash	Sample	Initial Cu mass (mg)	Cu in leaching liquid (mg)	Cu in organic phase after extraction (mg)	Cu in water phase after stripping (mg)	Cu recovery yield (%)
A	**1**	39.1	35.3	43.4	33.8	86
	2	39.1	35.0	44.6	32.4	83
B	**1**	15.5	13.1	14.1	10.7	69
	2	15.5	13.7	12.1	10.7	69
C	**1**	27.0	30.7	34.4	26.6	98
	2	27.0	30.8	32.1	24.3	90
D	**1**	7.3	5.5	5.0	5.6	77
	2	7.3	5.3	5.1	5.6	76
E	**1**	12.5	7.0	6.1	6.8	54
	2	12.5	6.3	5.8	6.3	50

Table 17 – Amount of copper recovered after each step of the acid leaching method.

Ash	Sample	Initial Cu mass (mg)	Cu in leaching liquid (mg)	Cu in organic phase after extraction (mg)	Cu in water phase after stripping (mg)	Cu recovery yield (%)
A	**1**	39.1	-	-	-	-
	2	39.1	-	-	-	-
B	**1**	15.5	14.4	11.2	12.5	81
	2	15.5	14.2	11.7	12.2	79
C	**1**	27.0	26.1	31.5	26.4	98
	2	27.0	29.7	33.1	27.6	102
D	**1**	7.3	6.6	5.1	4.6	64
	2	7.3	6.2	4.8	4.6	63
E	**1**	12.5	9.5	7.3	6.5	52
	2	12.5	10.1	7.9	6.7	53

3.3. Characteristics of leached ashes

In the end of the experimental procedure all the ash residue were dried and storage. In order to know the effects that the both leaching methods had in the chemical characterization of the ashes, they were analysed by XRD.

Below it will be displayed the different diffractograms obtained with the XRD analyses. First, the results from the raw ashes are going to be compared with the results of the ammonium nitrate leaching method.

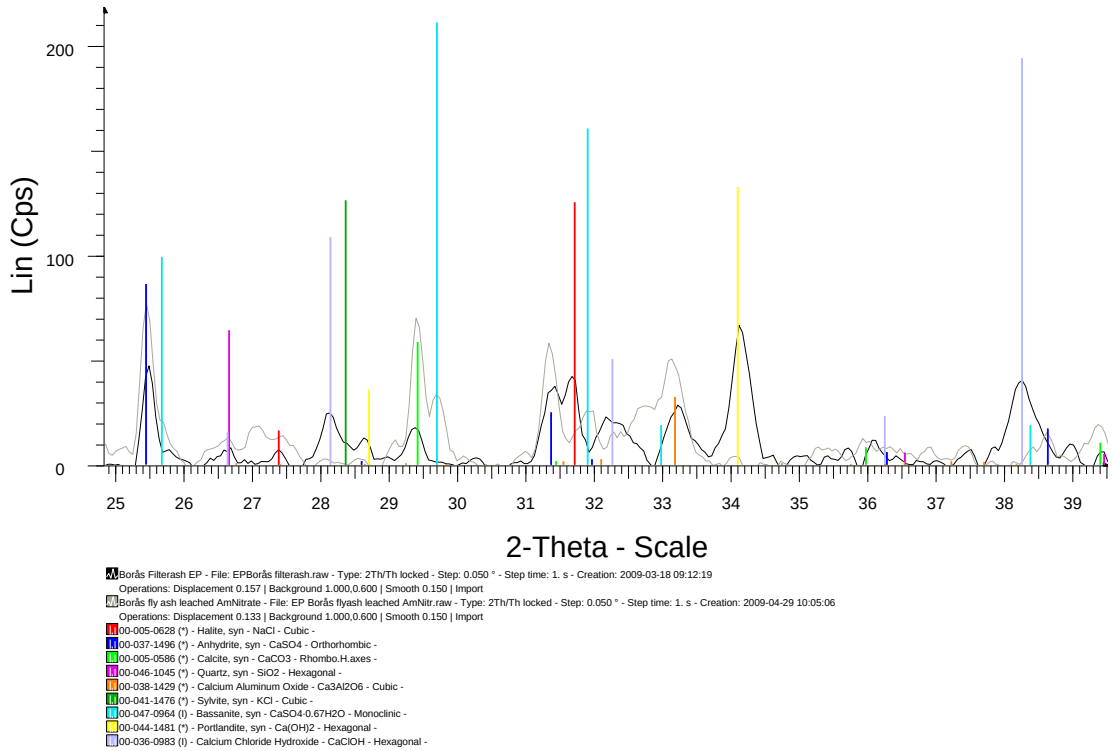

Figure 11 – Comparison of the chemical characterization of ash A in raw state and after ammonium nitrate leaching.

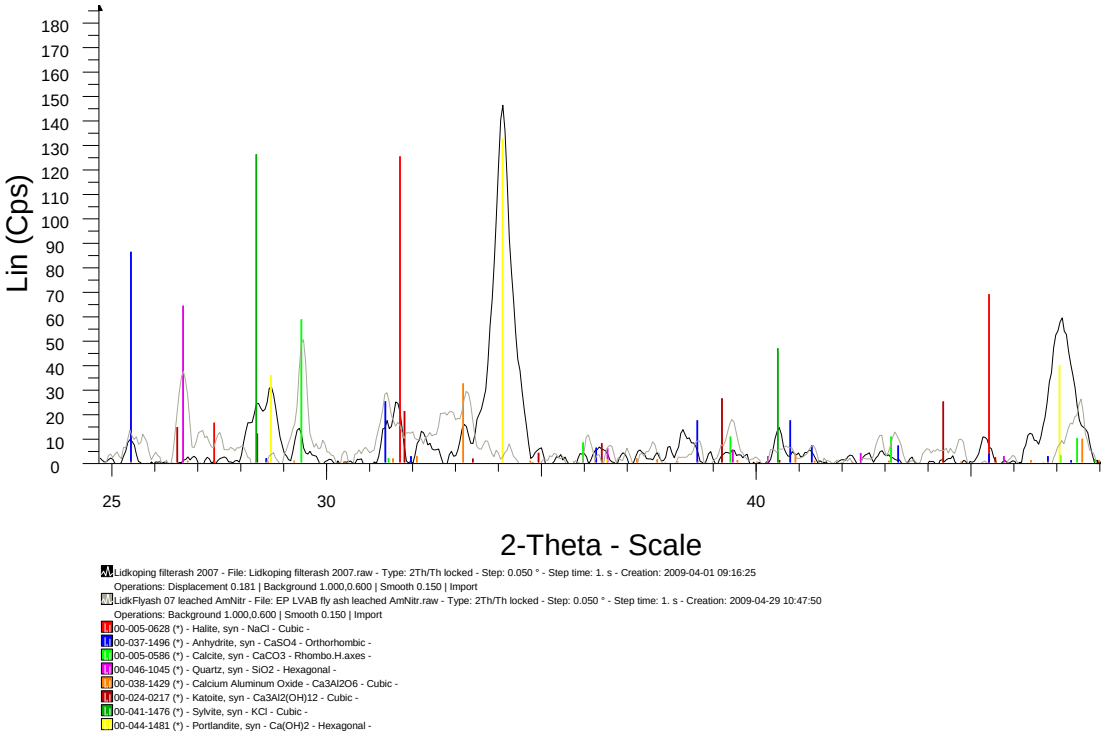

Figure 12 – Comparison of the chemical characterization of ash B in raw state and after ammonium nitrate leaching.

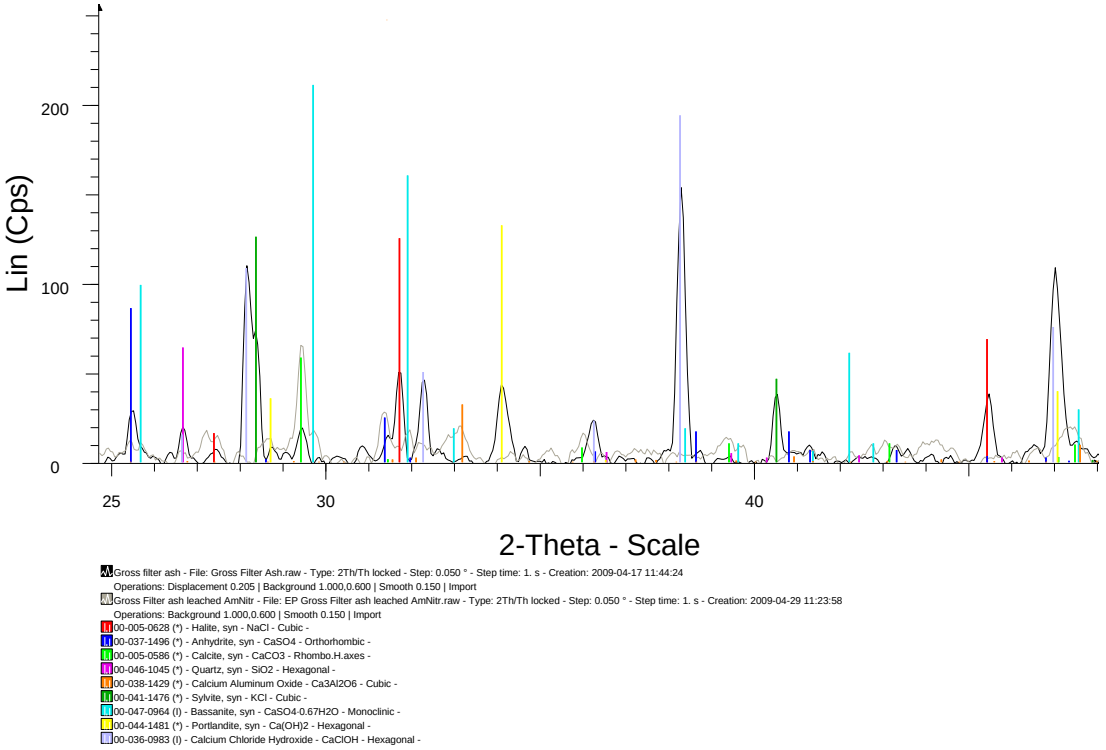

Figure 13 – Comparison of the chemical characterization of ash C in raw state and after ammonium nitrate leaching.

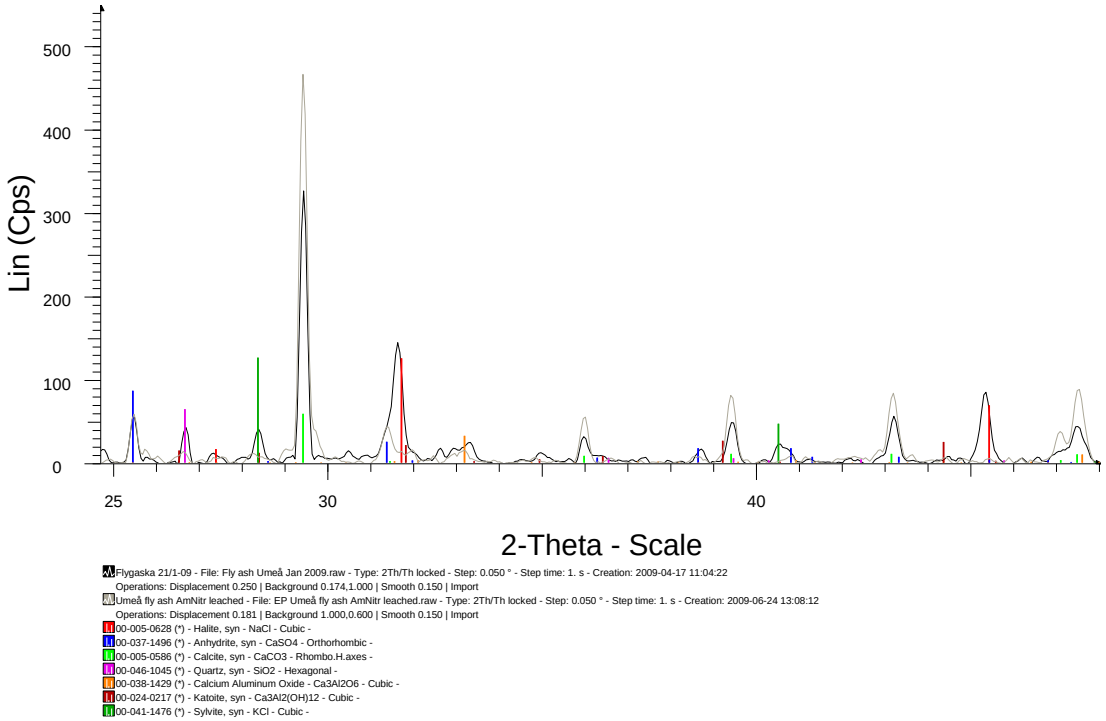

Figure 14 – Comparison of the chemical characterization of ash D in raw state and after ammonium nitrate leaching.

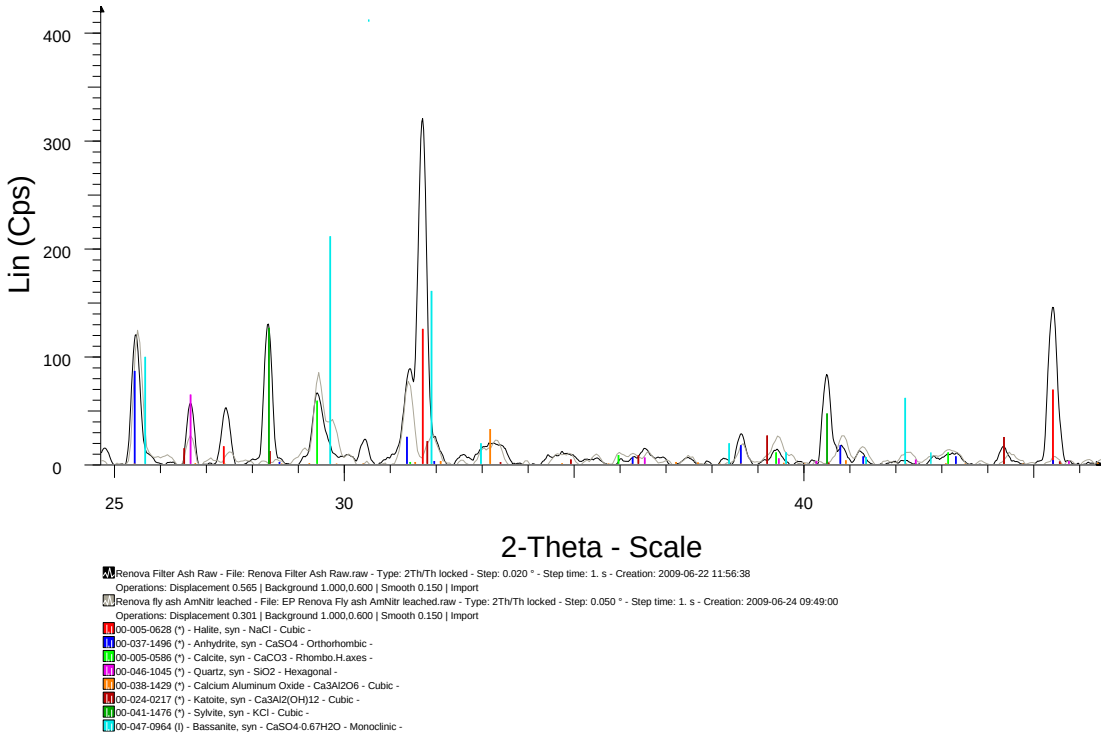

Figure 15 – Comparison of the chemical characterization of ash E in raw state and after ammonium nitrate leaching.

After analysing this diffractograms, it is possible to realize the differences between both ash residues. The ammonium nitrate leaching caused changes in the elements presented in the ashes.

In almost all the ashes, both NaCl and KCl were dissolved and were not found. The same happened to $Ca(OH)_2$ and CaClOH in the ashes that contained those compounds. It is also important to stress out the formation of $CaSO_4 \cdot 0{,}67H_2O$ in ash A, C and E. The $CaCO_3$ amount increased in all the ashes.

It is not possible to see any pattern based on the changes in the other compounds.

Now the results from the comparison between the raw ashes and the ashes after acid leaching are going to be shown. To refer that do not exist data for the ash B residue acid leaching. So, it was not possible to compare it with the respective raw ash.

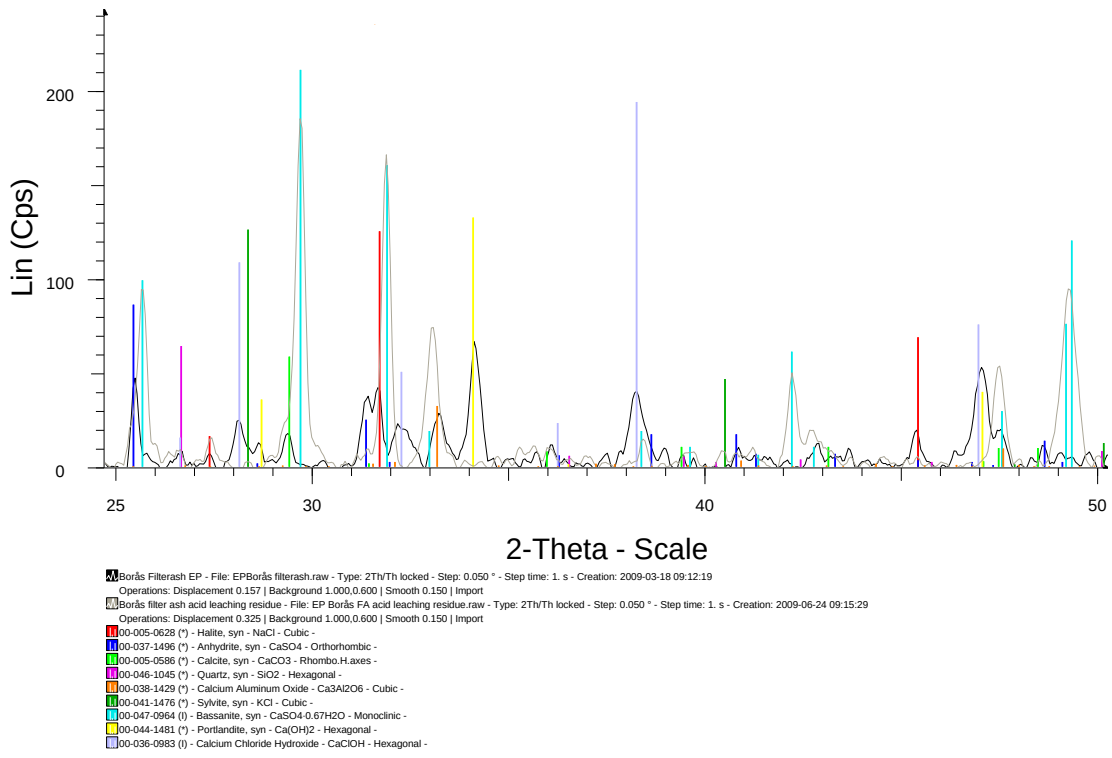

Figure 16 – Comparison of the chemical characterization of ash A in raw state and after nitric acid leaching.

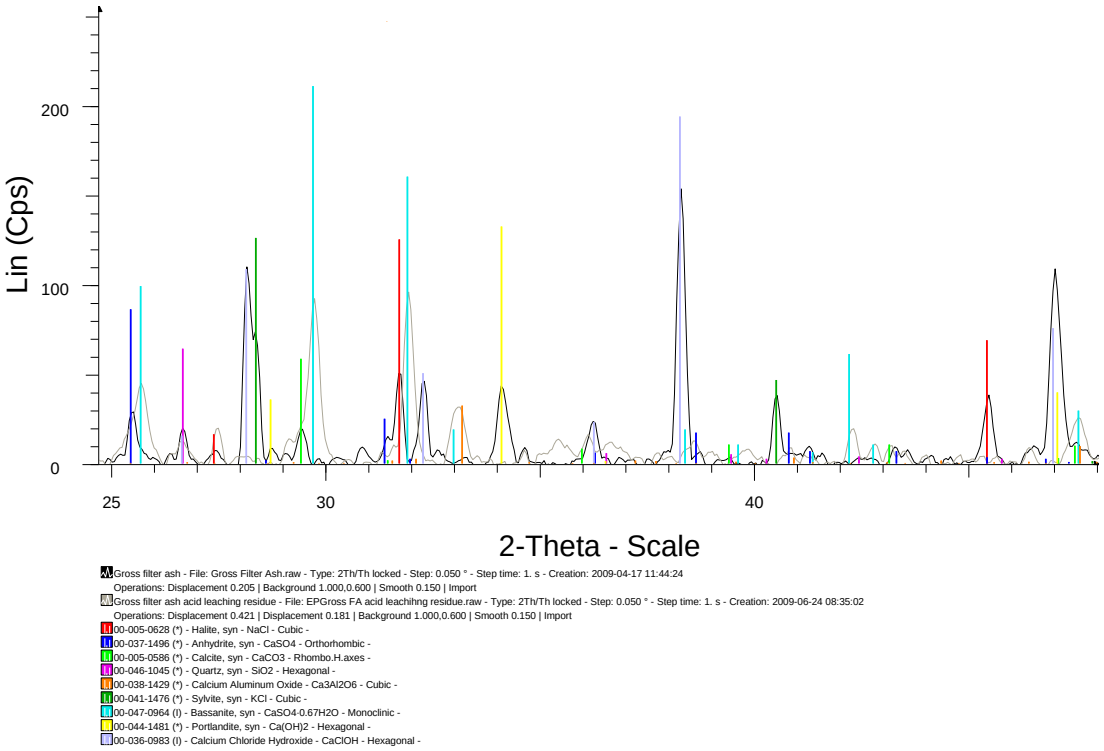

Figure 17 – Comparison of the chemical characterization of ash C in raw state and after nitric acid leaching.

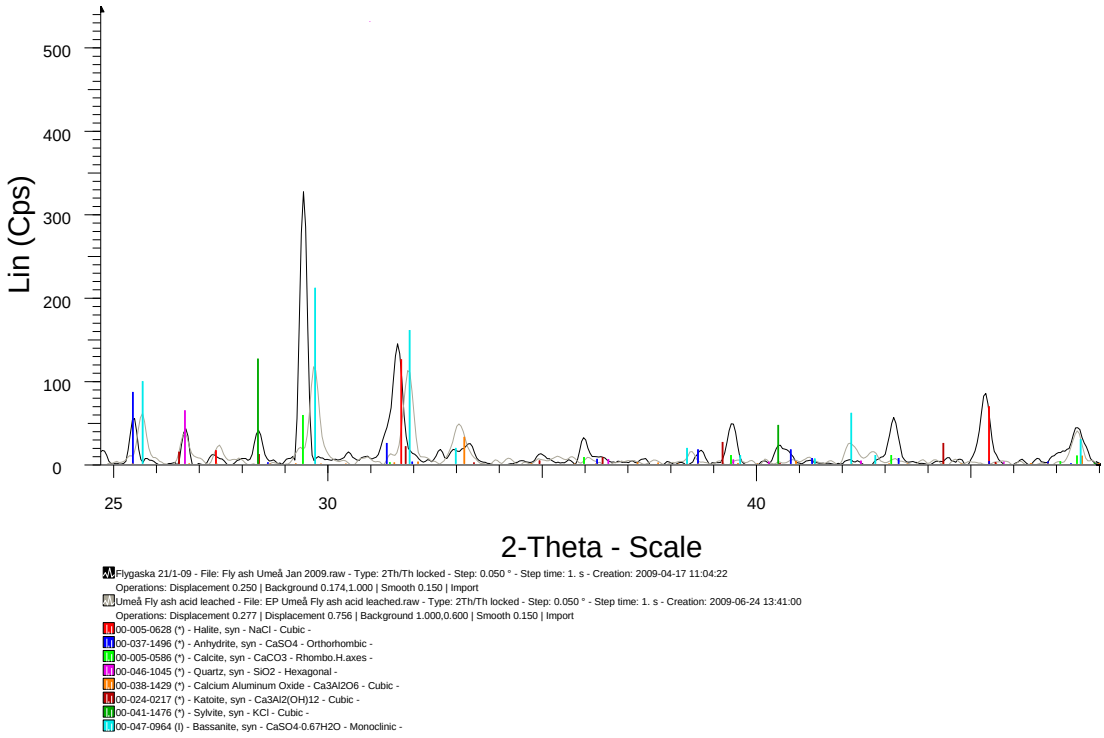

Figure 18 – Comparison of the chemical characterization of ash D in raw state and after nitric acid leaching.

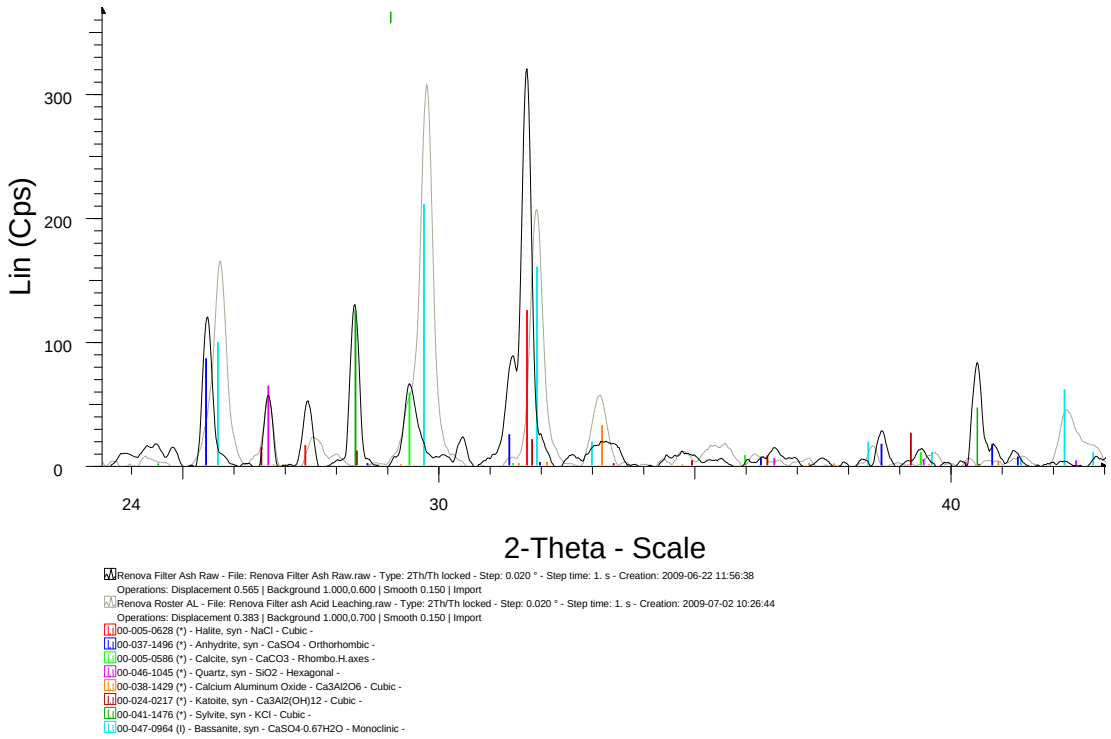

Figure 19 – Comparison of the chemical characterization of ash E in raw state and after nitric acid leaching.

After the analysing these diffractograms, it is possible to see what happened to the chemical compounds after the acid leaching.

As it happened in the ammonium nitrate leaching, both NaCl and KCl were not found in the ashes after the acid leaching, for almost all the ashes. Both compounds were dissolved by the acid. The $CaSO_4$ registered also a decreasing in the amount, and in ash D and E it is not even found. The analyses showed that SiO_2 remained in the same quantity after the leaching. Again, in the ashes which contained $Ca(OH)_2$ and CaClOH, those compounds were not found after the acid leaching. About the $Ca_3Al_2O_6$, it was observed an increasing of the amount in two of the BFB ashes, while in the ash D it was not found and in ash E the quantity remained the same. The amount of $CaCO_3$ decreased in almost all the ashes after the acid leaching. Finally, as it happened after the ammonium nitrate leaching, was observed the formation of $CaSO_4 \cdot 0{,}67H_2O$ in all ashes.

In order to facilitate the comparison of these results, two tables are going to show the changes in the ashes after both leaching methods. These tables are going to compare BFB ashes and GFC ashes separately.

Table 18 – Changes in the chemical characterization of BFB ashes after both leaching methods.

	Ash A - BFB		Ash B - BFB		Ash C - BFB	
Compounds present in Raw ash	**Am. Nitr. leaching ash residue**	**Acid leaching ash residue**	**Am. Nitr. leaching ash residue**	**Acid leaching ash residue**	**Am. Nitr. leaching ash residue**	**Acid leaching ash residue**
NaCl	not found	same amount	not found	-	same amount	not found
KCl	not found	not found	not found	-	not found	not found
$CaSO_4$	more amount	less amount	same amount	-	less amount	less amount
$CaCO_3$	more amount	same amount	more amount	-	more amount	less amount
SiO_2	same amount	same amount	more amount	-	less amount	same amount
$Ca(OH)_2$	not found	not found	not found	-	not found	not found
CaClOH	not found	not found	-	-	not found	not found
$Ca_3Al_2(OH)_{12}$	-	-	same amount	-	-	-
$Ca_3Al_2O_6$	more amount	more amount	same amount	-	more amount	more amount
$CaSO_4 \cdot 0{,}67\ H_2O$	formed	high formation	-	-	formed	high formation

Table 19 – Changes in the chemical characterization of GFC ashes after both leaching methods.

	Ash D - GFC		Ash E - GFC	
Compounds present in Raw ash	**Am. Nitr. leaching ash residue**	**Acid leaching ash residue**	**Am. Nitr. leaching ash residue**	**Acid leaching ash residue**
NaCl	not found	not found	not found	not found
KCl	not found	not found	not found	not found
$CaSO_4$	same amount	not found	same amount	not found
$CaCO_3$	more amount	less amount	more amount	less amount
SiO_2	less amount	same amount	less amount	same amount
$Ca_3Al_2(OH)_{12}$	not found	not found	not found	same amount
$Ca_3Al_2O_6$	same amount	not found	same amount	same amount
$CaSO_4 \cdot 0{,}67\ H_2O$	-	formed	formed	formed

4. Discussion

The leaching results showed in the previous section demonstrate that the ashes are different from each other, since they have different leaching data between them. They present different leaching results in both methods as it was expected. In the ammonium nitrate leaching method, the ash C presented the best leaching results (114 %), whereas the ash E with 51 % of leached Cu is the ash with the lowest results. In the acid leaching method, once again the ash C is the one with the best results (110 %). The ash with the lowest results is the ash E, with 76 % of leached Cu. With these results, it is possible to say that there is no direct relation between the amount of Cu present in each ash and the correspondent amount of leached Cu. However, the differences in leaching efficiency can be the result of differences in copper speciation in the ashes, i.e. the copper content may be bound in different compounds. Not much is known about the actual speciation of Cu in ashes since the relatively low concentration makes it difficult to find a method that can identify the compounds in situ. Work along this line is being done at the department of Environmental Inorganic Chemistry Chalmers University of Technology using synchrotron based Extended X-ray Absorption Fine Structure spectroscopy. Preliminary results indicate copper mainly in oxidation state II and that the nearest neighbour atoms are oxygen or other Cu atoms. No data are available on fly ash from grate fired boilers so far.

In the extraction step for the ammonium nitrate method, the results were near 100 % for almost every ash. This confirms what was said before. The extraction organic agent, LIX 860 N-I, is Cu selective and it is very effective recovering the Cu from the water phase.

In the same step of the acid leaching that does not happen. Despite of the results not being very low, they are much lower than 100 %. That makes this method less efficient in the extraction step than the other one. One explanation for this is the high dissolution power of the acid in the leaching step. During that step, the acid dissolves more easily a bigger quantity and variety of other metals than the ammonium nitrate does. That will influence the extraction step. In the second step of the acid leaching, there will be more metals and in

bigger amounts available to compete with Cu for the LIX 860 N-I. That can be one reason for the lower results achieved in the extraction step of the acid leaching.

In the stripping step, the results from the acid leaching are better than the others (those from the method with ammonium nitrate leaching). Comparing both tables 11 and 15, the results from the ammonium nitrate method are not satisfactory. In the end of the procedure, it was expected to have all the Cu in the water phase, but that does not happen for any ash. In ash A, B and C the results are low (between 70 and 80 %) and for the other ashes the results are bigger than 100 %. Analysing the data for the remaining Cu in the organic phase that was not stripped, it is possible to see that every sample still have Cu in the organic phase, which means that not all the Cu was stripped from the organic to the water phase. Thus, the parameters used in the stripping step have to be optimised.

In the same step for the acid leaching method, the results are better if it is taken in consideration the results for water phase stripping. Only ash B present results higher than 100 %. All the others have results a little lower than 100 %. The percentage values are still under 100 %, but at least they are closer than the ammonium nitrate ones. The AAS offers reliability when measuring water phase samples, but the same does not happen with organic samples. The results from the amount of Cu that was not stripped from the organic phase are high and bigger than the ones in the ammonium nitrate method. This confirms that are still Cu present in the organic phase even if it is not too much, due to the uncertainties of the measurement in organic phase samples. It is important to say that this method is not well developed yet. It is possible that with some more experiments and adjustments it gives the right results, needed to do a proper comparison between this and the ammonium nitrate leaching method.

It is important to say that despite of the fact the ammonium nitrate results are not as they were expected, they do not make this an impracticable method. It would be necessary to have the acid leaching method developed at the level of the first one to allow a correct comparison.

The results presented in the literature are in agreement with the results obtained in the acid leaching. Van Herck P. *et al*. shows that sequential extraction can recover Cu from ashes by acid leaching and the pH influence it. The pH results in his work confirm what happened in the acid leaching. The final pH of the leachate is bigger than the initial pH. That

is due to the alkalinity of the ash, that by the time some metals are being dissolved, it makes the pH rise [14].

More information about the influence pH has under the leaching is given by Kyung-Jin Hong and co-writers [15]. They proved that the leaching percentage increases with the decreasing of the pH in the acid leaching. Acid had its optimal leaching conditions at low pH values (pH 4 or less).That is one reason for the low pH (2.2) used in this leaching method.

In this acid leaching extraction, the leaching agent was the nitric acid. One question that might come to light is what could happen if the leaching agent was different? Would the results be different, or equal? Previous work says that the leaching depends on what acid is used as leaching agent [14]. The results are influenced by the type of the acid. They show that with hydrochloric acid, most of the Cu stayed in the ash, whereas with acetic acid the leaching results were very high.

Kyung-Jin Hong and co-writers also say that the greater the acid concentration is, the higher leaching values are. In this work, that was difficult to put in practice. In the beginning, 3 M HNO_3 was used and accordingly to the information provided, that acid should give a higher leaching percentage. But then it was necessary to rise the pH to 2.2 in order to reach the organic extraction agent optimal conditions. It gave problems as it was already reported previously.

After analysing the experimental results, it is important to understand why the ashes behave so differently between them. Despite of the ashes originating from only two different types of incinerators, they came from different places and were produced in different years. That is one reason that can explain the different composition and behaviour of the ash when leached. This is reinforced by Van Herck and co-writers. They say that the composition of the ash influences the leaching results. They exemplify that when extractions are made with ashes containing different amounts of Ca and Al, the leachate step pH changes, influencing the leaching amount. That is due to the alkaline characteristics of Ca and Al, which make the pH values increase.

One disadvantage of this acid leaching method is that it requires a large amount of acid, which is going to complicate the handling of the acidic residues [15]. The nitric acid is poisonous, corrosive and it is also a strong oxidizer [16]. In the case of ammonium nitrate, it is possible to say that it is an oxidizer and very explosive [16]. So, they are both dangerous compounds that require caution when handled.

Kyung-Jin Hong and co-writers also compare two methods, an acid leaching method with HCl and a method using NTA, nitrilotriacetic acid, EDTA, ethylendiaminetetraacatate and DTPA, diethylenetriaminepentaacatate as leaching agents. They say that one advantage of using chelating agents is their ability to work with moderate pH. In those pH values, the chelating agents managed to extract more Cu than the acid, but with low values of pH, the acid leaching was as effective as the other method. Even when the results are similar, the acid leaching method has the inconvenience of producing acidic residues. One more advantage of chelating agents leaching method is being pH independent, while the acid leaching method is pH dependent [15].

It is also important to know in the end of the procedure, the amount of other metals leached from the ash. It should be possible by analysing the ash residue from the leaching by ICP-MS. Such thing was not implemented in this work due to the lack of time.

Maybe at this time, it cannot be possible to properly compare both leaching methods. In the future, after more work, adjusts and experiments it will be possible to know which one is the best method for Cu extraction from MSW fly ash.

5. Conclusions

- Cu leaching behaviour is different in each ash;
- The acid leaching method presents better leaching results than the ammonium nitrate leaching method;
- Ash C showed the higher leachability while ash E was the one with the lowest leachability;
- In the extraction step, the ammonium nitrate leaching method presents better results than the acid leaching method;
- In the stripping step, the acid leaching method presents better results than the ammonium nitrate leaching method;
- The acid leaching method is influenced by the pH. This method has better results at low pH values;
- The composition of each ash influences the leaching. This effect need further investigation;
- The acid leaching method presented many experimental problems, unlike the ammonium nitrate one;
- It is possible to recover Cu from MSW fly ash by both methods;
- The acid leaching method needs some adjusting so both methods can be totally compared and a conclusion can be reached about which method is the best for Cu extraction from MSW fly ash.

6. Further work

This work is one more help to the development of the knowledge about MSW fly ash. In the end of this thesis, it is possible to realise that many questions were raised and remained unanswered. More work is needed in order to understand and solve those questions.

Next, some issues that need further investigation are going to be reported.

- More work to understand clearer the pH influence over the leaching step of the ashes and its consequences;

- Investigate the ashes D and E leaching results under a pH value of 9;

- More investigation about the different behaviour of the ashes in the leaching step;

- More work to overcome the difficulties in the acid leaching method;

- Further analyses to know what metals and in which quantity are leached together with Cu from the ashes;

- Evaluate the efficiency of this methods in a real-life scale;

- More investigation about ways to turn Cu available in the market and investigate the economic revenues.

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