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Thermal Process of Flue Gas Desulphurization Gypsum

Diploma Thesis

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Declaration

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Prague, 26th April 2021

Rachel Samuel

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Thermal Process of Flue Gas Desulphurization Gypsum

SUMMARY

The strong pressure on the quality of air led to the desulphurization of smoke coming from the power plant facilities burning the brown coal. The by-product coming from desulphurization contains a large amount of sulphur, which is important nutrient for crop.

The samples were taken from 4 different the electrical power plants burning the brown coal in the Czech Republic. The aim of this study was to see the effect of pyrolysis under an inert atmosphere at two different temperatures 600 °C and 800 °C, as a thermal treatment on the characteristics of flue gas desulphurization gypsum.

Determining the influence of pyrolysis treatment on total and available content and pH values and electrical conductivity (EC) changes. The flue gas desulphurization gypsum (FGDG) was tested for determine selected elements in three groups: Macronutrients (Ca, K, Mg, P, S), Micronutrients (Cu, Fe, Mn, Mo, Zn, Ni) and Toxic elements (As, Cd, Cr, Pb).

The increasing of the temperature had the influence on weight loss after pyrolysis, when FGDG-A had lost 4.1 % of its weight at 600 °C, while it lost 54.5 % of its weight at 800 °C, and for FGDG-D the samples lost 8.8 % of its weight at 600 °C, when it lost 19.2 % at 800 °C, and the pH of FGDG-D at 800 °C had reached 11.22 und. On the total content of macronutrients Ca and S had increased at the 800 °C to reach 279.8 g/kg and 178 g/kg respectively for FGDG-A. The available contents of macronutrients S were higher at 600 °C in FGDG-A and FGDG-B (22.72 mg/kg and 26.27 mg/kg) respectively. For toxic elements, total content the increasing of temperature was good to decrease the concentration of As and Cr, at 800 °C (3.5 mg/kg and 2.6 mg/kg) respectively in FGDG-C, and same for availability, the high temperature affected FGDG-B and FGDG-C specially at 800 °C to be (51.6 mg/kg and 1.35 mg/kg) respectively.

This investigation reveals, that the increased temperature during the pyrolysis of flue gas desulphurization gypsum can affect both the total and available concentration of some elements.

KEYWORDS: Pyrolysis, gypsum, trace elements, calcium, sulphur

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1. Introduction

The current status of energy production, transportation, industry, inadequate waste management (burning), and growing population has a direct impact on the deterioration of air quality, according to data reported by the World Health Organization, near 91% of the world population lives in populated centres that exceeds the maximum values of contaminants in air (Sivarethinamohan *et al.*, 2020).

Coal is one of the world's most substantial and delivered on a large-scale as a fossil fuel. On the other hand, 14 billion tons of carbon dioxide (CO_2) is released in the atmosphere from burning coal production from power generation every year (World Nuclear Association, 2020). The improvement of the new clean coal technologies is an effort to deal with these problems, it refers to a range of systems and technologies that will reduce the health and environmental effects of air pollution from coal-fired power plants and heavy industry. The main gases that cause acid rain are (SO_2) and (NOx), which cause visible air pollution, sickness, and early death of people. FGDG is a by-product of coal-fired power plants SO_2 clean operation. When SO_2 gas is sequentially reacted with calcite ($CaCO_3$) and wet limestone gypsum ($CaSO_4$ $2H_2O$) is formed. When manufactured in this manner, FGDG is relatively inexpensive in comparison to commercial gypsum. FGDG has mainly been used in building, but it is also being considered for use in agriculture. In agriculture, gypsum treatments are useful because they are a source of sulfur and can be used as soil reform to improve soil structure, drainage, and aeration (Han *et al.*, 2016).

The aim of this Diploma Thesis will be to check quality of FGDG and analyze the effect of pyrolysis under two different temperature (600 °C and 800 °C) as a thermal treatment on the characteristics of flue gas desulphurization gypsum, like pH, and EC. To determine the influence of pyrolysis treatment on total and available content of trace elements and sulphur compounds present in FGDG.

KEYWORDS: Pyrolysis, gypsum, trace elements, calcium, sulphur

2. Hypothesis:

The strong pressure on the quality of air led to the desulphurization of smoke coming from the electrical power plants burning the brown coal. During desulphurization process the by-product, flue gas desulphurization gypsum (FGDG) is released contains a large amount of sulphur, which is important nutrient for crop. Unfortunately, the gypsum contains some contaminants which can limit the application to the soil. Before any application the FGDG has to be treated and properly controlled to decrease number of possible contaminants.

Thermal reductive treatment of flue gas desulphurization gypsum can influence the total and available content of trace elements and can also change the availability of sulphur for plants according to temperature applied.

3. Objectives of work

- To evaluate the effect of pyrolysis under two different temperatures (600 °C and 800 °C) as a thermal treatment on the characteristics of flue gas desulphurization gypsum, like pH, and EC.
- To determine the influence of pyrolysis treatment on total and available content of trace elements and sulphur present in flue gas desulphurization gypsum (FGDG).

4. Literature Review

4.1 Greenhouse gases

Greenhouse gas (GHG) is a gas that absorbs and emits radiant energy within the thermal infrared range (Mann, 2019). All people, animals, and even plants should live in areas that contain good air quality to live a healthy life, but for the reason of ongoing and developing life, we can say that the contamination of the air is increasing year after year. Not only the cities developments are the cause of this pollution, but also the population growth can cause contamination (Mabahwi *et al.*, 2014), The pollution of the air leads to global climate change, health effects on human, and for sure negative impacts on the environment. Major pollutants include of suspended matter ($PM_{2.5}$ or PM_{10}), nitrogen oxides such as carbon monoxides, sulfur oxides, arsenic, and metals such as copper, cadmium, and mercury and carbon dioxide (Sivarethinamohan et al., 2020). The increase of CO_2 in the atmosphere, this makes the atmosphere warmer by catching heat that leads to global warming, the amount the temperatures will increase if CO_2 is doubled from pre-industrial levels (Baird, 2012).

Climatologist agreed that urban developments have changed earth's atmosphere during the past two centuries. The radiation coming from UV will cause harm not only for human beings and to the environments, but it can also easily cross the glass walls of the greenhouse, UV transmission in greenhouses is determined by the glazing content. UV-A is transmitted by ordinary glass in the range of 65 to 75 percent, but UV-B is only transmitted in the range of 3 percent or less. UV stabilizers are added to most plastics used to glaze greenhouses to prevent them from degrading, but these stabilizers degrade over time, allowing more UV to pass through. even during winter (Lallanila, 2018).

Figure 1 shows the trends and behaviour of carbon dioxide (CO_2) emissions from 1990 to 2020 for the countries that are considered the major contributors to GHG according to EPA, it is possible to observe that China reports the highest increase in CO_2 emissions with a vigorous increase since 2002 as a major product of its industrial development; conversely the European Union is showing a slow decrease in its emissions since 2008 (Lallanila, 2018).

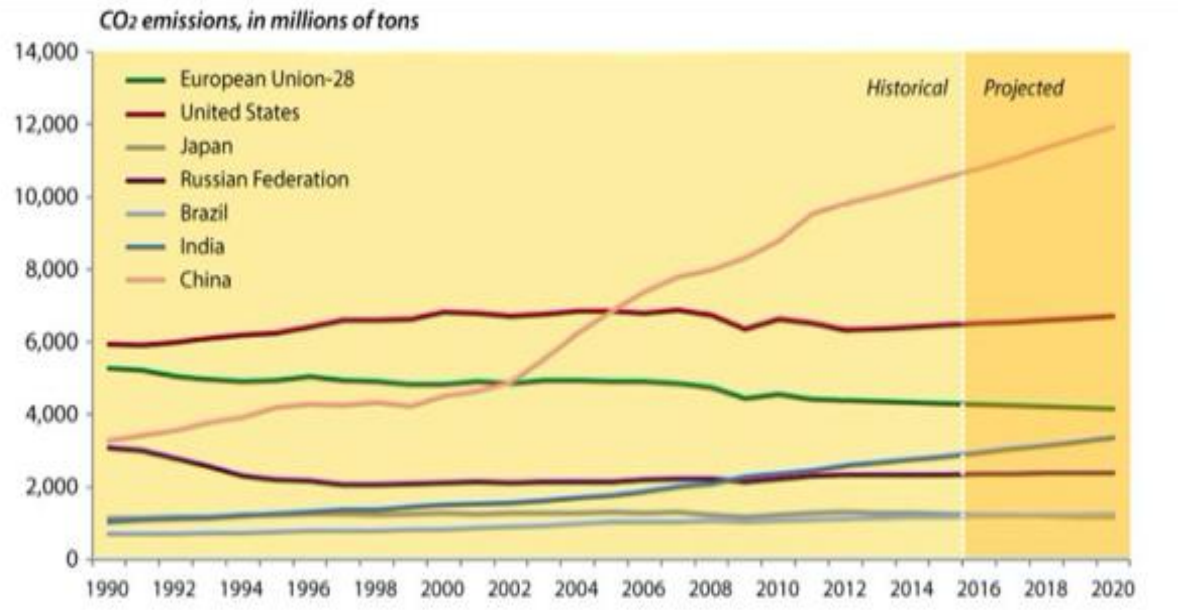

Figure 1. Greenhouse gas emissions for major economies expressed in CO2 emissions in millions of tons from 1990 to 2020 (Lallanila, 2018)

Increasing global warming, the knowledge of emissions of greenhouse gases features to electricity production from an environmental point of view has been an increasingly a major issue. Fuel placed a major risk on the environment, not just straight from burning, but also from mining and transportation, in this regard, tools, such as Life cycle assessment (LCA) and energy analyses of electricity generation systems undertaken this case widely for the last couple of decades (Odeh & Cockerill 2007). Figure 2 shows the different human activities that have a direct and indirect impact on global warming and climate change, showing the health and environmental consequences caused by these anthropogenic emissions causing climate change in a several ways which will be a major cause in increasing the anthropogenic greenhouse gas emissions, for example (transportation, energy generation, agriculture, industry and economy), all of those activities cause air pollution which is responsible for heat stroke, UV radiation that can cause skin cancer, skin burn and eye damage, high temperatures which will lead to sunburn, weather events and disasters, rising sea level (Gao *et al.*, 2018).

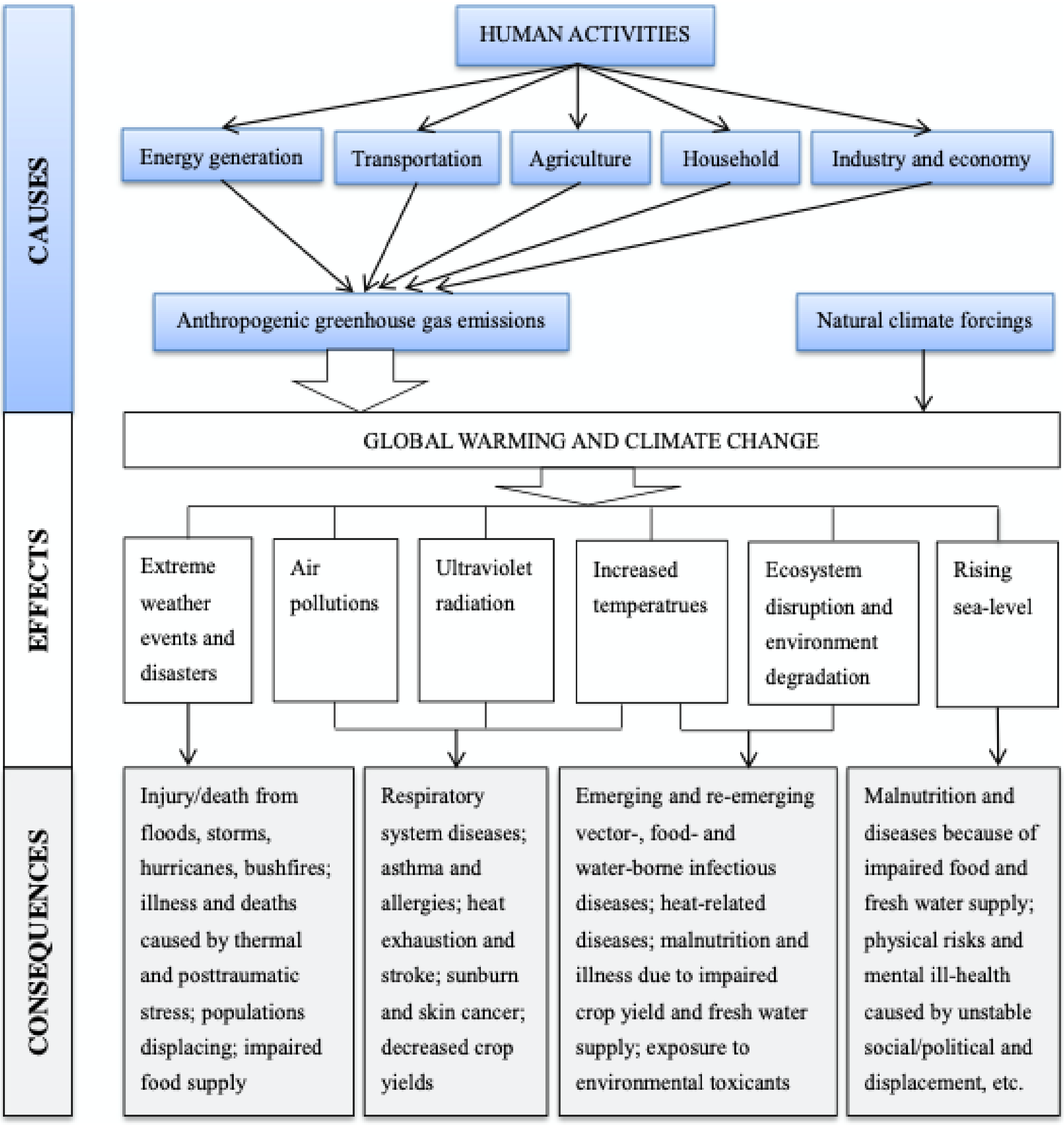

Figure 2. Schematic summary of climate change determinants and potential pathways through which climate change affects human health. (Gao et al., 2018)

Akdag & Yildirm (2020) carried out a study using retrospective data (1995 – 2016) from 28 EU countries regarding to the energy efficiency index and the greenhouse gas emission from energy, industrial, agricultural, waste management, land use, land-use change and forestry the study focused on how the energy efficiency was divided by the gross domestic product (GDP) by gross domestic energy consumption to give a yearly overview. The study reports registered activities in effect of energy demand and shows that energy demand is removed with the increase of gross domestic product. Greenhouse gas release from Kyoto basket which contain the six greenhouse gases: carbon dioxide (CO_2) as well as methane (CH_4), nitrous oxide (N_2O) and F-gases (hydrofluorocarbons, perfluorocarbons, nitrogen trifluoride (NF_3) and sulfur hexafluoride (SF_6) in the utilized gases that are measured in greenhouse, it is translated into a single indicator expressed in terms of CO2 equivalent using each gas's individual global warming potential. (Akdag & Yildirm, 2020).

The sulphur-related contaminants produce major issues that effects consistently the environment, the most common is acidic rain, which appears when nitrogen oxide (NO_2) and sulfur dioxide (SO_2) react with water and oxygen in the atmosphere. These acid gases are mainly developed from coal burning, in particular coal with high sulphur content, from electricity production (Taerakul, 2005).

4.2 Coal-Fired Power Plants

The first coal-fired power stations were built in the late 19th century. The coal-fired power plants are also outlined as “the electrical power generating stations where coal is the fuel to combust heat source” (Pešek *et al.*, 2005) is a physical and chemical mixed “flammable”, sediment rock composed of organic and inorganic matter. Organic portion of coal, contains carbon, hydrogen, oxygen, and a smaller amount of sulfur and nitrogen. Inorganic coal contains of ash formation that spread cross the coal (Miller, 2004; Pešek *et al.*, 2005).

In the Czech Republic, there are some negative consequences of power generation on environment. In 2003 63% of the electricity was made of coal mining. Around 34% of electric power was produced in nuclear power stations, 2% in hydroelectric power plants, and 1% derived from wind, solid bioenergetics, manufacturing, and urban waste burns and sewage gas. Since bituminous coal is mainly used for coke production, it has only been burned in two power plants. The main areas of lignite mining often referred to as brown coal, is a soft, brown, sedimentary rock developed from naturally compressed coal, occur in three places: North Bohemian Basin, Sokolov Basin, and South Moravian coal field (Pešek *et al.*, 2005).

All of the large power plants in the Czech Republic started the desulphurization process after the year 1990, that leads to the decrease of SO_2 outflow by 90% per capita. Nevertheless, there are still some of the dangerous substances being released to the atmosphere while burning the coal using the Clean Coal Technology (CCT), which were created to keep using coal to produce electricity while addressing the environmental liabilities of this fuel (Robl *et al.*, 2017), implementing a variety of new options for the control of sulfur oxides, nitrogen oxides, and particulate emissions from electric power plants operating on coal, for example, while firing the brown coal in fluidization furnace (350 $t.hr^{-1}$) around 80% of mercury (Hg), 5-10% of selenium (Se) and 70% of chlorine (Cl) are released. Those heavy metals that are released from the coal burning stay in the atmosphere for a long period and can be transported to many different places (Pešek *et al.,* 2005).

Table 1 shows the three major basins in the Czech Republic where lignite mining is carried out, its main utilization and the range and average of Arsenic content in the coal from the mentioned basins, Sokolov basin uses as source lignite to sub-bituminous coal for energy production, the average content of Arsenic content is 333 ppm, being the highest content among the 3 studied basins, and the lowest arsenic content between the three basin is the South Moravian coal field (Pešek *et al.,* 2005).

Table 1. Arsenic content in coal from different Czech basins (Pešek et al., 2005).

Basin	Rank	Utilization	Range (ppm)	Average (ppm)
North Bohemian Basin	Lignite to sub-bituminous coal	Energy production, home heating	0-1,101	40
Sokolov Basin	Lignite to sub-bituminous coal	Energy production, home heating	0-2,202	333
South Moravian coal field	Lignite	Energy production, home heating	4-194	28

4.3 Flue Gas Desulphurization Gypsum production

4.3.1 Flue Gas Desulphurization Technology

Flue Gas Desulphurization Gypsum (FGDG) is a commodity-specific of sulfur (S) dismissal from fuel burning gases in Flue Gas Desulphurization (FGD) method in coal-fired power plants. In the past few years, the coal-fired power plants were increasing while using SO_2 washing method to stay on the safe side of the environment, rules that were used to restrict acid in the atmosphere made by SO_2 emissions. Usually, the technology of FGD can be classified as Once-Through wet FGD technology, Once-through dry FGD technology and

Regenerative, once-through FGD processes: in this method, SO_2 is continuously bound to the absorbent, which will be used as a waste or by-product, these methods contain wet and dry category. or Regenerative processes: in this method, the absorbent is regenerated later than the uptake of SO_2, and in this method, the SO_2 that were caught will be released. It depends on how the solution is handled after it is absorbing the SO_2 (figure 3) (Pandey *et al*., 2005).

Once-through Wet FGD Technology: In an absorber, SO-containing flue gas comes into contact with two alkaline aqueous masonry. The concrete is normally made of both of lime (90% or more $Ca(OH)_2$), or limestone (90% or more $CaCO_3$). In the absorbent, SO_2 decomposes into sludge and began to react with the base liquid particles. The spent sorbent is disposed of as a wastewater dissolved SO_2, because it prevents the chemical reaction in the tanks, which will be holding the time for ground fine limestone and lime particles in the sludge to melt away and then the reaction will be done with disappearance of SO_2. The results of this reaction, that sulphite and sulphate crystallization has been found in the tend reaction, and the basic liquid of the sludge is used up (Srivastar & Jozewicz, 2001).

Once-through Dry FGD Technology: SO_2 is permanently attached to the sorbent in these systems (most frequently), which must be disposed of as waste or used as a byproduct (e.g., gypsum) (Pandey *et al.*, 2005)

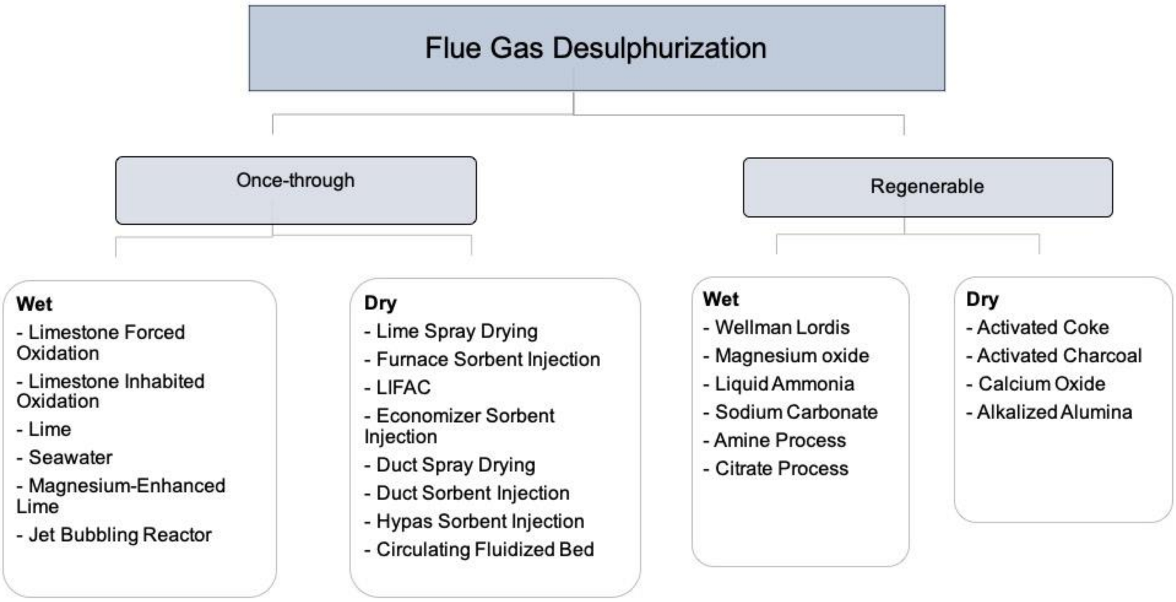

Figure 3. Classification scheme of Flue Gas Desulphurization Technology (Pandey et al., 2005)

4.3.2 The properties of Flue Gas Desulphurization

To enhance the performance of SO_2 emission reduction, flue gas desulphurization research and innovation have made progress to the issue that a certain method is accessible to include a wide range a location specific, scientific and economic dimensions (Pandey *et al.*, 2005).

FGDG is available in two forms: encapsulated and non-encapsulated, and is used in a number of applications. The most common beneficial application of FGDG is in the manufacture of wallboard (i.e., drywall made primarily of dihydrous calcium sulfate). FGDG can be used as a fixed retarder in concrete and grout, as well as an ingredient in cement and asphalt processing. The primary land application of FGDG is in agriculture, where it is used as a soil amendment and fertilizer. (Koralegedara *et al.*, 2019).

Several innovations are currently being developed to provide an alternative to usual burning methods. The wet oxidation, pyrolysis, and gasification processes are the most common. Pyrolysis has more benefits over other techniques. More useful products from pyrolysis include gas, oil, and solid char, which can be used as fuels or petrochemicals (Karayildirim *et al.*, 2019).

Despite the fact that the overall utilization of FGDG is growing all over the world, the value of its use is still down compared to its manufacture (Wang, 2018). The usage of FGDG as a useful result in farming is examined to improve the demand of FGDG and decrease the environmental-economic effect of disposition. The sustainability of the agricultural use of FGDG is determined by the observable decrease of the negative repercussions and the ability of the management systems to maintain the environmental strengths of this alternative (Wang & Yang, 2018), table 2 shows the FGDG production and utilization rate during the period 2009 - 2013 of two major producers (China and USA), China has a higher utilization rate in 2012 reached 69% compared to USA that reported 47 % in the same year (Wang & Yang, 2018).

Table 2. Generation and utilization of Flue Gas Desulphurization Gypsum (FGDG) in China and USA (Wang & Yang, 2018).

Country	**Year**	**FGDG production (MT)**	**Utilization (%)**	**Country**	**Year**	**FGDG production (MT)**	**Utilization (%)**
China	2009	43.0	55.8	**USA**	2009	16.3	49.7
	2010	52.3	68.8		2010	20.0	48.5
	2011	67.7	70.9		2011	22.7	47.1
	2012	69.0	71.7		2012	23.5	47.0

The FGDG production in both countries is different, in China it is about 70 MT (million tons), in USA it is about 20 MT (Wang & Yang, 2018).

China uses coal in energy production in higher proportion than any other country it is about 70%, most of the coal resources is for the energy production. About 80% of the coal usage in China is used straight for burning, coal-fired power plants. The most pollutant gas in China now is SO_2, which produced by human activities and it comes from the coal-fired flue gas large emissions (Wang & Deng, 2015).

The available amount of SO_2 in the air (1 – 5 ppm) is harmful for the human health, and with the reaction with oxygen and water it will form acid rain, which will be dangerous for the environment (Wang & Deng, 2015).

The world’s second largest country in the production of FGDG is the United State of America, earlier on 1990’s the FGDG production was around 2 MT. In year 2000 the production was around 9 MT, and in 2006 increased to 12 MT, and reached 20 MT in 2015. The main usage of FGDG in the United States is the fabrication gypsum board, and building cover and cement retarder (Wang & Deng, 2015).

4.3.3 Physicochemical properties of FGDG

Flue gas desulphurization gypsum (FGDG) is an industrial by-product generated during the flue gas desulphurization process in coal-fired power plants.

Flue gas desulphurization gypsum contains calcium sulfate ($CaSO_4$) as a main component, but it also contains Al, As, Ba, Ca, Cd, Cr, Cu, Fe, K, Mg, Mn, Pb, S, Si and Zn. Some of these components can be found as toxic elements, but it depends on the composition presents of coal burning and limestone, for instance, Na salts are used as an aid that can increase the content of Na in the final FGDG (Koralegedara *et al.*, 2019).

The chemical structure of FGDG changes due to the scheme of the electricity generation stations, terms of service, and use of materials. Physical and chemical characteristics of FGDG are clearly related to the class of coal than the main combustion and scrubbing technologies were used to erase sulfur (Wang & Yang, 2018). It is also the equivalent degree of humidity and it is a main component, $CaSO_4 \cdot 2H_2O$, of natural gypsum and has better technical characteristic. Mg and Si oxides are the major components in FGDG and natural gypsum because they both have alike chemical structure even with small components (Wang & Yang, 2018).

The availability of S and Ca in FGDG is very useful for growing crops and its yield, and it can be used the most in the soils that have extremely low levels of Ca (Wang & Yang, 2018).

In Table 3 is presenting the content of modern FGDG produced by 8 electricity generation stations in the USA from 2007 to 2010 according to Kost *et al.,* (2018), cited by Koralegedara *et al.,* (2019). This table shows that the modern FGDG includes low quantities of toxic elements, which make it more friendly to the environment (Koralegedara *et al.*, 2019).

Table 3. Content of elements in Modern Flue Gas Desulphurization Gypsum (FGDG) (Koralegedara et al., 2019)

Element	**Modern FGD (mg/kg)**
Al	140 - 2,120
As	1.35 – 2.99
Ba	6.91 - 123
Ca	160999 - 243000
Cd	0.08 – 1.12
Cr	1.8–13.2
Cu	< 0.378–3.25
Fe	334-1,230
K	183–700
Mg	600-7,430
Mn	0.97–160
Pb	1.33 – 1.84
S	143,000–209,000
Si	176-1,230
Zn	4.26–29

Source: Kost *et al.,* (2018) as presented by Koralegedara (2019)

Table 4 presents a comparison of FGDG characteristics from different studies evaluating coal-fired power plants, among the presented data, it is possible to identify the average content in percentage depending on the chemical composition of FGDG, particularly in the case of compounds such as SO_3, CaO, SiO_2, Al_2O_3 the study of Li & Wang (2019) reported the higher levels in comparison with the other studies, and MgO, LOI, has the highest number of chemical composition according to Telesco *et al.,* (2013).

Table 4. The comparison of Flue Gas Desulphurization Gypsum (FGDG) chemical composition from different studies

Chemical Composition (%)	**Telesco. A** (%)	**Li. J** (%)	**Li. Jing** (%)
SO_3	36.90	24.0 – 54.7	40.8
CaO	31.90	25.0 – 50.0	28.1
MgO	3.80	0.04 – 3.80	1
SiO_2	3.30	0.8 – 7.2	2.0
Al_2O_3	1.00	0.3 – 3.7	1.2
Fe_2O_3	0.30	0.1 – 0.9	0.5
TiO_2	0.05	0.05 – 0.07	0.07
P_2O_5	0.01	0.01	-
Mn_3O_4	-	0.01	-
Na_2O	-	0.01	0.3
K_2O	-	0.01 – 0.3	0.1

References: (Li & Wang, 2019; Li *et al*., 2015; Telesco *et al*., 2013)

In Table 5 the comparison shows the main trace elements found in the flue gas desulphurization, between three different studies and the range between the lowest and the highest. Wang & Yang (2018) and Li & Wang (2019) reported the same range content for Pb and Cr, in contrast Chen reported lower values <5.0 for Pb and <1.0 for Cr.

Table 5. Comparison of trace elements contents Flue Gas Desulphurization Gypsum (FGDG)

Trace Elements ($mg.kg^{-1}$)	**Li. J** ($mg.kg^{-1}$)	**Wang. J** ($mg.kg^{-1}$)	**Chen. L** ($mg.kg^{-1}$)
As	<2.6	<2.6	<11
Pb	3 – 218	3 – 218	<5.0
Cr	65 – 91	65 – 91	<1.0
Cd	<0.01	<0.01	<1.0
Zn	2.5 – 14.3	2.5 – 14.3	4.8

References: (Chen *et al*., 2008; Li & Wang, 2019; Wang & Yang, 2018)

4.4 The role of Nitrogen and Sulphur in plant nutrition

Nitrogen and sulfur are major plant nutrients that are present in proteins and a number of other organic compounds. In terms of their uptake, there is a similar relationship between N and S (Coleto et al., 2017).

Since nitrogen and sulphur are key protein components, having the right N:S ratio, and improving crop yields and quality. Sulphur and nitrogen interact at several levels in the plant, including uptake, assimilation of NO_3^- and SO_4^{2-}, and the formation of N and S metabolites. When the amount of absorbed sulphur is low, the minimum law can apply, this means that high nitrogen fertilization would have an effect on plants' sulphur consumption. As a result, the amount of sulphur and its derivatives in plants decreases. These nutrients are required in both human and animal diets (Klikocka & Marks, 2018)

4.4.1 Nitrogen

Plants need a considerable number of elements, among these nitrogen is the most required, corresponding to 1-5% of the overall plant dry weight, which is an integrated component of proteins, chlorophyll, nucleic acid, hormones, amides and secondary metabolites. The available content of nitrogen in the soil play an important role in plant growth, plants depend on two sources of nitrogen that are taken up by roots, which are nitrate (NO_3^-) and ammonium (NH_4^+). Depend on plant energy and temperature meanwhile (NH_4^+) uptake at lower temperature, usually nitrate is higher uptake than ammonium (Marschner, 2012).

Approximately 60% of the plants with nitrogen fertilizer worldwide, were utilized for cereal crops (FAO, 2006). With the purpose of increasing of crop production, around 100 million tons were added internationally of nitrogen fertilizers in 2008 Because nitrogen fertilizer has achieved the best quality of fertilizers that will let the grain yield grow in a better way, and it/s good for the environment. (FAO, 2008).

The low availability of N in soil will affect in a negative way on the production of the plants and environmental competiveness, the deficiency of N in plant will be noticed on the plants leaves, since chloroplast and chlorophyll synthesis are inhibited, the leaves begin to wilt and dry out, turning a yellowish brown to a brown color (Marschner, 2012).

4.4.2 Sulphur

Plants also need sulphur to continue growing, but it takes two sources of sulphur, for the upper parts is Sulphur dioxide (SO_2), and roots will take sulphate (SO_4^-) and go through the xylem and phloem (Marschner, 2012). S substance change heavily among the species, aligning 0.1 to 6% of dry weight. Sulphur is present in oxidation states, such as (SO_4-^2), which is the chemical structure the plants take from the soil to feed itself with S (Fuentes-Lara *et al.*, 2019). Sulphur and nitrogen have the same general characteristics absorption, like development of amino acids, proteins and coenzymes (Marschner, 2012). The available amount of sulphur needed by plants is highly dependent on its Nitrogen nutrients (Fuentes-Lara *et al.*, 2019).

Sulphur (S) is important for the growth of plants, as it is significant role in the protein nutrient. Sulphur gives the green color that cover plants, practically in alfalfa it takes from the soil sulphate (SO_4^{2-}) because it quite responsive to leach in sandy soils (Sahota, 2005).

Sulphur shortcoming in soil is supposed to get higher as a result of the rise of high performance of harvest types, use of Sulphur-free fertilizers, and removal of sulphur from industrial waste. (Chen *et al.*, 2005).

Plants in the dry weight contain 0.1 and 0.5 % of sulphur, and the protein that the plants build take from sulphur are significantly different between the protein fractions of particular cells and within plant types (Marschner, 2012).

4.4.3 Sources of Nitrogen and Sulphur

One of the main environmental issues is acid rain which occurs when sulphur dioxide (SO_2) and nitrogen oxides (NO_X) react in the atmosphere with water and oxygen. The combustion of coal, especially high in sulfur coal produces the majority of these acidic gases. Acid rain also contains nitrogen, which is a source of concern. It causes nitrate to be deposited in aquatic environments (Taerakul 2005). The nitrogen leaking from the plant-soil system can cause pollution problems, even in air and water (Marschner, 2012).

Coal-fired power plants are one of the major sources of sulfur and nitrogen oxide emissions in the atmosphere. As flue gas cools during the emission process, sulfur dioxide and sulfur trioxide are converted to sulfuric acid (H_2SO_4). (Amster 2019).

Acid rain can break up the environmental stability which will be a major endanger to human life. The third region in the world that got affected with acid rain is China. It has taken place in the coastal areas of southwest and south China the mostly because of the acid precipitation, and south area of Yangtze River has turned the main point of acid rain in the whole world (Li et al., 2021).

4.5 Pyrolysis process

Pyrolysis is a thermal process that allows to transform and decompose organic substances where relatively high temperatures (300 - 1000°C) are applied to organic matter materials under low oxygen or anoxic conditions or inert atmosphere, producing three basic products, syngas, bio-oil and biochar (Carey *et al.*, 2015; Frišták *et al.*, 2017). The gaseous fraction contains H_2, CH_4, CO, CO_2, and some other gases, the liquid fraction consists of in tar/oil, containing acetic acid, methanol, and acetone, and finally the solid fraction is char, which is a solid carbonaceous residue combined with some inert materials (Fytili & Zabaniotou, 2008). Pyrolysis process can be described by the following equation:

$$Pyrolysis = Feedstock + Heat \rightarrow CO + H_2 + CO_2 + CH_4 + Oil + Char$$

This process is less pollutant than more conventional methods, such as incineration or combustion, the resulting solid carbonaceous residue (char) closes securely in the heavy metals (like mercury and cadmium). Pyrolysis products can be used as fuels or feedstocks for several applications, such as petrochemicals (Karayildirim *et al.,* 2006).

It's important to differentiate between pyrolysis and gasification. Gasification is a process that converts organic materials into combustible gas or flammable gas, using 20 to 40% of the oxygen required for complete combustion. on the other hand, pyrolysis is aimed to produce mainly char, gas or liquid, which is called also bio-oil and can be used as fuel (Fonts *et al.*, 2012).

Figure 4 shows a pyrolysis setup, consisting in a chamber, coupled with an electric heater and gas inflow to provide an inert atmosphere, also for treating the produced synthesis gases this setup contains a cooling system with a filter with the purpose of remove tar compounds at the end. Gas bag collects the gases for analysis using gas chromatography (Tran *et al.*, 2020).

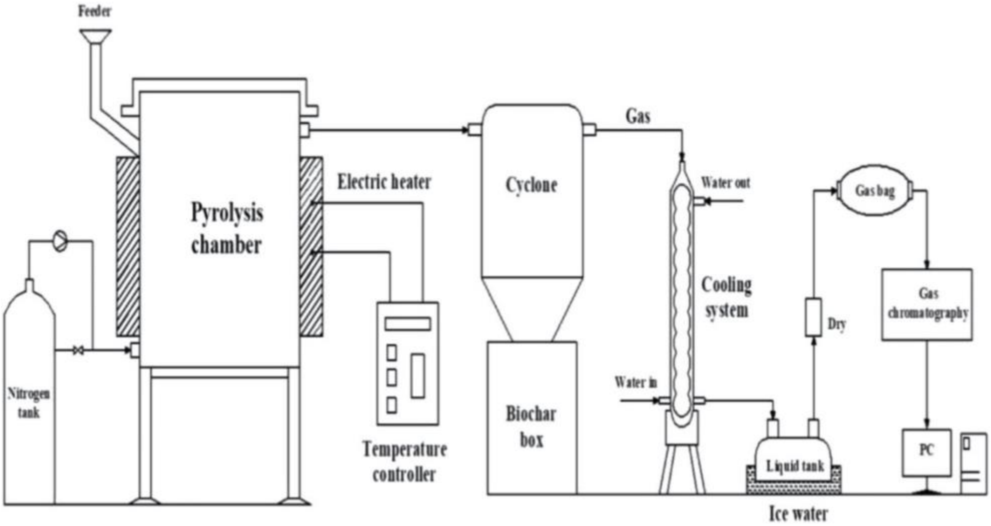

Figure 4 - Scheme of Pyrolysis process (Tran *et al.*, 2020)

4.5.1 Pyrolysis Conditions

The conditions for pyrolysis are mainly pyrolytic temperature, heating rate, and residence time. It can be categorized as fast and slow, depending on the differences of its characteristics.

Slow Pyrolysis

Is performed at a lower heating value increase, which is about 0.1 to 1 °C/s, and is used at low pyrolytic temperature, in the range of 300 to 400 °C, and the gas residence time is about 5 – 30 minutes (Raheem *et al.*, 2018).

Fast Pyrolysis

A pyrolysis reaction with higher heating rate, 10 – 200 °C/s, higher pyrolytic temperature 450 – 600 °C and the gas residence time is 0.1 – 0.3 s. This pyrolysis method is used mainly when its required to increase the yields in the production of gas and bio-oil/asphalt (Raheem *et al.*, 2018).

The available technologies for fast pyrolysis are; (A) Ablative pyrolysis, this process uses larger particles of material and is typically limited by the rate of heat supply to the reactor, (B) Fluid bed and circulating fluid bed pyrolysis, which transfers heat from a heat source to the material by a mixture of convection and conduction and (C) Vacuum pyrolysis which has slow heating rates but removes pyrolysis products as rapidly as in the previous methods (Bridgwater *et al.,* 1999).

4.6 Gasification and Liquefaction

Other than the common pyrolysis process, there are three connected technologies that might be a possibility to improve useful resources (for instance: energy, chemical feedstocks, fiber, and steel) that come from waste tires, which are pyrolysis, gasification, and liquefaction (Muzenda, 2014).

Gasification is a thermochemical method that is more reactive than pyrolysis. In general, it happens in a temperature between (700 – 1400 °C) which is higher temperature than pyrolysis and liquefaction. It includes the utilization of air, oxygen (O2), hydrogen (H2). Vapor or water as a reactant. The effective energy from the gasification method is approximately noted as 76% (Muzenda, 2014).

Liquefaction is a thermochemical transformation of an natural solid to petrol like liquid. Liquefaction is usually used in the making of liquid composed of heavy microscopic compounds with the same characteristics, however not identical, for such the petroleum based fuels (Muzenda, 2014).

Pyrolysis, Gasification and Liquefaction (PGL) can also decrease the quantity of residual material that are still available for disposal (CIWMB, 1995). At the present time, the use of PGL is suitable for the transformation of carbonaceous materials to fuels, and their present might turn as the supply of natural resources get used up (Muzenda, 2014).

According to reports, the gasification process has a 76 % of energy release. Gasification of waste tyres is an appealing utilization route because the gaseous materials are easily handled, transported, and fed into existing boilers and combustors with minimal modifications. Waste tyre steam gasification has the ability to produce high-quality syngas. Traditional gasification systems, on the other hand, necessitate high temperatures to decompose the feedstock and initiate reforming reactions, which reduces the process' overall performance (Muzenda, 2014).

4.7 Treatment and Disposal Alternatives of Flue Gas Desulphurization Gypsum (FGDG)

4.7.1 Beneficial uses of Flue Gas Desulphurization Gypsum (FGDG)

The physical and chemical characteristics of FGDG can offer many useful applications in two ways: encapsulated and non-encapsulated. The main beneficial use of FGDG in wallboard manufacture (it mainly contains of calcium sulfate dehydrate). It is also a main component part in cement for asphalt and concrete production (Koralegedara *et al.*, 2019).

FGDG were first used in agricultural uses as a fertilizer and soil improvement. As reported by American Coal Ash Association, (2016), 54% of the whole FGDG produced in USA was used in wallboards creation, and 8% in cement concrete asphalt production. Moreover, 17% of the entire FGDG manufacture was used in ground applications such as inorganic fill up, farming, and dig reformation. Nevertheless, under these useful applications, approximately 43% of the whole FGDG production was wheeled around in landfill sites, as shown in figure 5 (Koralegedara *et al.*, 2019).

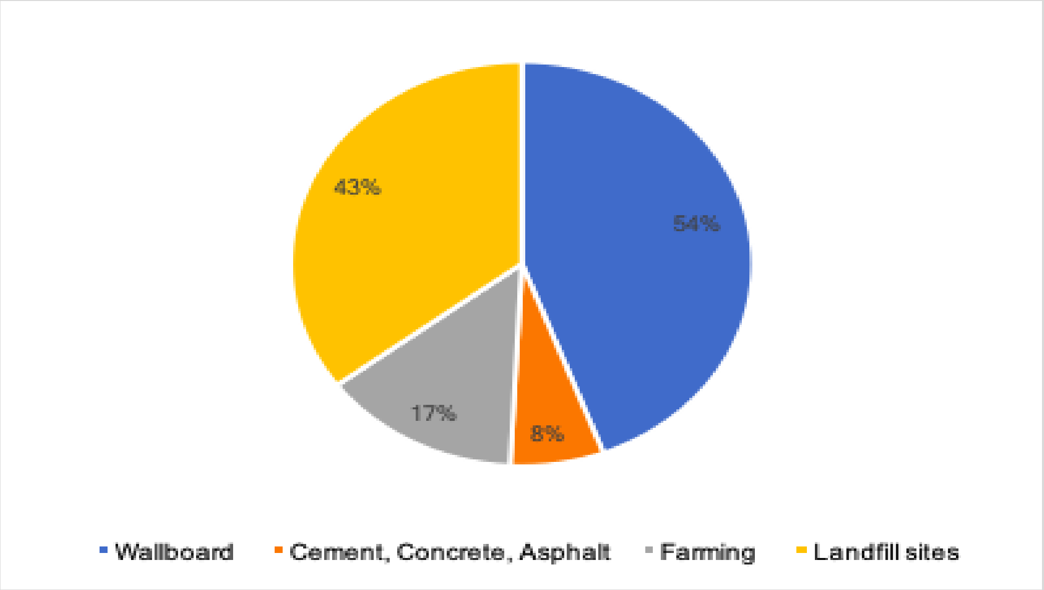

Figure 5 - Most common applications of flue gas desulphurization gypsum

According to the European Coal Combustion Products Association, in 2009, FGDG was the second largest byproduct generated in the EU countries. FGDG finds applications in wallboard manufacture or be used in the cement industry. Other uses such as agricultural lime substitute, amendments for improving soil properties, construction material for roads (ECCPA, 2009).

The application of FDGD to weathered soils increases plant Ca^{2+} and (SO_4^{2-}) sorption activity, resulting in improved nitrogen uptake. It's important to remember that all types of gypsum are not liming agents and have no effect on soil pH. FGDG, on the other hand, may help to alleviate the phytotoxic effects of excess soluble Al in acid soils. It reacts with Al^{3+} and eliminates it from the soil solution, reducing the toxic effects dramatically (Panday *et al.*, 2019)

4.8 Major nutrient available in Flue Gas Desulphurization Gypsum (FGDG)

FGDG is a direct source of macronutrients, providing plants with easily accessible calcium (Ca^{2+}) and sulfate (SO_4^{2}) ions (Panday *et al.*, 2019).

Oxygen availability is important for the production of calcium sulphate or calcium sulfite. Removal of SO_2 from wet FGD is highest than 90% and the quantity of absorbents utilized in wet FGD can be resolved from SO_2 (Srivastava. 2000).

As the limestone-based scrubbing is one of the most used method for FGDG, the following equation summarizes the presence of SO_2 in flue gas and the limestone dissolution and subsequent oxidation of calcium sulfite for FGDG production (Koralegedara *et al.*, 2019):

$SO_{2(g)} + CaCO_{3(s)} + 2H_2O_{2(aq)} = CaSO_3{\cdot}2H_2O_{(aq)} + CO_{2(g)}$

$CaSO_3{\cdot}2H_2O_{(aq)} + \frac{1}{2}O_{2(g)} \leftrightarrow CaSO_4{\cdot}2H_2O_{(s)}$

4.9 Policy and regulations for FGDG

The FGDG production has been increasing after flue gas desulphurization technology was implemented in coal-fired power plants, it was reported by the Cross-State Air Pollution Rule (CSAPR) the statement from U.S. EPA in 2011, specifying that SO_2 emissions from coal burning should be decreased before it discharged to the environment. Although the FGDG production has been increasing as a result of this strict measurements its utilization is still low.

In the case of the Czech Republic the regulation used to determine the use of FGDG as soil amendment is the Decree No.229/2017 (Amending Decree No. 377/2013 Coll.) Coll on the storage and use of fertilizers. This Decree incorporates the relevant regulation of the European Union, the Council Directive 91/676 / EEC concerning the protection of waters against pollution caused by nitrates from agricultural sources. Through this decree Czech Republic regulates the method for the storage of fertilizers and auxiliary substances and capacity of storage premises, the use of fertilizers and adjuvants on agricultural land and forest land.

5. Material and Methods

5.1 Flue Gas Desulphurisation Gypsum

In this study the Flue Gas Desulphurization Gypsum (FGDG) used as a feedstock for the pyrolysis process was sourced from four different Coal-fired power plants located in the Czech Republic. The samples were provided only of condition of anonymity and are therefore labeled as FGDG-A, FGDG-B, FGDG-C, and FGDG-D. Among the studied coal-fired power plants, all used brown coal for the electrical energy production, and wet limestone is the most common flue gas desulphurization technology implemented.

FGDG-A: total installed capacity 295 MW
FGDG-B: total installed capacity 820 MW
FGDG-C: total installed capacity 960 MW
FGDG-D: total installed capacity 149 MW

No further information about the source of the FGDG is present as this research work is subject to data protection agreement with the producers.

After retrieving the FGDG samples from the coal-fired power plants they were grinded, sieved, and stored in desiccator before use.

5.2 Pyrolysis

Figure 6, presents the schematic diagram of the experimental setting for pyrolysis process. The system used a horizontal quartz tube, Nitrogen gas cylinder and volatiles collection system.

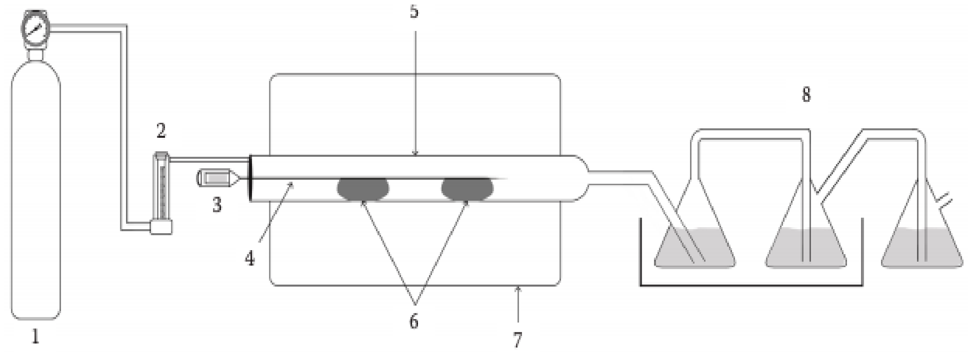

Figure 4. Schematic of the laboratory pyrolysis apparatus. 1 – the source of N_2; 2 – gas flow-meter; 3 – thermometer; 4 – thermometer probe; 5 – quartz tube; 6 – ceramic sample holders; 7 – electric furnace; 8 – volatiles collecting system (Mercl et al., 2020)

Pyrolysis process was carried out in an electric laboratory furnace Carbolite® Typ 301 (Carbolite Gero; UK) (Figure 7).

Figure 5. Furnace Carbolite® Typ 301 and Nitrogen source

Well-mixed grinded samples by duplicates (1 g, particle size <1 mm) were placed in crucibles (ceramic-made). These samples were put into a cylindrical tube, made of quartz with 4.5 cm internal diameter and 95 cm length, giving a total reactor volume of 0.6711 L (Figure 8). The sample was kept in the operating furnace for 30 min, to maintain an oxygen-free atmosphere during the process, nitrogen (99.99 %) was supplied to the system at a rate of 100 L/h.

Figure 6. Sample setting

Each run was executed with two different temperatures; 600 °C and 800 °C, for the pyrolysis process the oven was pre-heated and once the set temperature was reached (600 °C and 800 °C), the tube was then loaded with the sample and injected with a continuous stream of nitrogen, which was permanently manually controlled, the sample stayed under these conditions for 30 minutes. Pyrolyzed samples were stored in plastic containers and then deposited in a desiccator.

The volatiles were absorbed on three conical flasks filled as follows: the first two by chloroform ($CHCl_3$) and the third one by nitric acid (HNO_3). These were kept in ice bath to collect condensable vapors. After the condenser, the gases were vented.

5.3 Total content of elements

Total content of elements was determined by inductive coupled plasma-optical emission spectrometry (ICP – OES) after high pressure microwave digestion. 0.3 g of dry sample were decomposed in digestion vessels with 10 ml of nitric acid (65%). The mixture was then heated in the high-pressure microwave digestion equipment, as shown in figure 9, Ethos 1 (MLS GmbH, Germany) for one hour and 20 minutes for cooling the samples, samples were then transfer to test tubes completing the final volume of 20 ml with demineralized water. (Kairies *et al.*, 2006)

Figure 7. Samples in microwave digestion

5.4 Determination of pH values and electrical conductivity (EC)

For FGDG characterization pH and EC were determined using a saturated solution of sample and demineralized water, using a 1:50 ratio of sample and solution. Therefore 0.3 g of FGDG was weighed and 15 ml of demineralized water was added and shaken for 2 hours, at 180 rpm and at 25 °C, and settled down for 1 hour. The pH of the samples was measured using pH meter Sentron SI400 pH meter (Sentron Europe BV, Leek, Netherlands) (figure 10). The electrical conductivity measurements were carried out using a WTW Series Inolab Cond. 730 with a WTW Tetracon 325 electrode (Xylem Analytics GmbH & Co, German) at room temperature (Desutter et al., 2014). As shown in figure 11.

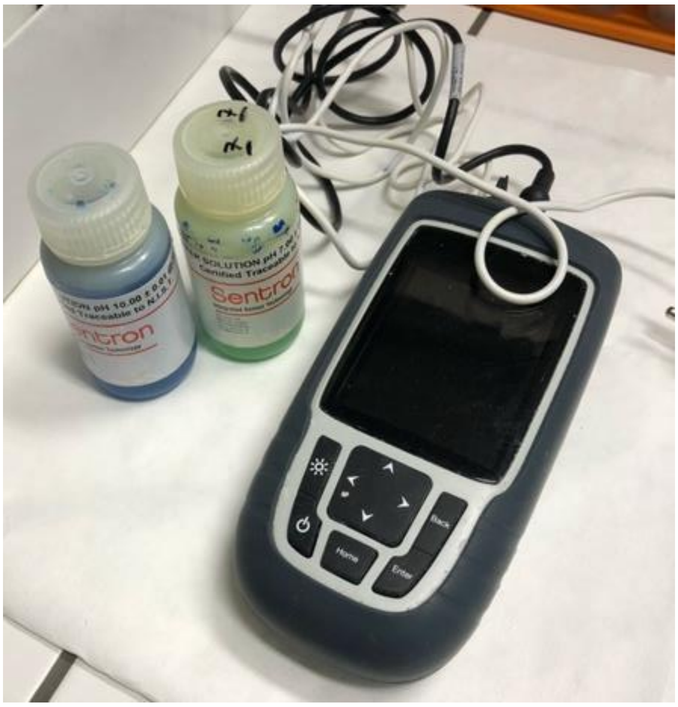

Figure 8. pH meter Sentron SI400

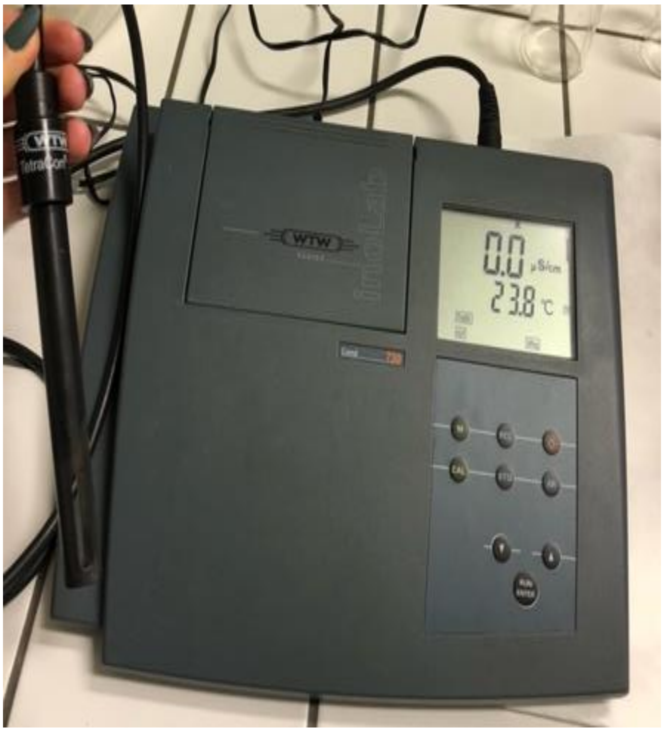

Figure 9. EC meter, WTW Series Inolab Cond. 730 with a WTW Tetracon 325 electrode

5.5 Determination of available content of elements

The available content of elements was detrmined by means of acetic acid extraction 0.2 g of pyrolyzed FGDG was mixed with 8 ml of 0.11 M CH3COOH (pH 2.0), then the mixture was shaken for 16 h at 120 rpm at 25 °C, this process was followed by centrifugation at 6000 rpm (9400 g) for 10 minutes using Rotina 420 R Andreas Hettich GmbH & Co. KG as shown at figure 12, the supernatant was transferred to test tubes for analysis. The concentrations were determined by an inductively coupled plasma optical emission spectrometer, ICP-OES, Agilent 720 (Agilent Technologies Inc., USA)

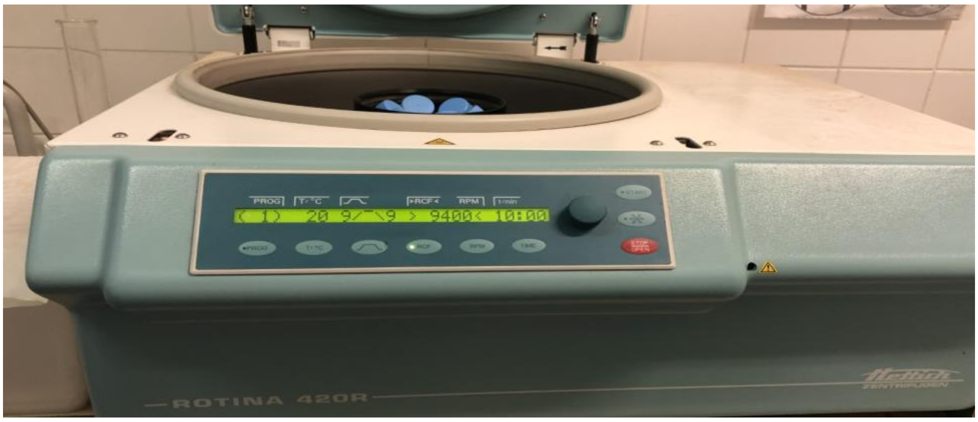

Figure 10. Centrifugation, Rotina 420 R

5.6 Statistical analysis

The analysis was focused on the changes in total and available concentration under the two temperatures for all elements in the different interest groups (macronutrients, micronutrients, and toxic elements). The data for both total and available contents were analyzed using the same procedure. Before the analysis, the data were explored to check for elements with observations below the detection limit, if the number of observations below the detection limit was below 40% the element was excluded from the analysis. Then, the data was explored using summary tables and graphics to better describe the trends and finals concentrations of each sample under different temperatures. Subsequently, additional plots regarding the changes in proportion of the available concentration under the different treatments were performed.

For the statistical analysis as such we performed multiple ANOVA models with each element as the response variable and the temperature and Sample as explanatory factor variables. Each ANOVA was followed by a post-hoc Tukey Honest Significance test for pairwise comparison between the different levels of the factors, the results of this test were presented graphically for ease of comparison. In all cases the significance levels was taken to be 0.05 and the analysis were carried in R software (R Core Team, 2020).

6. Results

The FGDG pyrolyzed samples were analyzed in terms of water content determination, pH, electrical conductivity (EC), total and available content of elements. These analyses were performed in a set of elements assembled in three different groups: Toxic elements (As, Cd, Cr, Pb), Macronutrients (Ca, K, Mg, P, S) and Micronutrients (Cu, Fe, Mn, Ni, Zn).

The samples were labeled as FGDG-A, FGDG-B, FGDG-C and FGDG-D, also they were analyzed by duplicates for testing two different temperature 600 °C and 800 °C, and pyrolysis reaction time of 30 minutes.

6.1 Determination of water content of FGDG and weight loss after pyrolysis

Table 6, presents the results obtained after drying the samples before being pyrolyzed at 105 °C to eliminate residual humidity, it is possible to observe that some samples had a higher water content, this depends on the FGDF characteristics. It can be observed for sample FGDG-D the moisture was 40 %, in the other hand sample FGDG-B contained 14 % of humidity. In that case sample FGDG-D had the highest water evaporation value.

Table 6. Moisture determination in Flue Gas Desulphurization Gypsum (FGDG) samples (%)

Sample	**FGDG-A**	**FGDG-B**	**FGDG-C**	**FGDG-D**
Dry at 105 °C (%)	72.46 ± 7.50	86.05 ± 4.97	83.95 ± 10.30	60.21 ± 8.16

Weight losses during pyrolysis were made on the raw FGDG samples on two different pyrolytic temperatures 600 °C and 800 °C as shown in table 7. It was found that the weight loss increased with the increasing temperature~~,~~ FGDG-A lost 54.5 % of its weight at 800 °C during the process, and FGDG-D have lost 19 % also at 800 °C, while at 600 °C all of the samples lost no more than 9 % of its weight.

Table 7. Flue Gas Desulphurization Gypsum (FGDG) weight loss after pyrolysis (%)

	Sample	**FGDG-A**	**FGDG-B**	**FGDG-C**	**FGDG-D**
Condition					
600 °C		4.19 ± 0.18	4.63 ± 0.08	4.33 ± 0.09	8.79 ± 0.0
800 °C		54.78 ± 69.66	5.39 ± 0.02	5.87 ± 0.05	19. 21 ± 0.05

6.2 Determination of pH and electrical conductivity (EC)

Table 8 shows the pH of the different pyrolyzed FGDG samples. It was observed that the pH ranges should be between 7 and 10 und.

The results presented in table 8 shows that the pH of FGDG-A, FGDG-C and FGDG-D samples were increased by the increase of temperature and it moved in the alkaline range for the tested temperatures 600 °C and 800 °C. In case of FGDG-B sample pH was 6.87 ± 0.18 und. Before pyrolysis, increased to 8.95 ± 0.14 und. at 600 °C and decreased to 7.22 ± 0.3 und. at 800 °C acidic at raw and increased at 600 °C and the again decreased at 800 °C.

On the other hand, electrical conductivity increased consistently from raw samples to pyrolyzed samples at 800 °C. For FGDG-B sample the results as show at 600 °C it increased and reached 2.66 ± 0.02mS/cm, and decreased again at 800 °C to 2.5 ± 0 mS/cm, and at FGDG-A has increased from 2.53 ± 0.27 mS/cm at raw, to 3.43 ± 0.05 mS/cm at 600 °C, to 4.6 ± 0.09 mS/cm at 800 °C, and also for FGDG-C, the results increased with the temperature from 2.4 ± 0.03 mS/cm at raw to 3.11 ± 0.01 mS/cm at 600 °C to 4.64 ± 0.07 mS/cm at 800 °C, also for FGDG-D the electrical conductivity has increased during 600 °C to 4.88 ± 0.24 mS/cm and more when reached 800 °C to 9.89 ± 0.09 mS/cm.

Table 8. pH values and electrical conductivity (EC) determination for flue gas desulphurization gypsum (FGDG) samples

Sample		**pH (und).**	**EC (mS/cm)**
	Condition		
FGDG-A	Raw	7.62 ± 0.27	2.53 ± 0.27
	600 °C	10.85 ± 0.07	3.43 ± 0.05
	800 °C	11.13 ± 0.09	4.6 ± 0.09
FGDG-B	Raw	6.87 ± 0.18	2.43 ± 0.19
	600 °C	8.95 ± 0.14	2.66 ± 0.02
	800 °C	7.22 ± 0.3	2.5 ± 0
FGDG-C	Raw	6.9 ± 0.09	2.4 ± 0.03
	600 °C	10.61 ± 0.06	3.11 ± 0.01
	800 °C	11.09 ± 0.03	4.64 ± 0.07
FGDG-D	Raw	10.43 ± 0.02	1.29 ± 0.05
	600 °C	11.10 ± 0.02	4.88 ± 0.24
	800 °C	11.22 ± 0	9.89 ± 0.09

6.3 Total content of macronutrients in flue gas desulphurization gypsum pyrolyzed samples

The total content of macronutrients in the samples was dominated by the Ca followed by S, this was the case for all samples. In all cases the concentration of both elements was above 100 g/kg. The other elements were much less concentrated in all samples with a varying concentration. From macronutrients analysis, it was found that calcium and sulphur in FGDG-A, were increasing by the increase of temperature, Ca went from (272.3 ± 47.16 g/kg before pyrolysis to 176.7 ± 22.53 g/kg at 600 °C to its maximum 279.8 ± 41.92 g/kg at 800 °C). While for K, Mg and P the higher concentrations were found at 600 °C 0.82 ± 0.36 g/kg, 0.68 ± 0.06 g/kg and 0.23 ± 0.12 g/kg respectively, as shown in figure 13.

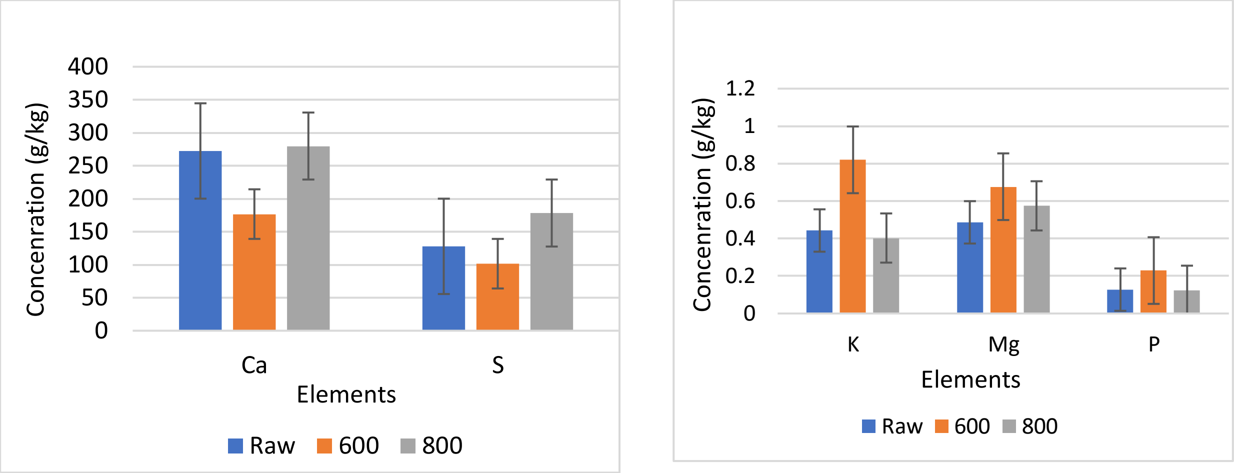

Figure 11. Total content of macronutrient in flue gas desulphurization gypsum (FGDG-A (g/kg))

Calcium in FGDG-B went from (238.4 ± 2.52 g/kg before pyrolysis, to 287.4 ± 22.3 g/kg at 600 °C, to 291.7 ± 49.4 g/kg at 800 °C), S reported similar values at 600 and 800 °C, being 203.6 ± 19.8 g/kg and 204.6 ± 38.9 g/kg respectively. For K and P, the concentration was increasing at 600 °C, in the case of Mg its concentration was maintained in a similar range (3.062 ± 0.37 g/kg in the raw sample, to 3.37 ± 0.07 g/kg at 600 °C and 3.58 ± 0.07 g/kg at 800 °C), as shown in figure14.

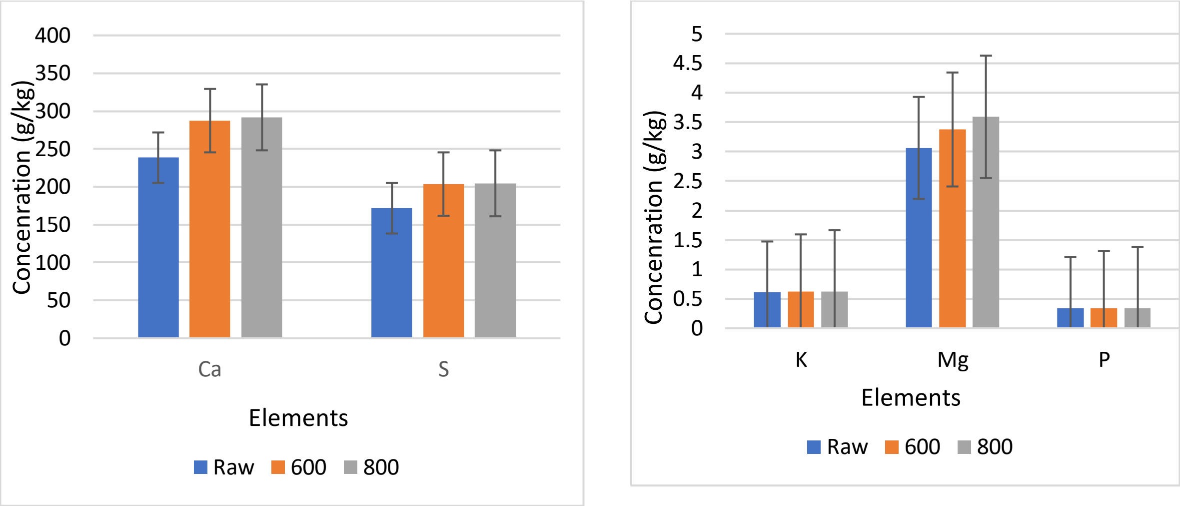

Figure 12. Total content of macronutrient in flue gas desulphurization gypsum (FGDG-B (g/kg))

The presence of macronutrients in FGDG-C is presented in figure 15, where it can be observed for Ca and S the maximum concentration (335.3 ± 5.06 g/kg and 227.0 ± 5.05 g/kg) at 600 °C, when the presence of P is very low (0.05 ± 0.02 at raw, 0.05 ± 0 at 600 °C, 0.044 ± 0 g/kg at 800 °C) regarding to K the concentration were decreasing by increasing the temperature (0.39 ± 0.15 g/kg at raw, 0.354 ± 0.07 g/kg at 600 °C, 0.30 ± 0.03 g/kg at 800°C) and Mg (1.60 ± 0.02 g/kg at raw to 1.62 ± 0.13 g/kg at 600 °C to 1.52 ± 0.12 g/kg at 800 °C).

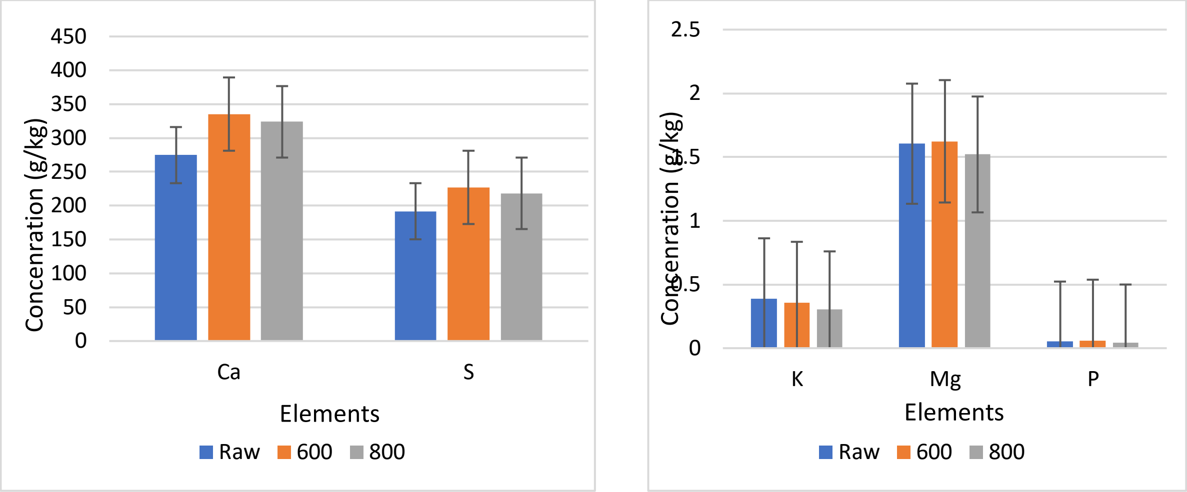

Figure 13. Total content of macronutrient in flue gas desulphurization gypsum (FGDG-C (g/kg))]

Macronutrients presence in FGDG-D is displaced in figure 16 shows Ca and S concentration at 600 °C where higher (Ca: 369 ± 31.24 g/kg, S: 168 ± 22.4 g/kg), for Mg the concentration where increasing with the high temperature (1.964 ± 0.18 g/kg at raw to 2.38 ± 0.02 g/kg at 600 °C to 2.598 ± 0 g/kg at 800 °C), and the higher for K was at 600 °C (1.5 ± 0.04 g/kg).

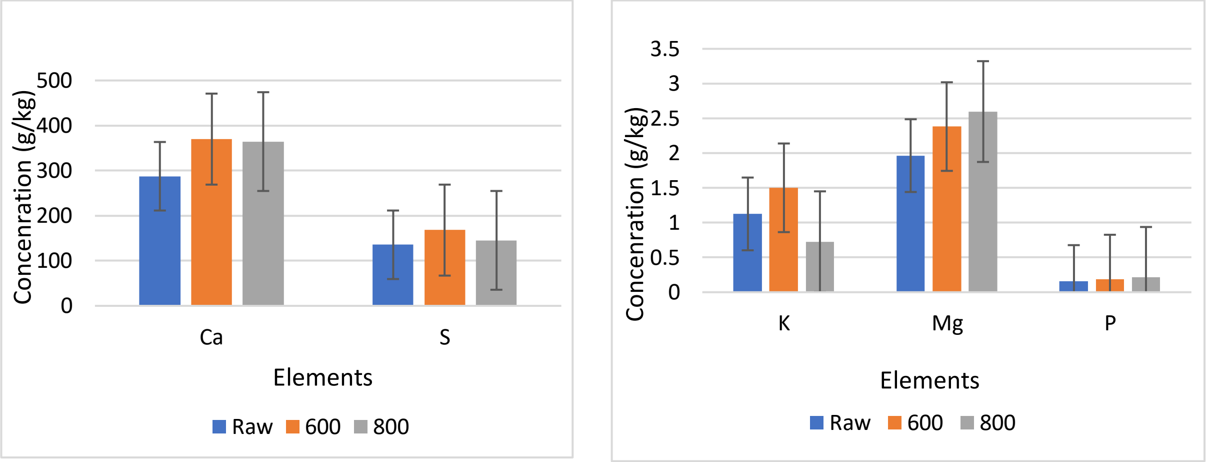

Figure 14. Total content of macronutrient in flue gas desulphurization gypsum (FGDG-D (g/kg))

6.4 Available Content of Macronutrients in flue gas desulphurization gypsum pyrolyzed samples

The available concentration of macronutrients in the samples followed a pattern really similar to the total concentration with the Ca and S being the most abundant in all samples, however the available concentration of S was higher than the one of Ca. The available concentration of S varied between 49.63 ± 23.35 and 11.91 ± 0.32

g/kg, while for the Ca the concentration varied between 1.81 ± 0.17 g/kg and 0.05 ± 0 g/kg. For the rest of the elements the variations were 0.26 ± 0.01 g/kg to 0.07 ± 0.01 g/kg for the K, 1.67 ± 0.06 g/kg to 0.02 ± 0.01 g/kg for the Mg, and 0.12 ± 0.01 g/kg to 0.01 ± 0 g/kg for the P. The highest average for available concentration of Ca was found on FGDG-D (0.73 ± 0.93 g/kg) while the lowest was found in FGDG-B (0.08 ± 0.03 g/kg). For K, the highest concentration was found on S FGDG-D (0.16 ± 0.01 g/kg) while the lowest was found in FGDG-A (0.08 ± 0.01 g/kg). In the case of Mg, the highest average concentration was found on FGDG-B (1.2 ± 0.05 g/kg) while the lowest was found in FGDG-A (0.51 ± 0.04 g/kg) while for the P, the highest average concentration was found on FGDG-B (0.09 ± 0.03 g/kg) while the lowest was found in FGDG-C (0.01 ± 0 g/kg). Among investigated nutrients S was the most abundant element in the available fraction, the highest average concentration was found on FGDG-D (25.95 ± 20.62 g/kg) while the lowest was found in FGDG-A (19.11 ± 4.06 g/kg). As shown in table 9.

Table 9. Available of elements in flue gas desulphurization gypsum (FGDG) –Macronutrient elements (g/kg)

FGDG	Condition	Ca	K	Mg	P	S
FGDG-A	Raw	0.25 ± 0.03	0.07 ± 0.01	0.53 ± 0.02	BDL	14.72 ± 0.74
	600 °C	0.35 ± 0.03	0.09 ± 0.01	0.53 ± 0.08	BDL	22.72 ± 0.29
	800 °C	0.31 ± 0	0.08 ± 0	0.47 ± 0	BDL	19.91 ± 0.21
FGDG-B	Raw	0.05 ± 0	0.16 ± 0.09	0.99 ± 0.07	BDL	18.83 ± 0.14
	600 °C	0.07 ± 0	0.2 ± 0.02	0.95 ± 0.02	BDL	26.27 ± 1.18
	800 °C	0.11 ± 0	0.09 ± 0	1.67 ± 0.06	BDL	24.4 ± 0.62
FGDG-C	Raw	0.35 ± 0.04	0.14 ± 0.13	0.69 ± 0.01	BDL	14.06 ± 1.21
	600 °C	0.54 ± 0	0.07 ± 0	1.18 ± 0	BDL	25.23 ± 0.1
	800 °C	0.44 ± 0.01	0.12 ± 0	1.48 ± 0.06	BDL	23.01 ± 1.35
FGDG-D	Raw	0.2 ± 0	0.26 ± 0.01	1.12 ± 0	BDL	11.91 ± 0.32
	600 °C	0.19 ± 0	0.11 ± 0	1.19 ± 0.01	BDL	16.32 ± 0.95
	800 °C	1.81 ± 0.17	0.12 ± 0.04	0.02 ± 0.01	BDL	49.63 ± 23.35

BDL: Below detection limit (P < 0.1 mg/l)

The following figures contains the available content in percentage for the evaluated samples. In figure 17, it is possible to notice the percentage of the relative availability of macronutrients for FGDG-A. Mg availability decreased at 600 °C (78 %), and increased with the temperature to (81 %) at 800 °C, S and P reported its maximum at 600 °C (22 % and 8 % respectively), For K the relative availability has increased with the temperature 12 % at 600 °C to 20 % at 800 °C. On the other hand, the relative availability of Ca portions was very law that didn’t even get higher than (1%).

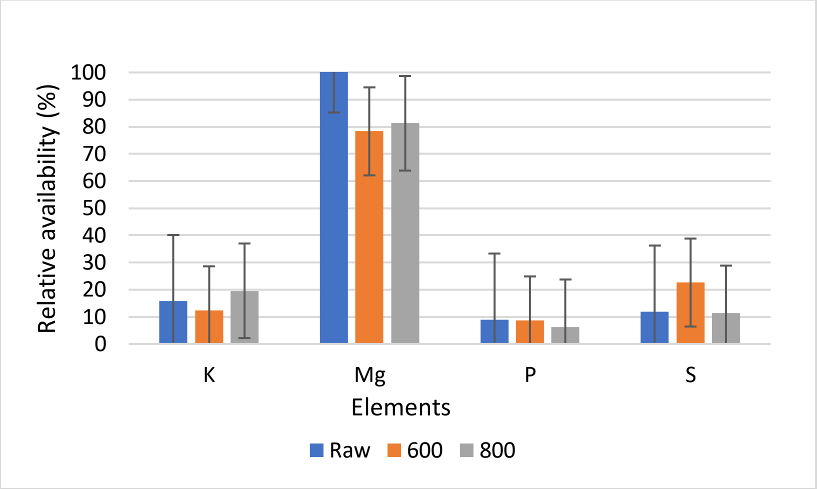

Figure 15. Relative availability content of Macronutrient in flue gas desulphurization gypsum (FGDG-A (%))

In figure 18, the relative availability in FGDG-B for Mg also registered the highest at 800 °C with percentage of 46 %. S relative availability for the two temperatures as close (13 % at 600, and 12 % at 800 °C). For P and K, the relative availability portions were higher at 600 °C and decreased at 800 °C (P 35 % at 600 °C, 27 % at 800 °C, K 32 % at 600 °C, 14 % at 800 °C). And Ca portions was very low (0.02 % at raw, to 0.03 at 600 °C, to 0.04 % at 800 °C).

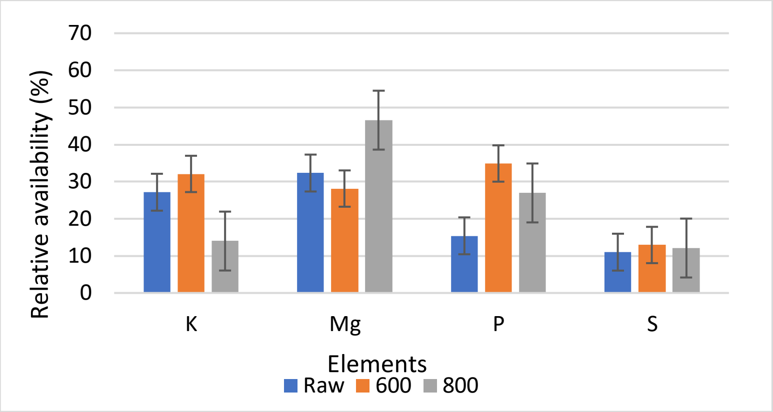

Figure 16. Relative available content of Macronutrient in flue gas desulphurization gypsum (FGDG-B (%))

In figure 19, FGDG-C relative availability of Mg has increased with the temperature (42 % at raw, to 73 % at 600 °C, to 98 % at 800 °C), for K the highest relative availability percentage was 40 % at 800 °C. P and S, highest relative availability was at 600 °C (14 %, 11 %) and then decreased at 800 °C (10 % and 10 %)

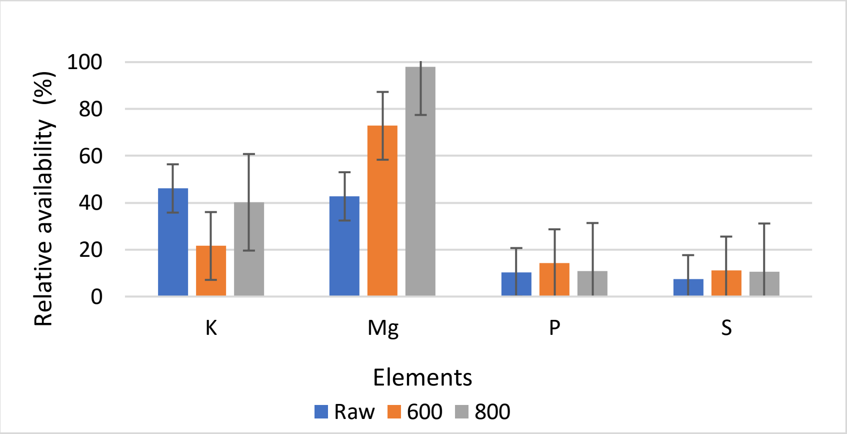

Figure 17. Relative available content of Macronutrient in flue gas desulphurization gypsum (FGDG-C (%))

Figure 20 shows that FGDG-D relative availability of Mg at 600 °C reached its higher value 49 %, and decreased to 0.9 % at 800 °C. P portions were below detection limit, and Ca didn’t pass the 1 % (0.06 % at raw, to 0.05 % at 600 °C, and 0.5 % at 800 °C). S portions has increased with the temperature from 9 % at 600 °C, to the highest 34 % at 800 °C, but for K the highest was at 800 °C with 16 %, and then decreased at 600 °C to 7 %.

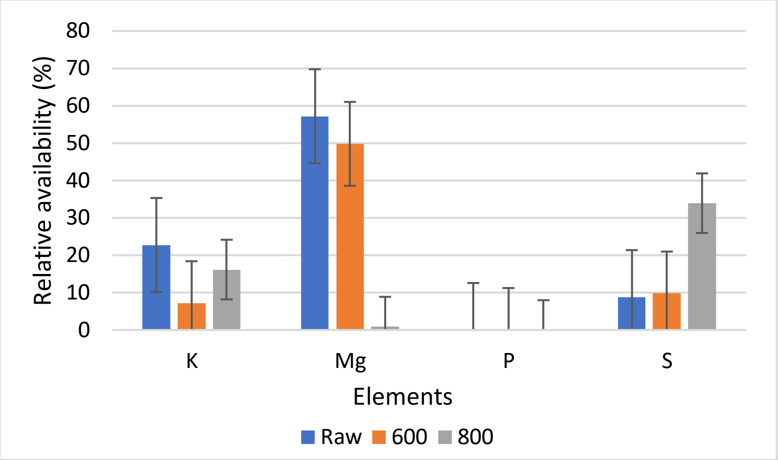

Figure 18. Relative available content of Macronutrient in flue gas desulphurization gypsum (FGDG-D (%))

6.5 Statistical analysis

6.5.1 Anova and TukeyHSD test for the total concentration of macronutrients

The analysis of variance for the total concentration of macronutrients revealed that temperature had a significant effect on Ca, K and Mg, while P and S the differences between samples were significant. The p.value of the elements goes like Ca (< 0.01), K (0.01), and Mg (0.01) as the samples were shown in table 10 to be a significant factor for all elements.

Table 10. Anova evaluation for the total concentration of the macronutrients

Element	term	df	sumsq	meansq	statistic	p.value
Ca	Temperature	2	15780.14	7890.07	6.93	< 0.01
	Sample	3	47003.60	15667.87	13.76	< 0.01
	Residuals	18	20499.94	1138.89	-	-
K	Temperature	2	0.39	0.20	5.69	0.01
	Sample	3	1.91	0.64	18.52	< 0.01
	Residuals	18	0.62	0.03	-	-
Mg	Temperature	2	0.38	0.19	5.85	0.01
	Sample	3	24.51	8.17	250.64	< 0.01
	Residuals	18	0.59	0.03	-	-
P	Temperature	2	0.01	0.00	1.33	0.29
	Sample	3	0.25	0.08	42.68	< 0.01
	Residuals	18	0.04	0.002	-	-
S	Temperature	2	3641.88	1820.94	2.69	0.09
	Sample	3	23282.26	7760.75	11.48	< 0.01
	Residuals	18	12172.53	676.25	-	-

The post-hoc pairwise comparisons showed which pairs of levels in each factor (Temperature and Sample) were significantly different with each other. As discussed above the difference between temperatures were only significant for the Ca, K and the Mg, in the case of the Ca the only difference was found between the raw (the sample measure before pyrolysis) and the 800 °C treatment. And for K there was a significant difference for 600 °C and 800 ºC. In the case of the Mg both the 600 °C and raw, and 800 ºC and raw treatments were significantly different but between 600 ºC and 800 ºC there was no significant different, and for P and S there were no significant different in any of the temperature or raw with the temperatures, as shown in figure 21.

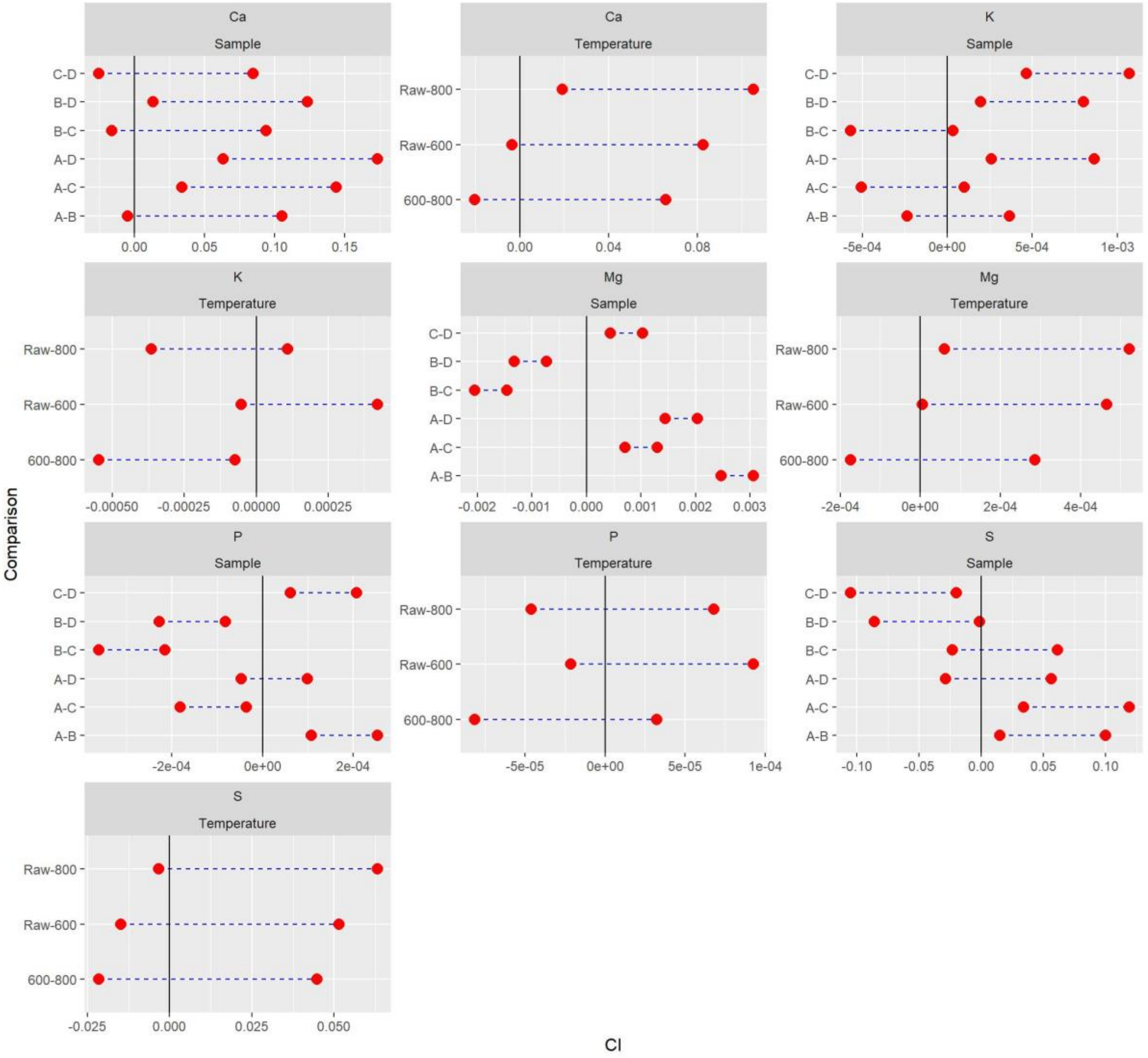

Figure 19. Pairwise comparison trough TukeyHSD test for the effects of temperature and Sample in the total concentration of macronutrients

6.5.2 The Anova and TukeyHSD test for the available concentration of macronutrients

The Anova for the available concentration of macronutrients found a significant effect of temperature for the P (0.03) and the S (0.03), Mg (0.03) significant difference for samples. As in the case above the sample was found in table 11 to be significant for most elements expect the S.

Table 11. Anova evaluation for the available concentration of the macronutrients

Element	term	df	sumsq	meansq	statistic	p.value
Ca	Temperature	2	0.00	0.00	3.26	0.06
	Sample	3	0.00	0.00	3.13	0.05
	Residuals	18	0.00	0.00	BDL	BDL
K	Temperature	2	0.00	0.00	1.82	0.19
	Sample	3	0.00	0.00	2.27	0.11
	Residuals	18	0.00	0.00	BDL	BDL
Mg	Temperature	2	0.00	0.00	0.21	0.81
	Sample	3	0.00	0.00	3.71	0.03
	Residuals	18	0.00	0.00	BDL	BDL
P	Temperature	2	0.00	0.00	4.76	0.03
	Sample	2	0.00	0.00	57.84	< 0.01
	Residuals	13	0.00	0.000	BDL	BDL
S	Temperature	2	0.00	0.00	4.39	0.03
	Sample	3	0.00	0.00	0.56	0.65
	Residuals	18	0.00	0.00	BDL	BDL

The pairwise comparison shows a significant difference for the P between the Raw and the 800 °C treatment and between the Raw and the 600 °C treatment, but no significant difference was found between the 600 and 800 °C treatments. For the S, the only significant difference was found between the Raw and the 800 °C treatment while the other two comparisons (Raw vs 600 and 600 vs 800 °C) did not show any significant difference, as shown in figure 22.

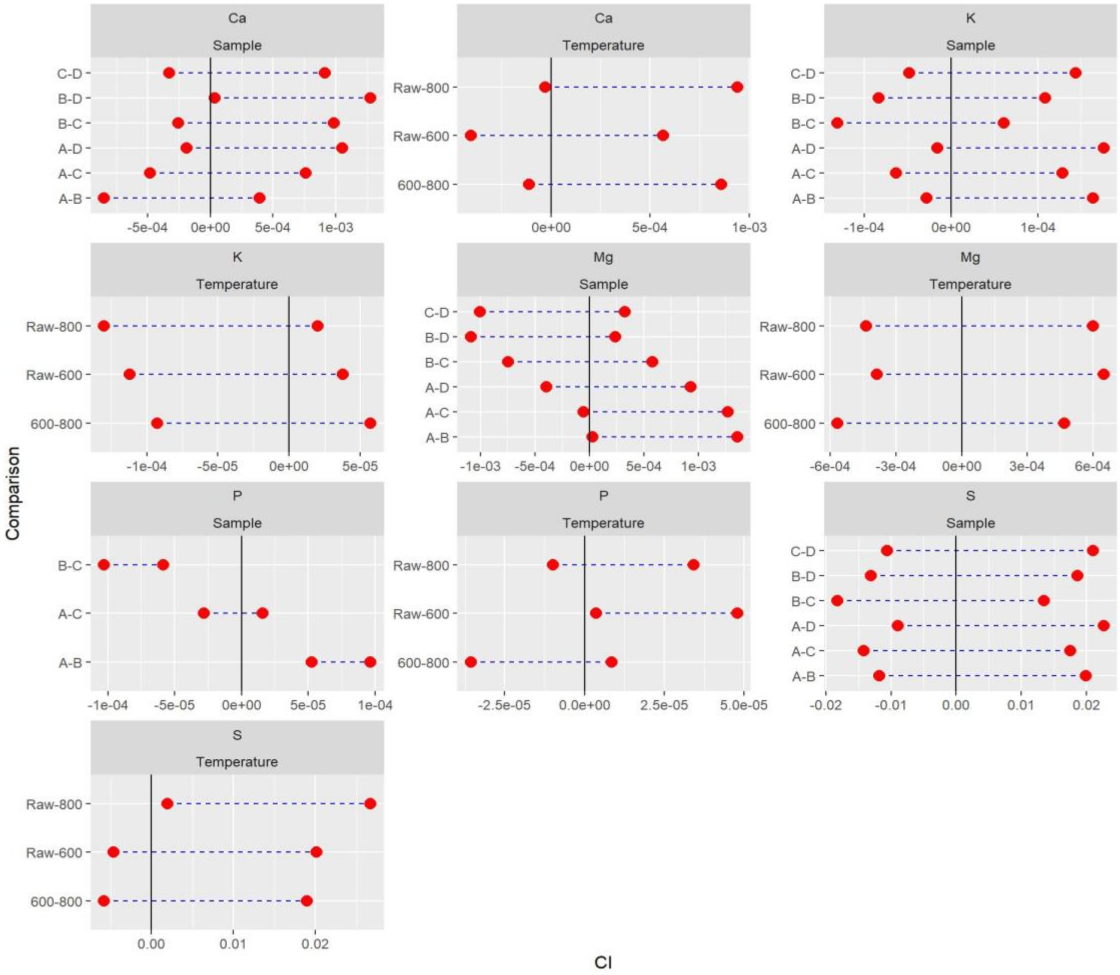

Figure 20. Pairwise comparison trough TukeyHSD test for the effects of temperature and Sample in the available concentration of macronutrients

6.6 Total Content of Micronutrients in flue gas desulphurization gypsum pyrolyzed samples

In the case of the micronutrients, the Fe was by far the most abundant micronutrient with concentrations varying between 611.06 ± 219.24 mg/kg and 4784.97 ± 3.14 mg/kg, followed by Mn (13.29 ± 1.33 mg/kg to 95.43 ± 2.46 mg/kg), the Zn (6.23 ± 1.25 mg/kg to 67.92 ± 59.24 mg/kg), the Cu (1.41 ± 0.85 mg/kg to 32.69 ± 4.04 mg/kg) and finally Ni (0.97 ± 0.08 mg/kg to 6.15 ± 0.05 mg/kg). The highest average concentration per sample were also analyzed. The highest average concentration of Cu was found on FGDG-D (23.87 ± 9.36 mg/kg) while the lowest was found in FGDG-C (1.86 ± 0.48 mg/kg). For the Fe, the highest average concentration was found on FGDG-D (3353.08 ± 57.92 mg/kg) while the lowest was found in FGDG-C (717.62 ± 93.46 mg/kg). In the case of the Mn the highest average concentration was found on FGDG-D (80.51 ± 4.34 mg/kg) while the lowest was found in FGDG-C (15.12 ± 2.7 mg/kg). The highest average concentration of Ni was found on FGDG-D (5.21 ± 0.29 mg/kg) while the lowest was found in FGDG-C (7.47 ± 1.98 mg/kg). And finally, the highest average concentration of Zn was found on FGDG-D (35.69 ± 20.03 mg/kg) while the lowest was found in FGDG-C (7.47 ± 1.98 mg/kg) as shown in table 12.

Table 12. Total content of elements in flue gas desulphurization gypsum (FGDG) – Micronutrients (mg/kg)

FGDG	Condition	Cu	Fe	Mn	Ni	Zn
FGDG-A	Raw	4.67 ± 2.16	684.68 ± 57.58	19.62 ± 1.96	1.22 ± 0.06	6.28 ± 1.73
	600 °C	6.28 ± 0.64	1120.3 ± 66.06	26.55 ± 5.91	1.37 ± 0.19	15.86 ± 12.68
	800 °C	5.76 ± 0.39	1017.06 ± 81.98	19.58 ± 3.2	1.28 ± 0.1	22.92 ± 24.45
FGDG-B	Raw	1.8 ± 0.76	800.72 ± 105.71	77.1 ± 4.95	1.81 ± 0.43	8.87 ± 0.3
	600 °C	13.67 ± 2.1	1034.74 ± 30.78	70.43 ± 5.82	1.49 ± 0.22	16.55 ± 13.42
	800 °C	10.18 ± 2.98	1229.52 ± 16.25	73.9 ± 3.15	1.74 ± 0.27	22.9 ± 16.88
FGDG-C	Raw	1.41 ± 0.85	611.06 ± 219.24	18.22 ± 4.16	1.23 ± 0.42	6.23 ± 1.25
	600 °C	1.81 ± 0.25	756.16 ± 44.16	13.85 ± 2.45	0.97 ± 0.08	9.75 ± 2.8
	800 °C	2.36 ± 0.73	785.66 ± 64.6	13.29 ± 1.33	1.22 ± 0.12	6.42 ± 1.66
FGDG-D	Raw	14.05 ± 4.27	3223.41 ± 116.32	65.73 ± 3.44	4.41 ± 0.32	17.46 ± 0.38
	600 °C	24.86 ± 0.43	4050.86 ± 54.31	80.39 ± 7.13	5.07 ± 0.51	21.69 ± 0.47
	800 °C	32.69 ± 4.04	4784.97 ± 3.14	95.43 ± 2.46	6.15 ± 0.05	67.92 ± 59.24

6.7 Available Content of Micronutrients in flue gas desulphurization gypsum pyrolyzed samples

In the case of the micronutrients, the Fe was again the most abundant micronutrient with concentrations varying between 174.76 ± 2.21 and 0.21 ± 0 mg/kg, followed by Mn (41.99 ± 1.41 to 10.43 ± 0.23 mg/kg), the Zn (7.07 ± 6.89 to 1.42 ± 0.09 mg/kg), the Cu (11.06 ± 1.58 to 0.44 ± 0.01 mg/kg) and finally Ni (1.42 ± 1.16 to 0.32 ± 0.04). The highest average concentration per sample were also analyzed. The highest average concentration of Cu was found on FGDG-B (5.12 ± 1.34 mg/kg) while the lowest was found in Sample C (0.67 ± 0.27 mg/kg). For the Fe, the highest average concentration was found on FGDG-A (92.11 ± 5.46 mg/kg) while the lowest was found in FGDG-D (0.66 ± 0.58 mg/kg). FGDG-B had the highest average concentration of Mn (46.46 ± 0.94 mg/kg) while the lowest was found in FGDG-C (11.02 ± 0.58 mg/kg). Consequently, the highest average concentration of Ni was found on FGDG-C (0.8 ± 0.01 mg/kg) while the lowest was found in FGDG-D (0.41 ± 0.17 mg/kg) and the highest average concentration of Zn was found on FGDG-B (4.1 ± 2.85 mg/kg) while the lowest was found in FGDG-D (2.08 ± 0.05 mg/kg). Table 13 shows the mean ± stand for micronutrients

Table 13. Available of elements in flue gas desulphurization gypsum (FGDG) –Micronutrient elements (mg/kg)

FDGD	**Condition**	**Cu**	**Fe**	**Mn**	**Ni**	**Zn**
FGDG-A	Raw	2.27 ± 0.1	8.89 ± 3.85	13.35 ± 2.35	0.32 ± 0.04	2.26 ± 0.87
	600 °C	2.42 ± 0.54	92.69 ± 10.33	15.93 ± 1.65	0.31 ± 0	1.63 ± 0.15
	800 °C	2.13 ± 0.19	174.76 ± 2.21	15.46 ± 1.72	0.61 ± 0.06	3.38 ± 2.43
FGDG-B	Raw	2.06 ± 1.71	120.2 ± 13.8	72.78 ± 0.83	1.42 ± 1.16	3.28 ± 0.22
	600 °C	11.06 ± 1.58	52.74 ± 10.41	41.99 ± 1.41	BDL	7.07 ± 6.89
	800 °C	2.26 ± 0.74	24.06 ± 0.14	24.62 ± 0.59	BDL	1.96 ± 1.46
FGDG-C	Raw	0.44 ± 0.01	42.6 ± 2.07	11.6 ± 1.52	0.77 ± 0.01	1.42 ± 0.09
	600 °C	0.6 ± 0.08	105.11 ± 10.75	10.43 ± 0.23	0.78 ± 0.02	2.18 ± 0.97
	800 °C	0.96 ± 0.24	163.56 ± 68.01	11.02 ± 1.43	0.86 ± 0.01	2.95 ± 0.35
FGDG-D	Raw	1.17 ± 0.17	0.46 ± 0.05	24.65 ± 0.03	0.32 ± 0.04	1.77 ± 0
	600 °C	0.87 ± 0.29	1.32 ± 0.72	28.39 ± 0.55	0.6 ± 0.09	2.39 ± 0.11
	800 °C	BDL	BDL	BDL	BDL	BDL

BDL: Below detection limit (Cu < 0.005 mg/l, Fe < 0.005 mg/l, Mn < 0.001 mg/l, Ni < 0.005 mg/l, Zn < 0.002 mg/l)

Figure 23, represents the relative availability portion of micronutrients in FGDG-A, Mn recorded the highest relative availability at 800 °C with a percentage of 80 %, which had increased from 600 °C (61 %), Ni has increased with temperature from 22 % at 600 °C, to 48 % at 800 °C. Fe went from 1.2 % before pyrolysis to 17 % at 800 °C, for Cu the portions for both 600 and 800 °C were close as 38 % and 37 %, the portion of Zn before pyrolysis were higher in 39 % than after for 600 °C 14 % and 800 °C 21 %.

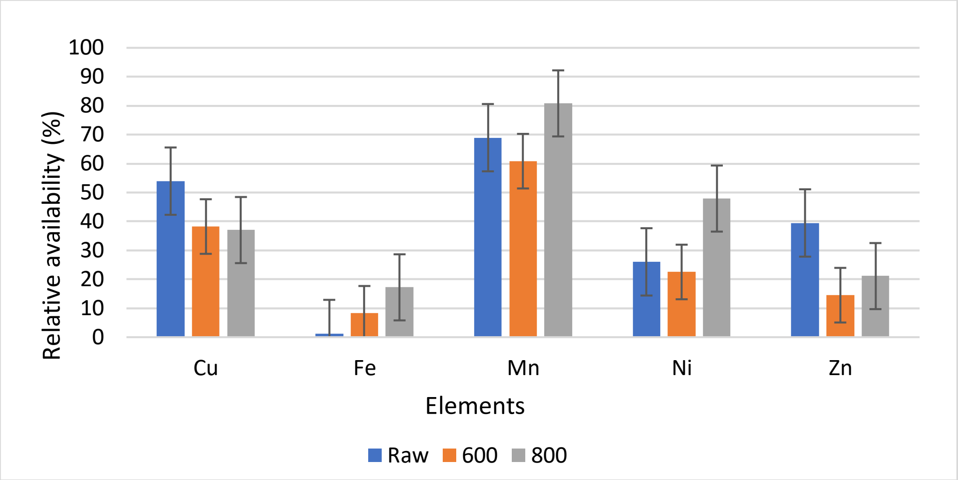

Figure 21. Relative availability content of Micronutrient in flue gas desulphurization gypsum (FGDG-A (%))

The relative availability of Cu in FGDG-B as shown in figure 24, was higher than the rest of micronutrients in all the evaluated conditions, while the relative availability of Ni reported values BDL for both 600 and 800 °C. The 600 °C of both Fe and Mn was higher than 800 °C (5 %, 60 % at 600 °C). For Zn, the portion increased at 600 °C to 38 %, and the decreased to 8 % at 800 °C.

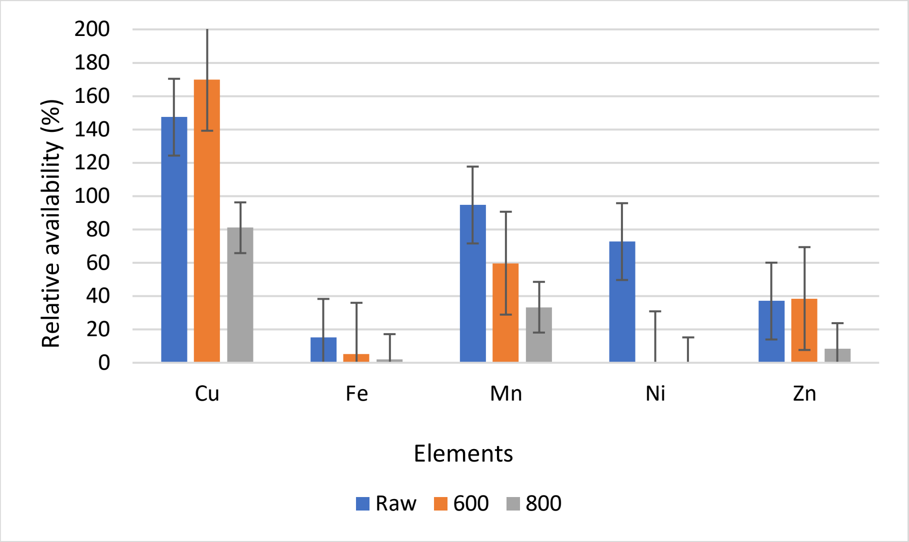

Figure 22. Relative availability content of Micronutrient in flue gas desulphurization gypsum (FGDG-B (%))

Figure 25, present the increasing of micronutrients in FGDG-C. Mn, Fe and Zn had increased by the increasing of temperature that goes from to 77 % at 600 °C, to 84 % at 800 °C for Mn, and 14 % at 600 °C, to 21 % at 800 °C for Fe, Zn goes from 24 % at 600 °C to 47 % at 800 °C. While for Cu and Ni the higher relative availability was at 600 °C (43 % and 80 %).

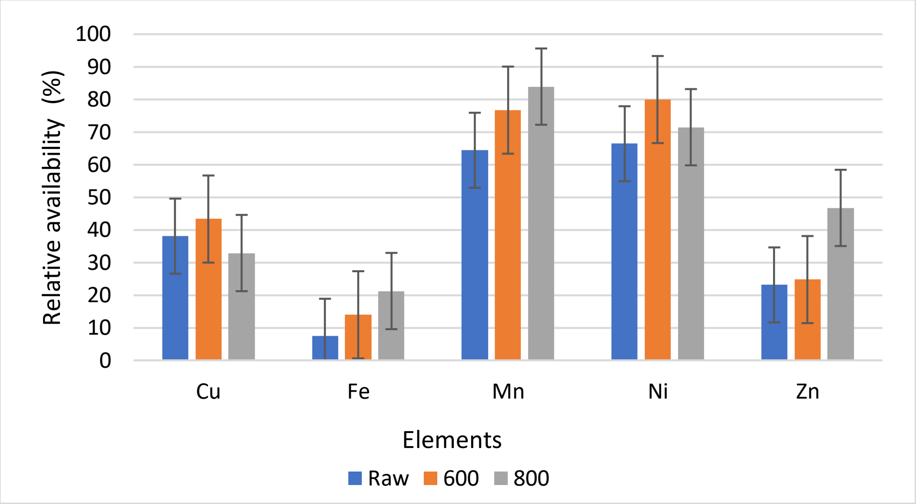

Figure 23. Relative availability content of Micronutrient in flue gas desulphurization gypsum (FGDG-C (%))

In figure 26 the availability of micronutrients in FGDG-D at 800 °C were below detection limit for all of the elements. For Mn, Ni and Zn the Relative availability of the micronutrient at 600 °C were similar as before pyrolysis (35 %, 11 % and 115 %), but for Cu the concentration had decreased at 600 °C to 3.5 %

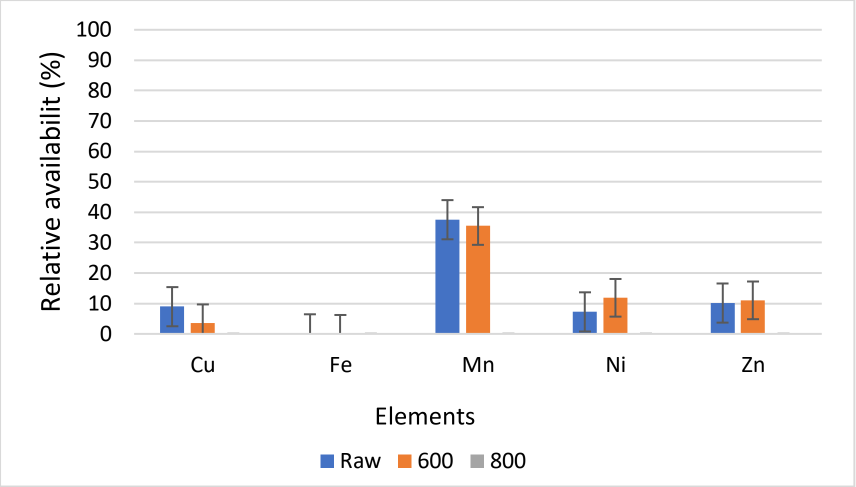

Figure 24. Relative availability content of Micronutrient in flue gas desulphurization gypsum (FGDG-D (%))

6.8 Anova and TukeyHSD test for the total concentration of micronutrients

The analysis of variance for the total concentration of micronutrients revealed that temperature had a significant effect on p.value Cu (< 0.01) and Fe (<0.01), while for the Mn and Ni has a significant difference for samples only, and Zn didn’t have any differences in temperature nor in samples. As with the macronutrients, the Sample was shown in table 14 to be a significant factor for all elements.

Table 14. Anova evaluation for the total concentration of the micronutrients

Element	term	df	sumsq	meansq	statistic	p.value
Cu	Temperature	2	245.55	122.78	7.07	< 0.01
	Sample	3	1681.44	560.48	32.28	< 0.01
	Residuals	18	312.50	17.36	-	-
Fe	Temperature	2	1610787.51	805393.75	10.70	< 0.01
	Sample	3	44282884.46	14760961.49	196.14	< 0.01
	Residuals	18	1354639.96	75257.78	-	-
Mn	Temperature	2	115.81	57.91	0.93	0.41
	Sample	3	20910.27	6970.09	112.48	< 0.01
	Residuals	18	1115.37	61.97	-	-
Ni	Temperature	2	0.86	0.43	2.30	0.13
	Sample	3	67.29	22.43	119.81	< 0.01
	Residuals	18	3.37	0.187	-	-
Zn	Temperature	2	1734.76	867.38	2.35	0.12
	Sample	3	2610.72	870.24	2.36	0.11
	Residuals	18	6640.02	368.89	-	-

Significant difference between temperatures were found for the Cu between the Raw and 600 ºC and Raw and 800 ºC treatments, while no difference was found between the 600 and 800 ªC treatments. For the Fe, significant difference was found between the Raw and the 800 ªC and between the 600 and 800 °C. Finally, the Zn, Ni, and Mn the o significant difference was not found in any temperature, as shown in figure 27.

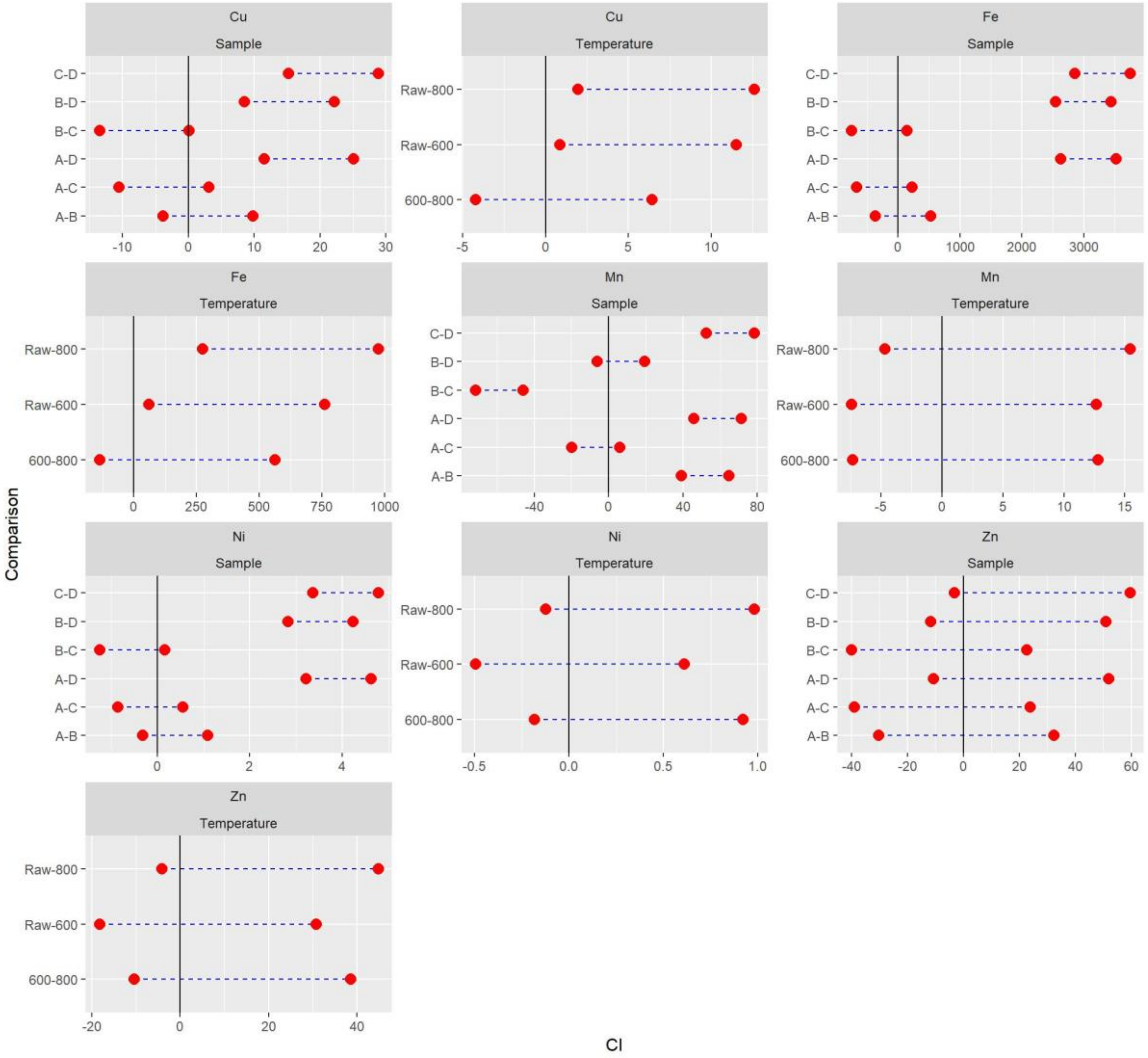

Figure 25. Pairwise comparison trough TukeyHSD test for the effects of temperature and Sample in the total concentration of micronutrients

6.9 Anova and TukeyHSD test for the Available concentration of micronutrients

The anova for the micronutrients didn't have any significant effect of the temperature any of the micronutrients, but had a significant difference for Samples in Cu, Fe and Mn. The sample was shown in table 15.

Table 15. Anova evaluation for the available concentration of the micronutrients

Element	**term**	**df**	**sumsq**	**meansq**	**statistic**	**p.value**
Cu	Temperature	2	23.25	11.63	2.19	0.14
	Sample	3	74.69	24.90	4.68	0.02
	Residuals	16	85.13	5.32	BDL	BDL
Fe	Temperature	2	14039.54	7019.77	2.54	0.11
	Sample	3	29776.52	9925.51	3.59	0.04
	Residuals	17	47049.28	2767.60	BDL	BDL
Mn	Temperature	2	632.17	316.09	2.80	0.09
	Sample	3	4537.15	1512.38	13.41	< 0.01
	Residuals	16	1804.04	112.75	BDL	BDL
Ni	Temperature	2	0.13	0.07	0.40	0.68
	Sample	3	1.13	0.38	2.22	0.13
	Residuals	14	2.37	0.170	BDL	BDL
Zn	Temperature	2	5.15	2.57	0.48	0.63
	Sample	3	15.52	5.17	0.96	0.43
	Residuals	16	86.04	5.38	BDL	BDL

The post-hoc test didn’t found any significant differences between the Raw and 600 °C and the 600 and 800 °C treatments, and the Raw - 800°C comparison was shown to no be significant, as shown in figure 28.

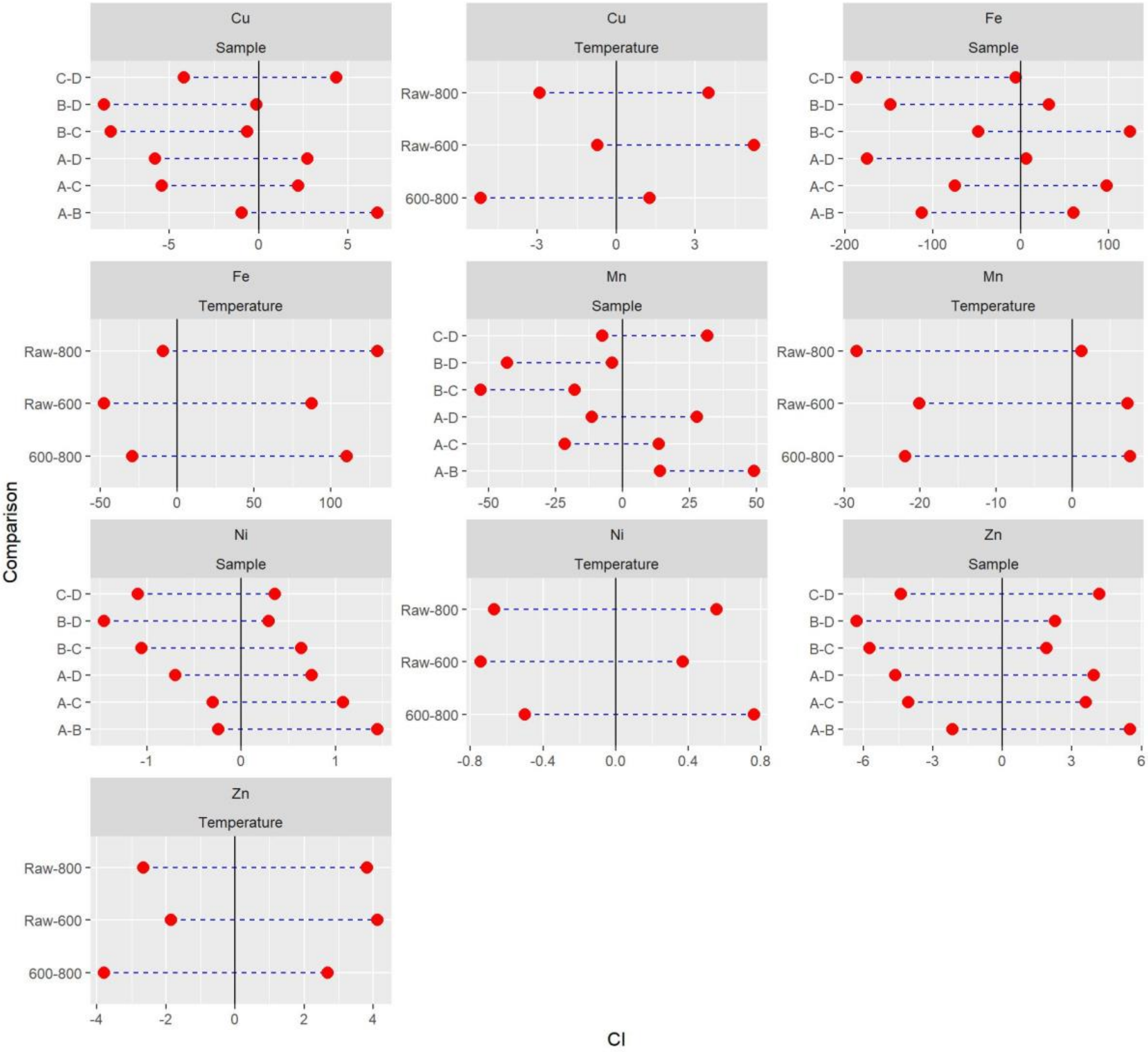

Figure 26. Pairwise comparison trough TukeyHSD test for the effects of temperature and Sample in the available concentration of micronutrients.

6.10 Total Content of Toxic elements in flue gas desulphurization gypsum pyrolyzed samples

In the case of the toxic elements, the As was by far the most abundant element with concentrations varying between 156.99 ± 16.11 mg/kg and 3.5 ± 0.65 mg/kg, followed by Cr (2.44 ± 0.36 mg/kg to 12.25 ± 0 mg/kg), the Pb (1.36 ± 0 mg/kg to 3.59 ± 0.2 mg/kg), and finally the Cd (0.07 ± 0.08 mg/kg to 0.61 ± 0 mg/kg), as shown in table 16. The highest and lowest values of nutrients per sample were as follows. The highest average concentration of As was found on FGDG-B (136.5 ± 25.88 mg/kg) while the lowest was found in FGDG-C (5.61 ± 2.59 mg/kg). For the Cd, the highest concentration was found on FGDG-A (0.27 ± 0.3 mg/kg) while the lowest was found in FGDG-C (0.07 ± 0.01 mg/kg). FGDG-D (9.82 ± 0.08 mg/kg) had the highest average concentration of Cr while the lowest was found in FGDG-A (2.68 ± 0.23 mg/kg). Finally, the highest average concentration of Pb was found on s FGDG-D (3.07 ± 0.36 mg/kg) while the lowest was found in FGDG-A (1.7 ± 0.54 mg/kg).

Table 16. Total content of elements in flue gas desulphurization gypsum (FGDG) – Toxic elements (mg/kg)

FGDG	**Condition**	**As**	**Cd**	**Cr**	**Pb**
FGDG-A	Raw	8.29 ± 1.42	BDL	2.44 ± 0.36	BDL
	600 °C	9.84 ± 0.7	BDL	2.89 ± 0.19	2.32 ± 1.08
	800 °C	7.22 ± 1.56	BDL	2.7 ± 0.18	1.41 ± 0.28
FGDG-B	Raw	107.4 ± 35.04	0.17 ± 0.08	3.07 ± 1	BDL
	600 °C	156.99 ± 16.11	0.17 ± 0.13	3.24 ± 0.18	2.09 ± 0.02
	800 °C	145.08 ± 0.16	0.07 ± 0.08	3.48 ± 0.06	BDL
FGDG-C	Raw	6.15 ± 3.38	BDL	2.75 ± 1.08	2 ± 0.26
	600 °C	7.19 ± 3.74	0.07 ± 0	2.72 ± 0.18	BDL
	800 °C	3.5 ± 0.65	BDL	2.65 ± 0.16	BDL
FGDG-D	Raw	26.21 ± 1.31	0.15 ± 0.06	6.86 ± 0.14	2.74 ± 0.19
	600 °C	33.93 ± 4.43	0.14 ± 0.09	10.36 ± 0.11	2.88 ± 0.7
	800 °C	39.37 ± 0.81	0.14 ± 0.01	12.25 ± 0	3.59 ± 0.2

BDL: Below detection limit (Cd< 0.001 mg/l, Pb < 0.02 mg/l)

6.11 Available Content of Potentially Toxic Elements (PTEs) in Flue Gas Desulphurization Gypsum pyrolyzed samples

The analysis of available concentration of PTEs only included the As and the Cr since both the Cd and Pb had more than 50% of observations below the detection limit. The most abundant PTE in the available fraction of all samples was As with concentration varying from 95.52 ± 0.56 mg/kg to 1.27 ± 0 mg/kg while the Cr varied from 0.79 ± 0.11 mg/kg to 0.22 ± 0.02. Regarding average concentration per sample, the highest average concentration of As was found on FGDG-B (78.77 ± 23.73 mg/kg) while the lowest was found in FGDG-D (1.61 ± 0.3 mg/kg). For the Cr, the highest concentration was found on sample C (0.56 ± 0.06 mg/kg) while the lowest was found in Sample B (0.25 ± 0.02 mg/kg), as table 17 show.

Table 17. Available of elements in flue gas desulphurization gypsum (FGDG) –Potentially Toxic elements (mg/kg)

FGDG	Condition	As	Cr
FGDG-A	Raw	2.17 ± 0.56	BDL
	600 °C	7.09 ± 0.23	0.26 ± 0.01
	800 °C	3.42 ± 0.11	0.5 ± 0.06
FGDG-B	Raw	89.17 ± 6.9	0.26 ± 0.02
	600 °C	95.52 ± 0.56	0.24 ± 0.02
	800 °C	51.61 ± 0.38	BDL
FGDG-C	Raw	2.12 ± 0.00	0.22 ± 0.02
	600 °C	2.64 ± 0.64	0.67 ± 0.07
	800 °C	1.35 ± 0.28	0.79 ± 0.11
FGDG-D	Raw °C	1.27 ± 0.00	BDL
	600 °C	1.84 ± 0.00	BDL
	800 °C	1.73 ± 0.00	BDL

BDL: Below detection limit (As < 0.03 mg/l, Cd < 0.001, Cr < 0.005 mg/l, Pb < 0.02 mg/l)

Figure 29 shows the relative availability of toxic elements in FGDG-A samples. As availability at 600 °C was higher than 800 °C, went from 27 % at raw, to 72 % at

600 °C, and decreased to 48 % at 800 °C. For Cr the availability increased with temperature from 9 % at 600 °C, to 19 % at 800 °C.

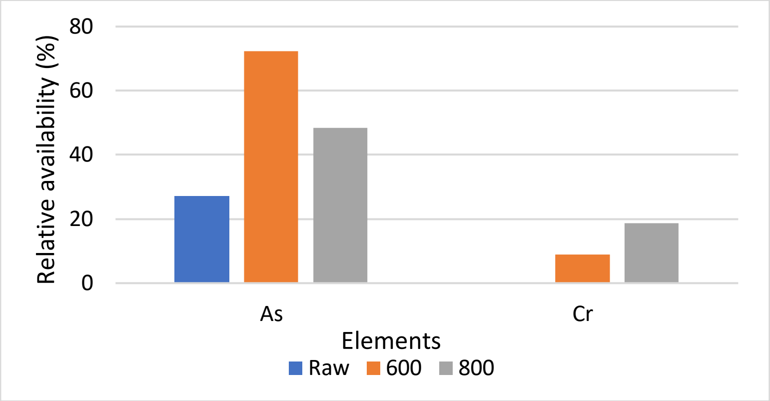

Figure 27. Relative availability content of Toxic elements in flue gas desulphurization gypsum (FGDG-A (%))

Figure 30 represent FGDG-B sample relative availability of As and Cr, As portion has increased through the two temperatures, it went from 88 % at raw, to 61 % at 600 °C, to 35 % at 800 °C, while Cr has 7 % at 600 °C, and below detection limit at 800 °C

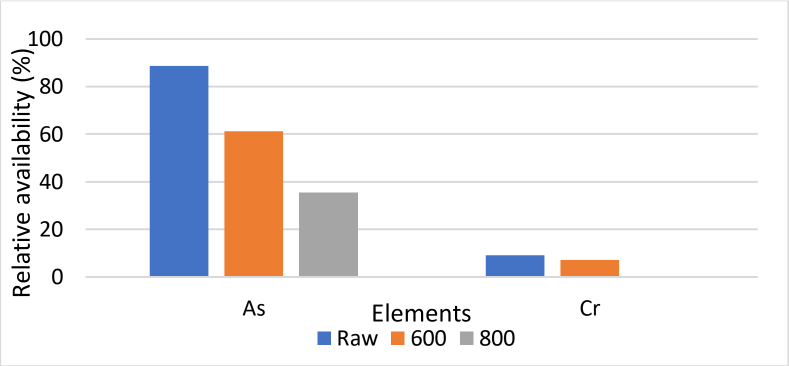

Figure 28. Relative availability content of Toxic elements in flue gas desulphurization gypsum (FGDG-B (%))

In figure 31, the relative availability of FGDG-C in As at 600 °C was higher than at 800 °C (61 % and 27 % respectively), and for Cr the availability increased with temperature from 9 % at raw, to 25 % at 600 °C, then to 30 % at 800 °C. For FGDG-D the available contents were below detection limits for raw samples at both temperatures.

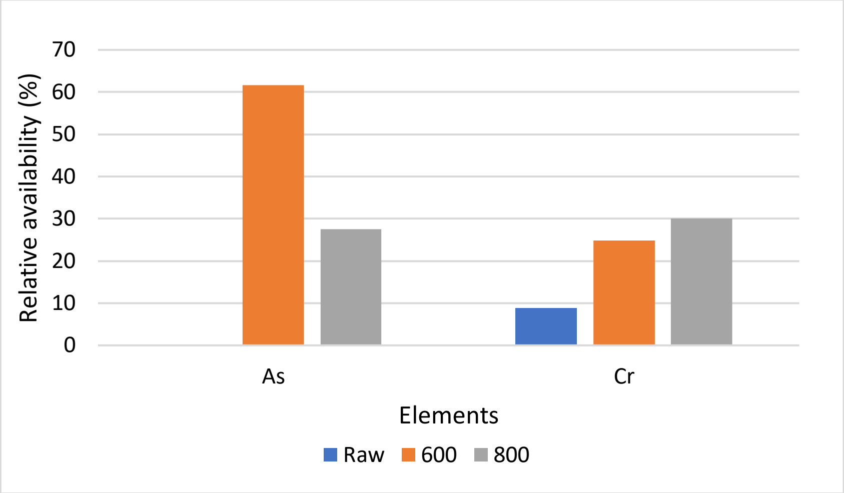

Figure 29. Relative availability content of Toxic elements in flue gas desulphurization gypsum (FGDG-C (%))

6.12 Anova and TukeyHSD test for the total concentration of toxic elements

The analysis of variance for the total concentration of toxic elements revealed that temperature had a significant effect only on Cr (0.05), while for the As, Cd the significant difference was only for samples and Pb the differences between temperatures were not significant. In contrast with the macro and micronutrients the Sample was not found in table 18 to be significant in all elements because it was not significant for the Cd.

Table 18. Anova evaluation for the total concentration of the toxic elements

Element	term	df	sumsq	meansq	statistic	p.value
As	Temperature	2	995.19	497.60	2.62	0.10
	Sample	3	68368.05	22789.35	119.91	< 0.01
	Residuals	18	3420.89	190.05	BDL	BDL
Cd	Temperature	2	0.03	0.01	0.92	0.42
	Sample	3	0.08	0.03	1.76	0.21
	Residuals	12	0.18	0.02	BDL	BDL
Cr	Temperature	2	9.29	4.65	3.56	0.05
	Sample	3	218.15	72.72	55.79	< 0.01
	Residuals	18	23.46	1.30	BDL	BDL
Pb	Temperature	2	0.13	0.07	0.22	0.80
	Sample	3	5.93	1.98	6.63	< 0.01
	Residuals	13	3.88	0.298	BDL	BDL

The pairwise comparison revealed that for the Cr the pyrolysis at 800 °C was significantly different from the Raw treatment but not from the 600 °C treatment. Additionally, as anticipated by the anova no significant difference was found between the different samples for the Cd, as shown in figure 32.

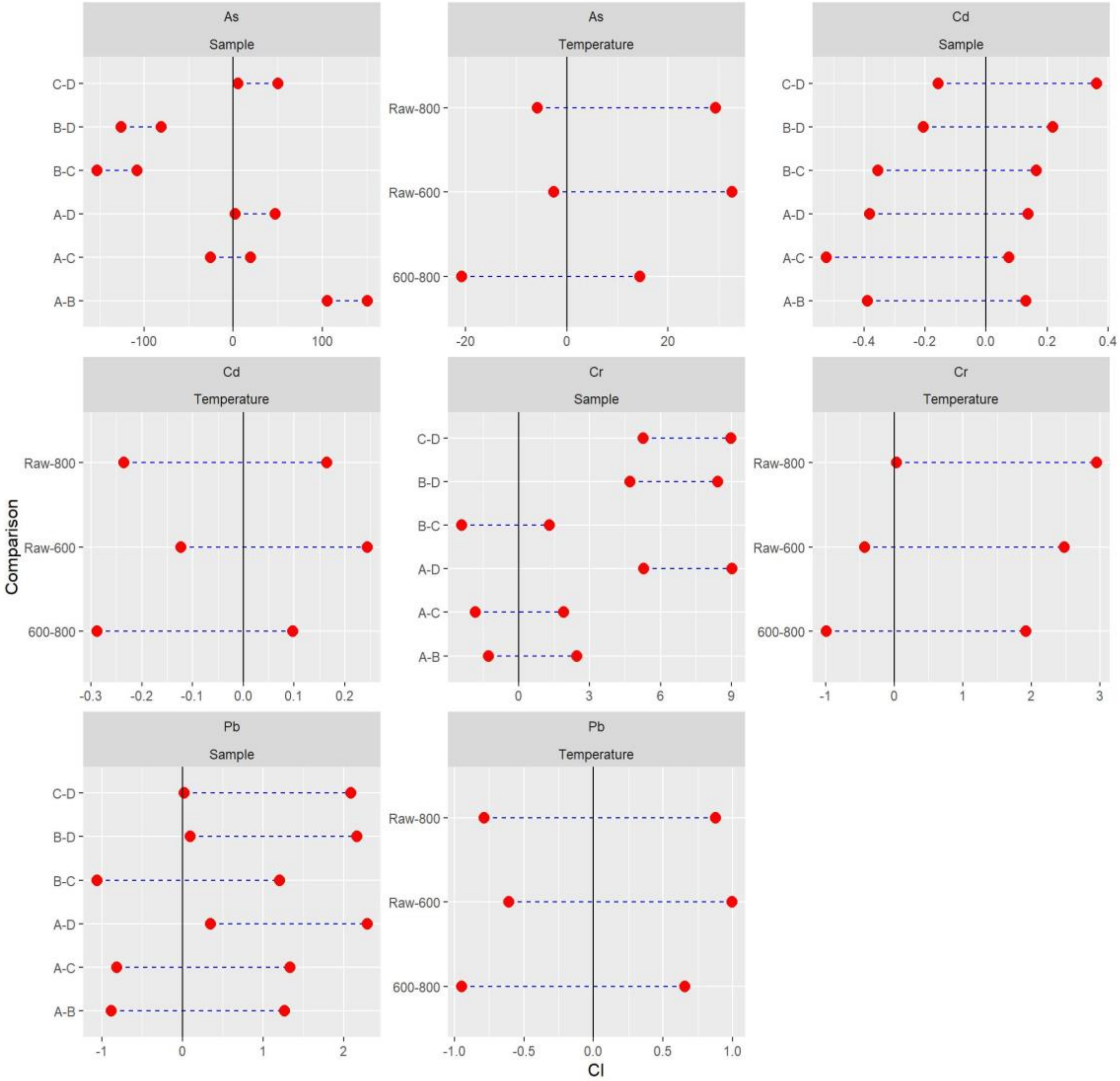

Figure 30. Pairwise comparison trough TukeyHSD test for the effects of temperature and Sample in the total concentration of toxic elements

6.13 Anova and TukeyHSD test for the available concentration of toxic elements

Finally, figure 19 shows the available concentration of toxic elements no significant effect of temperature was found for neither element, although the sample was significant in both cases As (0.04) and Cr (< 0.01).

Table 19. Anova evaluation for the available concentration of the toxic elements

Element	term	df	sumsq	meansq	statistic	p.value
As	Temperature	2	930.89	465.44	4.12	0.04
	Sample	3	24026.78	8008.93	70.96	< 0.01
	Residuals	14	1580.21	112.87	BDL	BDL
Cr	Temperature	2	0.34	0.17	11.38	< 0.01
	Sample	2	0.22	0.11	7.18	0.01
	Residuals	9	0.14	0.02	BDL	BDL

Regarding the sample the FGDG-B was shown to be significantly different from all the others sample in As. While for the Cr it has significant differences for 600 – 800 °, and Raw – 800 °C, while for Raw – 600 °C didn’t show any differences, as shown in figure 33.

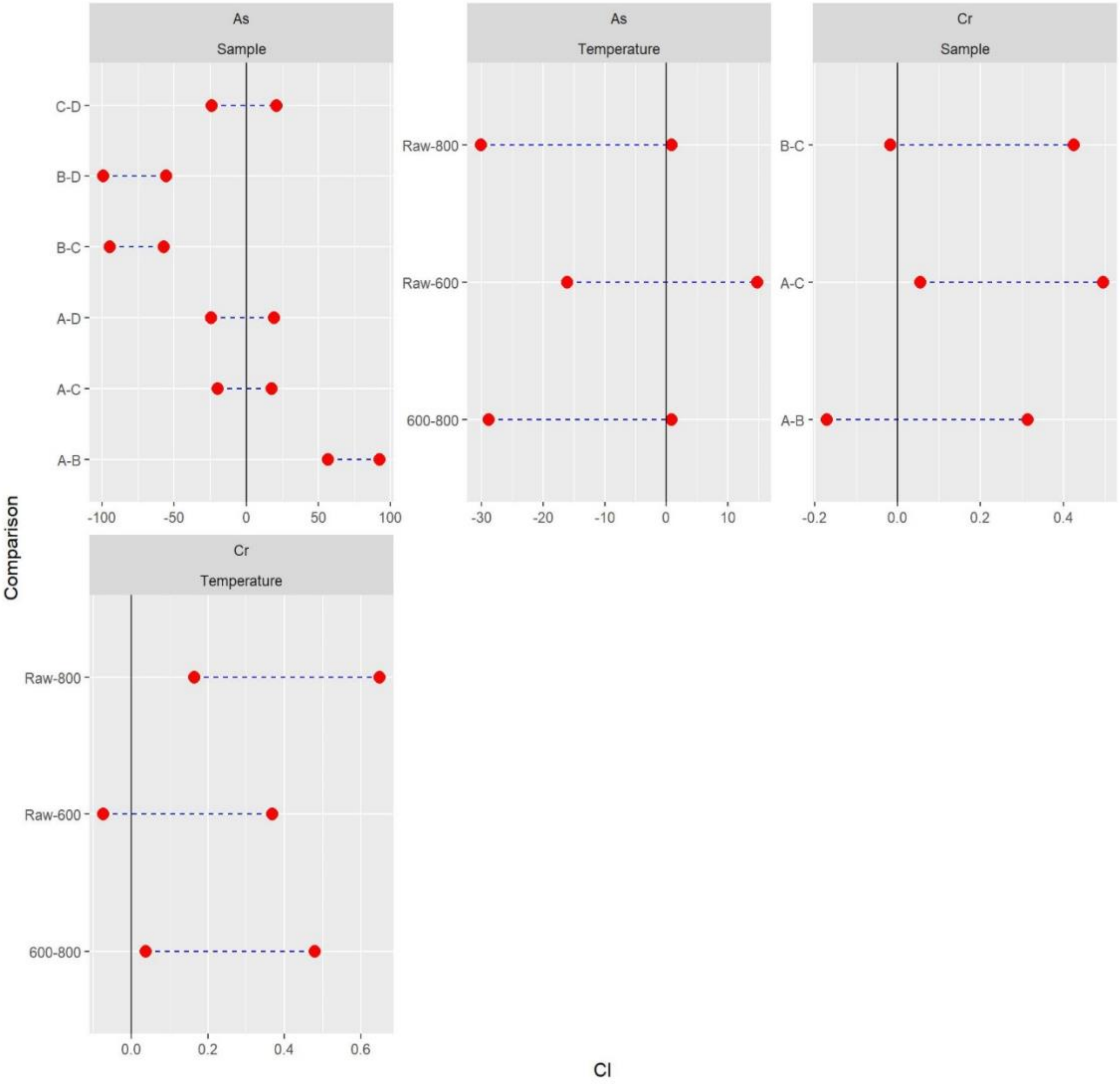

Figure 31. Pairwise comparison trough TukeyHSD test for the effects of temperature and Sample in the available of toxic elements

7. Discussion

Regarding pH, the samples were taken from four different power plants in the Czech Republic, in the case of FGDG-A the analysis samples reported pH of 7.6. This was in accordance with the results reported by Desutter *et al.,* (2014), where pH value for the analyzed FGDG-A was 7.5, while for FGDG-B and FGDG-C the pH reported in the analysis was 6.9. On the other hand, pH value in the analysis reported 10.43 in FGDG-D sample.

The pH values reported by Bagligar *et al.,* (2011) for non-stabilized FGDG samples varied between 8.4 – 8.8, being higher than the pH values found in FGDG-A, FGDG-B and FGDG-C and is affected by the content of unreacted base present in the product.

The use of FGD on agricultural lands could have both benefits and drawbacks (Knox *et al.,* 2006).

Electrical conductivity is a metric for how much soluble is found the soil, it's a crucial metric for determining the health of the soil. It has an effect on crop yields, crop suitability, plant nutrient availability, and soil microorganism development, all of which influence main soil processes such as greenhouse gas emissions including nitrogen oxides, methane, and carbon dioxide. The abundance of solube nutrients in the soil is indicated by the EC. The further negatively charged sites (clay and organic particles) in the soil, the higher the EC, and therefore the more cations (positively charged ions) must be retained in the soil, the lower EC values (0-2 mS/cm) (Fourie, 2019). The analysis sample reported values between 1.3 – 2.6 mS/cm, this was in accordance with the results reported by Desutter *et al.,* (2014), in this study values were above 2.6 mS/cm. While Bagligar *et al.,* (2011) reported EC values with range of 2.2 – 3.5 mS/cm for non-stabilized samples, because the concentrations of mineral elements needed by plants are higher in stabilized FGDGs than in non-stabilized FGDGs (original FGD material formed without receiving stabilizing materials) (Bagligar *et al.*, 2011).

Soil pH is an important parameter in the assimilation of various essential nutrients for plant production. To correct the pH of the soil, base calcium compounds are used. A large quantity of calcium carbonate is commonly used in this application (Lemos *et al.,* 2007). The analysis of total content of elements determination, focused on macronutrients, showed Ca higher concentration in FGDG-D as the analysis reported for samples before pyrolysis 287.6 g/kg, in concordance with the results described by Desutter *et al.,* (2014), with a slightly lower concentration of Ca 243 g/kg. Calcium concentration value for raw sample reported in FGDG-A was 211 g/kg, following with the results reported by Chen *et al.,* (2008) who obtained 213 g/kg, indicating similar results. Ca in FGDG is important because it promotes the flocculation and accumulation of clay particles, which decreases soil particle dispersion, also its application promotes rapid downward movement of Ca in the soil profile due to the high Ca content in soil solution (Wang *et al.,* 2018; Ernani *et al.,* 2006). On the other hand, S concentration was higher 209 g/kg, when compared to FGDG-D with a total content of 135 g/kg. S, raw FGDG samples, Chen *et al.,* (2008) reported a higher concentration 164 g/kg, while the analysis for FGDG-A 128 g/kg. The concentration of calcium in the soil was still higher in the gypsum treatments. With time, the differences in soil Ca between the gypsum plus lime treatment and the lime alone treatment grew. In comparison to lime alone, gypsum application resulted in higher soil Ca concentrations at deeper depths (Zoca & Penn, 2017)

Phosphorus analysis for raw samples has reported higher P concentration in FGDG-A with a total content of 0.13 g/kg, similar results are reported by Bagligar *et al.*, (2011) who obtained 0.054 g/kg. Using FGDG as a soil amendment has the ability to minimize P losses in runoff by raising infiltration and creating less soluble pools, according to (Endale *et al.,* 2014, Dou *et al.,* 2003). As reported from Stout *et al.*, (1999) using FGDG to convert soil P to less soluble forms can reduce the amount of soil P released into runoff. Chen *et al.*, (2016), recorded that FGDG decreased P loss in soil incubation tests and that a higher dose of FGDG resulted in a greater decrease in water-extractable P.

Total concentration of Ca after pyrolysis process reported higher value in the analysis of FGDG-D at 600 °C, 369.9 g/kg, the results described by Guo *et al.,* (2013), who reported 214 g/kg, and for S after pyrolysis at 600 °C the analysis has reported lower concentration 161 g/kg, this was similar to the total content of 203.6 g/kg for sample FGDG-B. Macronutrients total content after being pyrolyzed at 800 °C, has reported higher concentration for Ca and S for FGDG-B and FGDG-C, 204.6 g/kg and 218.2 g/kg respectively, this was in accordance with the result reported by Guo *et al.*, (2013) who obtained 256 g/kg for Ca, and 188 g/kg for S.

Continuing with the total content of elements review, this time concentrating on micronutrients, Cu had higher concentration in FGDG-D raw sample reporting 14.05 mg/kg, compared to FGDG-A with 4.7 mg/kg, while the results described by Desutter *et al.,* (2014) had concentrations of 0.8 mg/kg, but for Punshon *et al.,* (1999), the analysis reported lower concentration 0.001 mg/kg.

Manganese analysis had low concentration in the analysis of raw samples for FGDG-C 18.22 mg/kg, when the result describes by Desutter *et al.,* (2014), reported higher concentration of 161 mg/kg, also the value of Bagligar *et al.,* (2011) reported higher concentration than 94 mg/kg, while for Punshon *et al.,* (1999), the concentration was very low 0.002 mg/kg comparing with the other results.

Iron value for FGDG-D has reported a high concentration 3223.4 mg/kg, when the result of Baligar *et al.,* (2011), obtained concentration of 2700 mg/kg, while Desutter *et al.,* (2014), had higher concentration of 1379 mg/kg than, FGDG-B, 800.7 mg/kg, and the lowest concentration of Fe was reported by Chen *et al.,* (2008), who obtained a value of 222 mg/kg.

Total concentration of Fe after pyrolysis process has reported higher value in the analysis of FGDG-D at 600 °C, 4050 mg/kg, and at 800 °C, 4785 mg/kg, while the analysis of Guo *et al.*, (2013), has reported low concentration of 142 mg/kg and 132 mg/kg respectively for the same tested temperatures.

Total content of Cu after pyrolysis had reported for FGDG-D the highest concentration for Cu at 800 °C, the analysis has reported 32.7 mg/kg, meanwhile at 600 °C 24.9 mg/kg, when Guo *et al.*, (2013), has obtained lower concentration of 0.47 mg/kg for 600 °C and 800 °C.

Continuing with the results the available content of micronutrients, the higher value of Cu concentration was obtained for FGDG-B 1.71 mg/kg, in the result described by Punshon *et al.,* (1999), the value was 0.08 mg/kg. For Mn the result reported higher concentration for FGDG-B raw sample 72.8 mg/kg, while Punshon *et al.*, (1999), has reported low value of 0.01 mg/kg.

Continuing the study of the total content of elements, this time focusing on toxic elements, As in raw sample analysis has reported higher concentration in FGDG-B 107.41 mg/kg, when the result described by Chen *et al.,* (2008) had obtained value below 11 mg/kg. Also, Bagligar *et al.,* (2011) has reported concentration below detection limits for As, and Punshon *et al.,* (1999), has obtained value with lower concentration 0.03 mg/kg. FGDG has proven to be an effective soil amendment for soil reclamation, it has the potential to introduce additional heavy metals into the soil environment (Wang *et al.,* 2018). FGDG does not contain large amounts of heavy metals, according to some reports, and its application does not cause soil pollution (Koralegedara *et al.,* 2017).

Total content of As after pyrolysis has reported higher concentration for FGDG-B at 600 °C with a value of 157 mg/kg, when the result of Guo *et al.,* (2013), obtained concentration of 1.61 mg/kg for both temperature 600 °C and 800 °C. According to Chen *et al.*, (2015), Arsenic concentration in soils was found to be positively associated with the addition of FGDG.

Chromium analysis reported higher concentration at FGDG-D 6.9 mg/kg, similar to the results describe by Desutter *et al.,* (2014), who attained 5.1 mg/kg, this was in contrast with the results described by Chen *et al.,* (2008) with concentration below 1 mg/kg. While Bagligar *et al.,* (2011) has reported higher concentration reached 87 mg/kg, when Punshon *et al.,* (1999), has reported a low concentration value for 13.73 mg/kg.

According to the Decree Np. 474/2000 Coll. The limits value for toxic elements in fertilizers were found in paragraph 1b, the phosphorus-free mineral fertilizers, and soil improvers, by the Czech regulation:

For Arsenic, the limit of it presence is 20 mg/kg, which is higher than FGDG-A and FGDG-C after being pyrolyzed, while FGDG-B record higher concentration for 600 °C, 157 mg/kg, so the limit exceeded about 7x, and FGDG-D also has high concentration at 800 °C, 39 mg/kg.

And for Cadmium, the limit in the Czech Republic is 1 mg/kg, while the analysis has recorded lower concentration for all the FGDG samples.

While Chromium and Lead limit is 50 mg/kg and 10 mg/kg respectively, which is much higher than the FGDG samples after pyrolysis process (Decree No. 474/2000 Coll. 2000).

On the other hand, Cr value has reported concentration below detection limits for FGDG-A and FGDG-D, while for FGDG-C concentration was 0.22 mg/kg, in accordance with the results from Punshon *et al.,* (1999), has reported 0.05 mg/kg.

8. Conclusion

Four samples were taken from four different power plants in the Czech Republic, the samples were dried at 105 °C, and all of the humidity were taken out, then samples were pyrolyzed at two temperatures 600 °C and 800 °C for 30 minutes fast, and from pyrolysis, total, available content were analyzed.

For some elements, the total concentrations of FGDG samples were dependent on the pyrolysis temperature, Macronutrients contents of Ca, P, S, has increased with the pyrolysis temperature, as well micronutrients like Fe, Mn also increased with the temperature, and those elements are better to use as a soil amendment.

For few elements, the available concentration in FGDG samples after using the two-temperature in pyrolysis process played a big roll, like for macronutrients: Ca, P, S, in FGDG-A the highest value of S was 22 % at 600 °C, some of them increased at 800 °C, as S in FGDG-D which has the highest value at 800 °C for 34 %, but also had below detection limits. For micronutrients Cu, Fe, Mn most of the elements value didn't increased during the pyrolysis, and stay at its highest as the raw samples.

And for Toxic elements: the total concentration in the analysis shows that it presence is lower than the regulation limits in the Czech Republic, but for Arsenic, FGDG-B has recorded higher concentration at 600 °C for 157 mg/kg and at 800 °C 145 mg/kg, which are higher than the limit of it presence that should be 20 mg/kg, and also for Arsenic in FGDG-D has recorded values higher than the limits for both 600 °C and 800 °C, 34 mg/kg and 39.3 mg/kg respectively. For samples of FGDG-A and FGDG-C, the values didn't exceed the limits.

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