UNIVERSIDAD DE INVESTIGACIÓN DE TECNOLOGÍA EXPERIMENTAL YACHAY TECH

Escuela de Ciencias Químicas e Ingeniería

Biphasic agglomerate clay-iron oxide to the gas sweetening of natural gas.

Trabajo de titulación presentado como requisito para la obtención del título de Petroquímico

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Urcuquí, agosto 2019

UNIVERSIDAD YACHAY TECH

Urcuquí, 21 de agosto de 2019

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ACTA DE DEFENSA No. UITEY-CHE-2019-00002-AD

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Dedicatory

To all my family that give me the support during all this time but in special for my mom Matha Celín, my dad Nelson Luna, my sister Leandra Luna and my grandmother Iraldita because without them I would not be the person that I am.

To my mom, Martha, thank you for give me the life, for all the effort that makes every day in order to impulse me to reach my dreams, for teaches me that always is possible overcome any problem and for all the confidence that you give me.

To my dad, Nelson, thank you for teaches me that the work hard is the unique way to obtain anything, forgive me everything that I needed and for be an example of effort and overcoming.

To my sister, Leandra, thank you for taking care of me and always worrying about me, for give me all your sweetie and love and for be my best friend.

To my grandmother, Iraldita, thank you for all your advises and cares, for give me all your love during my life.

To all my friends that always accompanied me in all my university life and share with me the best anecdotes.

Acknowledgements

To Yachay Tech University, especially the School of Chemical Sciences and Engineering for give me the opportunity to study my career.

To the Inedita project, that give me the support to develop my graduation project.

To all my professors, but in special to José Ángel Rivera Ortega and Darío Alfredo Viloria that shared with me all their knowledge and experience to be an excellent engineer.

To the judge professors Marvin Ricaurte and Alex Palma for the support and guidance to improving my thesis project.

To LEMAT, that give the opportunity to make the Scanning Electron Microscopy and X-Ray diffraction techniques.

ABSTRACT

Natural gas is a mixture of light hydrocarbons such as methane, ethane, propane, butane and other substances; despite, its composition is mainly made of methane, the presence of impurities such as carbon dioxide, steam, hydrogen sulfide and others are the principal cause of operational problems in refineries relates with corrosion, poisoning of catalyzers, mechanical failures, etc. More over, the environmental impact is a bigger problem because all of these substances promotes acid rains and the greenhouse effect increase causing several problems in many places around the world. There are several process to remove the impurities in the pre-treatment step, but one of the most important is the sweetening of natural gas.

The Sulfur, in form of an acid gas known as hydrogen sulfide is removed by the use of technologies such as adsorption using solid beds, filtration with porous materials and chemical substance as amines in a procedure known as sweetening of gas. The present research analyze the behaviour of a pellet composed of a mixture of clay and iron oxides obtained from different places of the Ecuadorian regions. The valorization of these raw materials in the formation of pellets in order to use it in the adsorption of hydrogen sulfide is the main objective of the research. The formation of pellets is carried out by mechanic chemical techniques; the characterization of the pellet is done by powder X-ray Diffraction, Scanning Electron Microscopy and Energy Dispersive X-Rays Spectroscopy.

Keywords: *Natural gas, hydrogen sulfide, sweetening of gas, clay, iron oxide.*

RESUMEN

El gas natural es una mezcla de hidrocarburos ligeros tales como el metano, etano, propano, butano y otras sustancias. Sin embargo, su composición está basada mayoritariamente en metano, la presencia de impurezas como el dióxido de carbono, el vapor, el sulfuro de hidrógeno y otras son la causa principal de problemas operacionales en las refinerías relacionados con la corrosión, el envenenamiento de catalizadores, las fallas mecánicas, entre otros. Por otro lado, el impacto ambiental es un problema aun mayor debido a que todas estas sustancias promueven lluvias ácidas y el aumento del efecto invernadero causa varios problemas en muchos lugares del mundo. Existen varios procesos para eliminar dichas impurezas en la etapa de pre tratamiento, pero uno de los más importantes es el endulzamiento del gas natural.

El azufre en forma de gas ácido conocido como sulfuro de hidrógeno se elimina mediante el uso de tecnologías tales como la adsorción utilizando lechos sólidos, la filtración con materiales porosos y el uso de sustancias químicas como aminas en un procedimiento conocido como endulzamiento de gas. La presente investigación analiza el comportamiento de pellets con una composición de una mezcla de arcilla y óxidos de hierro obtenidos de diferentes lugares de las regiones ecuatorianas. El objetivo principal de la investigación es la valorización de estas materias primas en la formación de pellets para su uso en el proceso de adsorción de sulfuro de hidrógeno. La formación de pellets se realiza mediante técnicas químicas mecánicas; para la caracterización del pellet se realizó difracción de rayos X, microscopía electrónica de barrido y espectroscopia de rayos X de energía dispersiva.

Palabras clave: *Gas natural, sulfuro de hidrogeno, endulzamiento de gas, arcilla, óxido de hierro*

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CHAPTER I

Importance and justification

Nowadays, the tendency of the energy consumption is relating to the use of the natural gas such as a matrix energy with a low percentage of carbon in their composition. In fact, countries such as Russia, Japan, China, United States of America and others are the main nations in terms of consumption of natural gas and they continue increasing their values of energy consumption (BP, 2018). The problems relate to the environment are a main concern to several nations around the world. The climate change cause problems such as droughts, melting of ice poles, increasing of sea level and others.

Decarbonisation of the matrix energy is one of the solutions to the global warming; due to the energy consumption increase each day and the wastes too. Therefore, a responsible production of fuels guaranteed a reduction of typical pollutants in the atmosphere such as carbon dioxide, methane, nitrogen oxide and others (Barnes, 2019). One of the most important pre-treatment steps for the natural gas production is the gas sweetening and it consist in the removal of impurities such as carbon dioxide and hydrogen sulfide.

Hydrogen sulfide is one of the most toxic gases for the humans, for this reason it is essential to remove it from the natural gas. Exists several technologies to the gas sweetening process for example: chemical solvents, physical solvents, uses of membranes and adsorption with solid beds (Martinez, 2013). The use of solid beds consist in the transformation of sour gas into a contact tower to sweet gas using sorbents to capture acid gases, in the Figure 1 is shown a general scheme of the gas sweetening process.

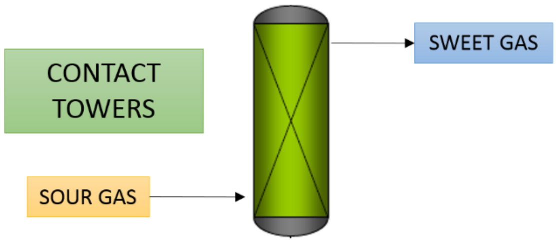

Figure 1: Scheme of gas sweetening.

Usually, the solid beds contain pellets made of metal oxides that reacts with the hydrogen sulfide. Iron oxides are one of the most used components for the gas sweetening due to a good removal capability and economic reliability in terms of operational costs (Tacuri, 2015). For this reason in this research is analyzed, the formation of a pellet based on clay and iron oxide with excellent mechanical resistance for the adsorption of hydrogen sulfide obtained from different places of Ecuador.

Problem statement

Ecuador is a region with a relevant hydrocarbon activity based on mainly in the extraction of oil. N new tendencies of the chemical engineering lead to transform the matrix energy into some more sustainable sources. Ecuadorian natural gas sources are principally obtained from the coast region in the Guayaquil bay, specifically at the Amistad field (Petroamazonas, 2018). In addition, associated gas is present in oil wells. In order to obtain the maximum profitable of natural gas sources and to reach the quality specifications it is necessary to remove its typical impurities such as hydrogen sulfide, carbon dioxide and water steam. According to the statistical report of production of natural gas of Petroamazonas EP the total production is 120.456 MMPCED, this value is relate to the production of the Amistad field and the associated gas of the amazon region.

The valorization of the ferruginous and titaniferous sands acquired from various coasts of the Ecuador for the extraction of the iron oxides and the use of clay such as an agglomerate for the formation of pellets with a good mechanical resistance remaining a noble reactivity with the hydrogen sulfide is the main problem. On the other hand, the new technology should be nearly competitive with the conventional technologies used for the removal of hydrogen sulfide.

General objective

- Develop a new technology based on Ecuadorian materials to the sweetening of natural gas, proving that a pellet formed by clay and iron oxide has the sufficient mechanical resistant and a good reactivity with the hydrogen sulfide.

Specific objectives

- Obtain raw material (sands and clays) from specific places of Ecuador.
- Analyze the structure and the chemical composition of the materials by X-ray diffraction and Scanning Electron Microscopy.
- Make pellets with iron oxide and clay
- Test reactivity of pellets to hydrogen sulfide.
- Test mechanical resistance of the pellets.
- Analyze the structure and chemical composition of the pellets after the reaction by X-ray diffraction and Scanning Electron Microscopy.

CHAPTER II

Introduction

Natural gas is a mixture of light hydrocarbons; its composition is mainly methane with a less proportion of other gases including ethane, propane and butane. The presence of impurities such as carbon dioxide, hydrogen sulfide, water steam, nitrogen, helium and others causes operational problems and reduces the final quality of natural gas (Younger, 2004). The typical composition of the natural gas is shown in Table 1.

Table 1: Typical composition of natural gas (Demirbas, 2010).

Component	Typical Analysis (vol%)	Range (vol%)
Methane	94.9	87.0-96.0
Ethane	2.5	1.8-5.1
Propane	0.2	0.1-1.5
Isobutane	0.03	0.01-0.3
n.Butane	0.03	0.01-0.3
Isopentante	0.01	Trace to 0.14
n-Pentane	0.01	Trace to 0.14
Hexane	0.01	Trace to 0.06
Nitrogen	1.6	1.3-5.6
Carbon dioxide	0.7	0.1-1.0
Oxygen	0.02	0.01-0.1
Hydrogen	Trace	Trace to 0.02

The natural gas can be found depending of the deposit it comes from, in a general way they are:

Associated gas. The gas dissolved in the oil reservoir is known as associated gas. Generally, it contains condensable hydrocarbons such as propane, butane and C_{5+}. For this reason, it is the feed for the Liquefied Petroleum Gas (LPG).

Gas reservoirs. The gas accumulated in rock formations that does not allow scape of the deposit, due to differences in permeability. The main product is the natural gas.

In addition, the natural gas can be classified for its composition. In a general way the different types of natural gas are:

Rich gas. It is the gas that the percentage of methane is low due to the presence of higher hydrocarbons such as ethane, propane, butane and$C_5{}^+$, all of these compounds can be liquefied.

Lean gas. It is the gas with a high quantity of methane and little traces of other hydrocarbons. In addition, it is known such a pour gas.

Sour gas. It is the gas with an acidic composition due to the presence of hydrogen sulfide (H_2S) and carbon dioxide (CO_2)

Sweet gas. It is the gas produced after of the removal of sour compounds.

The general use of the natural gas is related to the consumption as a fuel for the energy generation such that is used in the industry, transportation, and domestic use. The presence of impurities cause several environmental problems, in fact the main cause of acid rains is due to the presence of sulphur in the air pollution. For this reason, it is necessary to eliminate the acidic compounds of natural gas.

Natural gas in Ecuador

In Ecuador, the main source of the natural gas is obtained from the Amistad field in the extraction of the gas reservoir. The field is located in the Guayaquil bay at the southwest of country. However, exists other source of natural gas in forms as associated gas in several fields of petroleum across the Amazon region of the country. In general, the distribution of the Ecuadorian hydrocarbons source is indicated in the Figure 2.

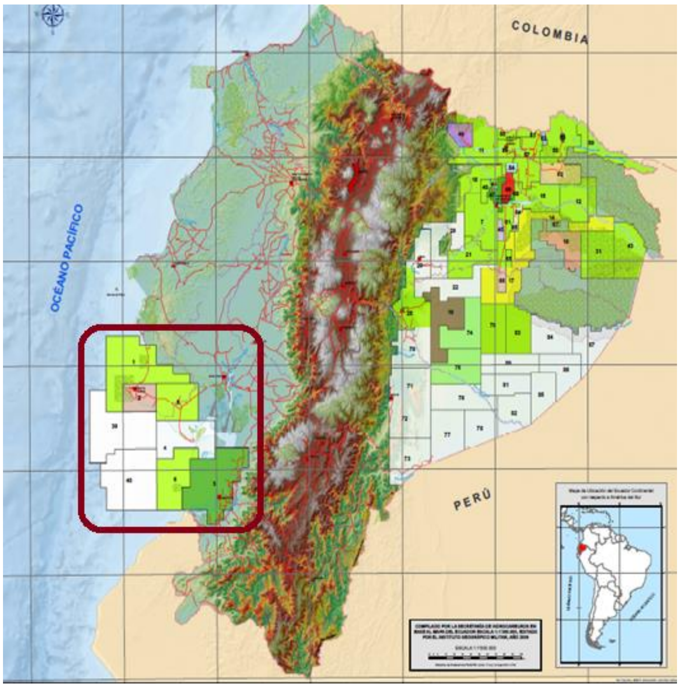

Figure 2: Ecuadorian distribution of oil sources (Secretaría de Hidrocarburos, 2015)

The petroleum fields of Ecuador are distributed in 60 blocks and the block number 6 is related to the Amistad field. The field operates in offshore conditions and in the 2017 its production of natural gas was approximately 45 MMPC (Petroamazonas, 2018). At the present year Petroecuador continue promoting projects in order to recovered the associated gas of the oil wells for energy consumption of the operations. In fact, the quantity of associate gas recovered from Amazon region is approximately 87.865 MMPC. In Ecuador, the quality specification of the natural gas is based on the norm NTE INEN 2489 and is shown in the Table 2.

Table 2: Quality specification of the Ecuadorian natural gas (INEN, 2009).

Specification	Minimum	Maximum	Methods of essay
Calorific power (MJ/m^2)	35.42	43.12	ASTM D 1945 ASTM D 3588 ISO 6976
Wobbie index (MJ/m^2)	45.8	50.6	ASTM D 3588 ISO 6976
Hydrogen sulfide (mg/m^3)		6.1	ASTM D 4084
Sulfur total (mg/m^3)		15.0	ASTM D 5504 ASTM D 6226
Inert (%)		5.0	ASTM D 1945
Wetness (mg/m^3)		65.0	ASTM D 1142 ISO 6327
Methane (%)	80		

Hydrogen sulfide

Hydrogen sulfide is a dangerous compound that is the cause of the sourness of the natural gas, the presence of this gas cause several corrosion problems in the industry. The exposure to this acid gas can cause the death if the concentration of the gas is higher than 16 ppm (Younger, 2004). The typical odor of this gas is similar to the rotten egg, however the person losses the capability to smell it after a few minutes of exposure.

Gas sweetening

The process of hydrogen sulfide and carbon dioxide removal is known as gas sweetening. Exists several steps to reach the quality specification of the natural gas and they varies depending of the kind of technology used for the process. However, to choose a kind of technology it is necessary to take in mind the following variables such as the gas composition, operational conditions, selectivity of acid gas, the volume of gas to be processed and others (Maddox, 1982).

In general, exists many processes to remove the hydrogen sulfide of the natural gas the most used are:

Chemical solvents. The process uses an active component that circulate into the flow stream and reacts with the acid compound. Usually it is used an alkanolamine such as monoethanolamine (MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA) (Kohl, 1997). Other compounds are used as salts of potassium carbonate and basic salts.

Physical solvents. The physical solvents does not react chemically with the impurities. The mechanism of this process is the physical adsorption in the solvent, the main interest of this process is the huge removal of acid gases with a high partial pressure (Martinez, 2013).

Membranes. The separation of the components is reached for the characteristics of affinity and diffusivity of the membrane. The acid gas, water and carbon dioxide are excellent diffusers, in consequence it is possible the movement of the compounds through the membrane. Due to the separation is not completely effective a certain quantity of hydrocarbons are dragged with impurities (Martinez, 2013).

Adsorption with solids. The materials are principally compound for metal oxides, such as iron, zinc, magnesium and calcium due to its selectivity to the hydrogen sulfide. The most active metal is the zinc; however, the iron oxide is the most used for economic aspects (Ricaurte, 2009). The material is considerate as a biphasic material due to the presence of the metal oxide and the support that generally is a ceramic of glass material.

Biphasic solid materials

A biphasic material has two different phases. Usually the implementation of a new phase is relates to the modification of specific properties such as porosity, selectivity, activity and others. The conventional solid materials used for the gas sweetening presents several operational problems relate to their mechanical resistance. In fact, the pressure drops and the high temperatures in the interns of a contact tower could destroy the materials.
For that reason, it is necessary to implement new materials that can resist the operational conditions, the new biphasic material is a composite of iron oxide and clay. The reasons to use these compounds are presented in the following sections.

Cationic clays

Clays are materials form by laminar layers. The term of clay is applied to materials with a particle size less than 2 um and between each family share similarities in their chemical composition and crystal structure (Uddin, 2016). There are several types of clays, which differ depending on the variation of cation composition and location. The general classification shows three groups: kaolinites, smectites and chlorites. Exists around of 30 different types of clays. Natural clays are mixtures of all of these (Adeyemo, 2017).

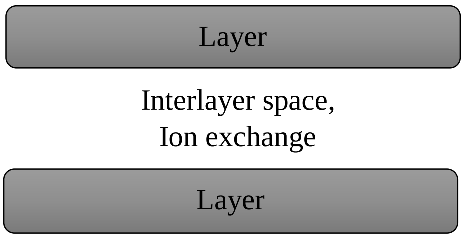

Figure 3: General structure of clay

Figure 3 shows the general structure of clays, layers are composed by tetrahedral and octahedral distributions, the interlayer space occurs the ion exchange and also there is a presence of water.

Kaolinite. The laminar distribution is 1:1. Kaolin is a soft, white plastic clay consisting dominantly of a hydrated aluminum silicate. The general structure is compound by the linked of several unit cells such as octahedral, tetrahedral and di-octahedral (Adeyemo, 2017).

Smectites. The laminar distribution is 2:1, the main composition of this type of clays is based on magnesium, and aluminum, the coordination of these compounds is octahedral in form of oxides or hydroxides. The main clay of this group is the bentonite and it is an aluminium phyllosilicate that differ respective to the main element, it could be potassium (K), calcium (Ca), aluminium (Al) and sodium (Na). Bentonites are excellent rheological and absorbent materials, in fact in industry they are used in drilling mud for oil and gas extraction (Adeyemo, 2017).

Chlorite. The laminar distribution is 2:1.1. The structure of these clays is dioctahedral and trioctahedral. It is compound mainly by chlorites and they are formed by the decomposition of micas and feldspar.

Due to the swelling characteristic of the clays, it is possible to act as an agglomerate of a composite to grant mechanical resistance properties. In fact, clay is used to form bricks for the construction industry and they hardness depends directly of calcination temperature.

Geographical location of clays in Ecuador

In the Ecuador exist several zones in which is possible to find natural clay, in the Figure 4 is shown the general distribution of the kind of clays. In the amazon region at the south of the country is the place in which exist the major presence of clay used for the formation of pellets due to its characteristics of natural agglomerant.

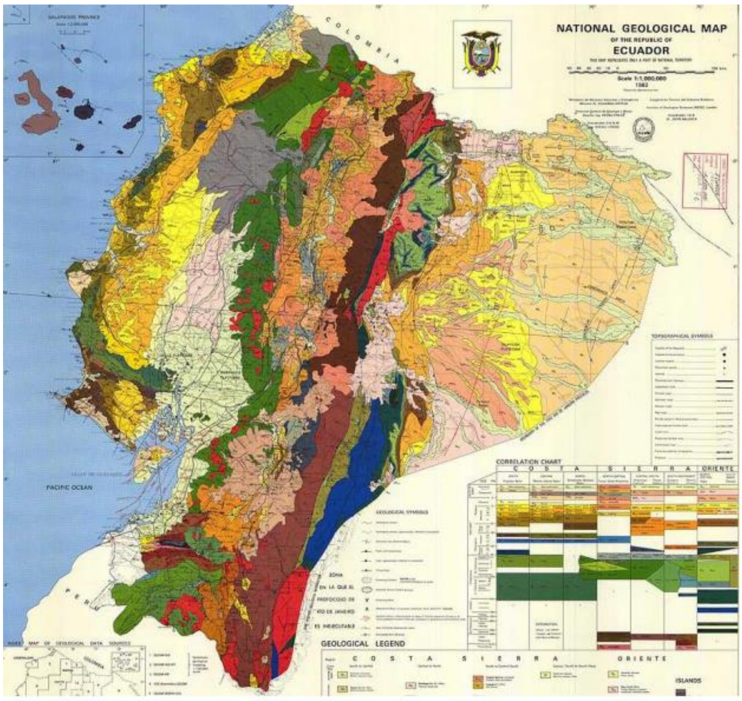

Figure 4: Geographical location of clays in the Ecuador (Ortega, 2014)

Iron Oxide

There are several kinds of iron oxides that varies with the composition of iron and oxygen and the most common iron oxides are wüstite (FeO), magnetite (Fe_3O_4), hematite (αFe_2O_3) and maghemite (γFe_2O_3). Ecuadorian coasts have an acceptable percentage of iron oxides in its sand principally composed by magnetite (Ortega, 2014).

Depending of the type of iron oxide the following reactions could take place with the hydrogen sulfide:

$$4H_2S_{(g)} + Fe_3O_{4(s)} \longrightarrow 4H_2O_{(l)} + S_{(S)} + 3FeS_{(S)} \quad (1)$$

$$6H_2S_{(g)} + Fe_3O_{4(s)} \longrightarrow 4H_2O_{(l)} + 2H_{2(g)} + 3FeS_{2(S)} \quad (2)$$

$$3H_2S_{(g)} + Fe_2O_{3(s)} \longrightarrow 3H_2O_{(l)} + Fe_2S_{3(S)} \quad (3)$$

Due to the heating treatment of the composite the possible changes of the oxidation state can occurs.

Exploitation of iron oxides

In Ecuador, there are several places in which the iron oxide is obtained, the Figure 5 shows a map in which indicate the places with the major presence of iron oxides in the land. Mompiche is the place with a major quantity of iron oxides in the composition of the sand due to its geographical location.

Figure 5: Map of the places in which exists iron oxides (Pinantoja, 2016).

CHAPTER III: Methodology

Sand treatment

Sampling

The sand was recollected from different coasts and the Andean region of Ecuador, due to make a comparison of the relative quantity of the iron oxides between these places. In the coast region the places are: Atacames, Tonsupa, Punta Galera, Mompiche, Montañita and Ancon. On the other hand, it was recollected a sample in the Cotopaxi province in the location of Quilotoa. Approximately 2 kg of sample was obtained for each location giving fourteen samples. The following procedure was realized:

- Localize the place to obtain the sample.
- Dig a square of 1 m^2 of surface and a 30 cm of depth
- From the border of the square obtain the sand.
- Dry the samples during 8 hours.

The differentiation of each sample is based on the following nomenclature:
S=Sand
Province: X=Cotopaxi, Y=Santa Elena, E=Esmeraldas, M=Manabí.
Location: Q=Quilotoa, A=Ancon, O=Olón, M=Montañita, V=Río Verde, T=Tonsupa, P=Pedernales, M=Mompiche, G=Punta Galera.

This work was carried out by Dayanna Vera with the main support of the professor Jorge Toro under INEDITA project. The Table 3 shows the identification used for each sand sample.

Table 3: Identification used for the samples of sand.

No	Code	Identification	No	Code	Identification
1	180716,1	SXQ-101	8	180730,1	SEV-201
2	180716,2	SXQ-102	8	180730.2a	SET-202
3	180717,1	SYA-103	10	180730.2b	SET-203
4	180717,2	SYA-104	11	180731,1	SMP-204
5	180718,1	SYO-105	12	180731.2a	SEM-205
6	180718,2	SYM-106	13	180731.2b	SEM-206
7	180718.3	SEM-208	14	180731,3	SEG-207

Sieving

The samples recollected were separated by using a sieve proportionated for the UNACEM, the characteristics of the equipment are shown in the Table 4. The objective is made the separation of the less particle size depending of the granulometry of the sieves.
The procedure of sieving consists in to put the samples in to the sieves and with a mechanical movement the sand flow through the openings of the sieves. The highest

particles were located in the top sieve, in consequence the separation of the particles taking place. In addition, it was calculated a distribution of particle size using the data of the weight of the sieves after sieving.

This work was carried out by Marlon Chimarro with the main support of the professor Jorge Toro under INEDITA project.

Table 4: Characteristics of the sieves using for the sieving treatment.

Sieves No	Brand	Material	Opening [µm]
1/2	Retsch Germany	Stainless steel	12500
1	Soiltest	Brass	6300
4	Retsch Germany	Stainless steel	4750
8	Retsch Germany	Stainless steel	2360
16	Retsch Germany	Stainless steel	1180
30	Retsch Germany	Stainless steel	600
50	Retsch Germany	Stainless steel	300
100	Retsch Germany	Stainless steel	150
Basal plate	Retsch Germany	Stainless steel	
Metallic cover	Retsch Germany	Stainless steel	

Magnetic separation

The sample SEM-208 had typical impurities of the sand obtained from coast regions such as quartz, minerals, salts and others. The magnetic characteristic of the iron oxide allows separating the impurities of the sample using a magnet. The procedure of the separation is:

- In a beaker put 250 g of sample.
- Add approximately 100 mL of distillated water
- Put a magnet below the beaker
- Make a homogeneous mixture
- Separate the water with the impurities.
- Continues adding water and making washes until the impurities disappear.

The iron oxides will be deposited in the bottom of the beaker due to the attraction forces of the magnetic field. In the Figure 6 is shown the separation due to the presence of the magnet.

Drying and Milling

The drying process consist in the heating of the sample for the water removal. The samples were dried during twelve hours at 60 ºC. In the figure 7, it is possible to identify the result of the drying.

The milling process consist in the reduction of the particle size. The sample was milled in a mortar of ceramic during 10 minutes until the appearance looks homogeneous.

Clay treatment

Sampling of natural clay

The clay was recollected from the south of Ecuador in the provinces of Morona Santiago, Zamora Chinchipe and Azuay. There are several differences in their appearance, due to their composition. In addition, the clay naturally was founded with a high wet percentage. The following procedure was realized:

- Localize the place of the sample
- With a shovel remove the organic material of the surface
- Obtain the sample from a 40 cm of depth.

A total number of eight samples were recollected, and in order to differentiate each one the following nomenclature was used:
C=Clay
Provinces: A=Azuay, Z=Zamora Chinchipe, O=Morona Santiago
Locations: N=Nabón, P=Panguintza, Y=Yantzaza, Q=Quiringue, L=Limón Indanza, N=Namírez.
The professor Jorge Toro under the INEDITA project carried out this work.

In the Table 5, it is shown the identification used for each clay sample.

Table 5: Identification of the clay samples

Number	Code	Identification
1	180807.1	CAN-301
2	180807.3	CZN-302
3	180808.5	CZP-303
4	180807.6a	CZY-304
5	180807.6b	CZY-305
6	180807.8	CZQ-306
7	180808.8a	COL-307
8	180808.8b	COL-308

Drying of natural clay

Initially the recollected samples had a huge amount of water in their composition; in consequence, it was necessary to dry the samples. The procedure was made in a oven with a temperature of 100 °C during 12 hours.
In order to calculate the wet percentage of the natural clays, it was measured the initial weight of the sample and the final weight after the drying.

Bouyoucous method

The method consists in the principles of sedimentation and usually uses the sodium hexametaphosphate as a dispersant agent. The principle of function is based on that the highest particle are deposited in the bottom of the vessel due to the gravity force.
This method was used for the separation of the impurities in the sample COL-308, CAN-301 and CZP-301 it was selected due to its appearance in comparison with the other clays, the procedure consist:

- In a beaker put 400 g of sample.
- Add to the beaker 1800 mL of distilled water
- With a stirred rod make a homogenous mixture.
- Instantaneously after to stop the stirring, pour the mixture in a measuring cylinder.
- After 15 minutes, when the sediments layer are formed with a pipet extract the clay in the middle of the phases.

Drying and Milling

The recollected sample was dried during 12 hours at a temperature of 60 °C. Subsequently, the dry clay was milling in a mortar during 10 minutes until the appearance looks homogeneous.

Pellet formation

The conventional technology for the pellet formation is the use of a pelletizer, however the pellets were made using a manual process with a spherical mold, the approximately diameter of the pellets are 1.0 cm. Once all the two materials are in conditions to form the pellets the following variations in the composition were made in order to know what is the most effective for the gas sweetening. The amount of mixture used for the formation of pellets is 15 grams.

Table 6: Clay percentage used in the pellets

CLAY (% m/m)	Iron oxide (g)	CLAY (g)
70	4.5	10.5
65	5.25	9.75
60	6	9
100	0	15

The process of the pellet formation consists in:

- In a beaker put 15 grams of the mixture (iron oxide and clay).
- Add water with a dropper until the mixture is homogeneous (8% m/m).
- Take a certain amount of the wet mixture and with the help of the spherical mold give the form of the pellet.
- Burn the pellets at 450 ºC during 15 hours in a muffle.

Mechanical resistance test

In order to prove the mechanical resistance of the pellets a simple test was performed. It consist in a free fall from a high of 50 cm, the pellet should support the test 3 or 5 times. The material of the surface with recipes the free fall is composed by wood.
If the pellet does not pass the test neither, continue to the test of reactivity.

Test of reactivity.

For the generation of the hydrogen sulfide, it was used iron sulfide and hydrochloric acid at 37% of concentration. The general formula of the reaction is:

$$2HCl_{(aq)} + FeS_{(s)} \longrightarrow FeCl_{2\,(s)} + H_2S_{(g)} \qquad (4)$$

For the reactivity test, a hermetic system that consist in a round flask capped with a septum. Three or four pellets and a test tube containing 1.0 g of FeS were placed into the flask. After plugging the flask and sealing it with parafilm it was added 3 ml of HCl into the test tube using a syringe. The reaction takes place during one week.

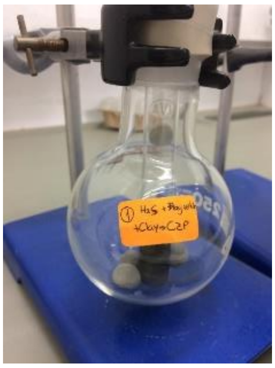

Figure 6: Hermetic system for the test of reactivity, containing the pellets.

Scanning Electron Microscopy methodology

For the preparation of all the samples was carried out with the following procedure:

- Put a small quantity of the sample in a vial.
- Prepare a solution 50/50 v/v of ethanol and distillated water
- With a dropper put the solution in the vial
- Realize a mixture between the sample and the solution.
- With a dropper obtain a small quantity of the mixture.
- Put the mixture in the pin.
- Dry the pin during 1 hour at 60 ºC.

The procedure of preparation could be realized for each sample even the sample is clay or sands.

The software used for the analysis of the results is the EDAX.

X-Ray Diffraction Methodology

For the preparation of all the samples was carried out with the following procedure:

- Dry the sample during 6 hours at 60 ºC

- Mill the sample with an agate mortar during 10 minutes with a constant movement.
- Weight 0.3 grams of sample
- Add 0.03 grams of zinc oxide
- Realize a homogeneous mixture between the sample and the zinc oxide
- Put the mixture in the pin slightly.

The procedure of preparation is the same for each sample even the sample is clay or sands.
The software used for the analysis of the results is the QUALX.

CHAPTER IV: Results and Discussion

Yield of iron oxide extraction

It was calculated the ratio between iron oxide and black sand, by the measure of the removal mass from the sample. The value is 26.48 % (m/m) of richness of iron oxides. The calculation of the value is the following:

$$Iron\,\frac{oxide}{black\ sand} = \frac{m_f}{m_0} = \frac{66.2\ g}{250\ g} \times 100 = 26{,}48\ \%\ \left(\frac{m}{m}\right) \qquad (5)$$

Figure 7: Separation of impurities using a magnet. The right site is before the separation and the left site is after the separation.

The total amount of iron oxide recollected is 66.2 grams and the removal impurities are 183.8 grams. In the Figure 7 is evident the differences between the sand before and after the process of magnetic separation.

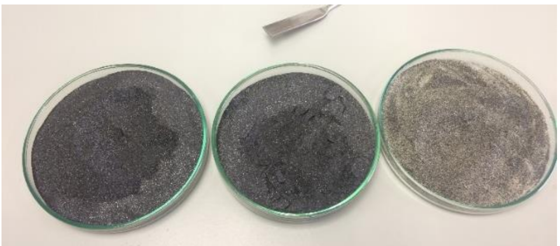

Figure 8: The sample after the magnetic separation. The petri box of the right side is the residue.

Figure 8 shows the results after the drying process, it is evident that the yield of the magnetic separation is relatively low.

Figure 9: Milling process result for the sand samples

Wet percentage of natural clay

In the Annex 1 in the Table 12 is shown the summarizing calculations. In the Figure 10 it is possible to know the wet percentage of the samples, the sample with the highest amount of water is the clay of the province of Morona Santiago in the locality of Limón Indanza. However, the average value for all the samples is 22.69 % of wetness and indicates that the clays had high percentages of water in their composition.

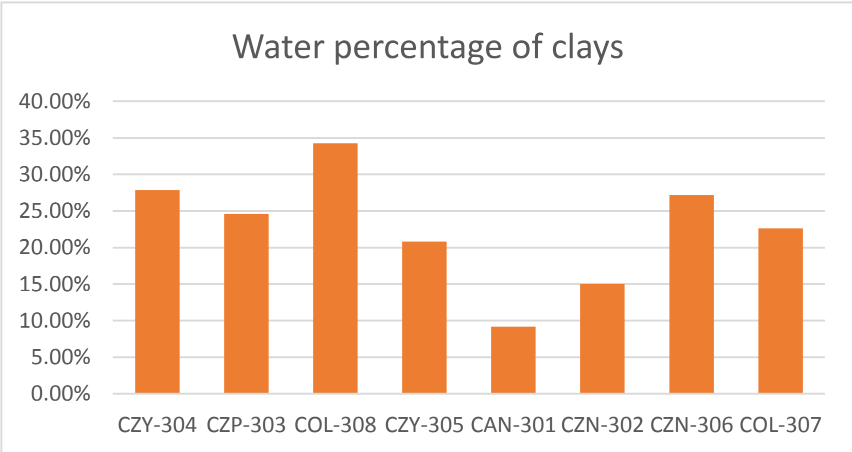

Figure 10: Water percentage in the eight samples of clay.

Yield of clay concentration

It was used three different clays obtained from distinct places of Ecuador in specific Morona Santiago, Zamora Chinchipe and Azuay. The characteristics to choose these three clays are due to its difference in their appearance and the agglomerate qualities. Three of them differ in colors red, orange and brown. The calculations of yields for all of them is the following:

$$\frac{final\ mass\ of\ clay}{initial\ mass\ of\ clay} \times 100 = \frac{m_f}{m_0} \times 100 \qquad (6)$$

Type of clay	Initial mass (g)	Final mass (g)	Yield (% m/m)
COL-308	800	178.83	22.35
CAN-301	800	154.8	19.35
CZP-303	400	90.41	22.60

Table 7: Yields of the clay concentration using the Bouyoucous method.

In the Figure 11 is shown the system used in the laboratory and it is evident how the sediments form layers due to the sedimentation

Figure 11: The Bouyoucous method for the treatment of the sample COL-308. In the right side the sedimentation was finished.

The Figure 12 shows the results of the drying and milling process of the samples of clay, it is evident that the quantity of water eliminated is huge.

Figure 12: In the left site the drying process and in the right the milling process of the clay.

Mechanical resistance results

After to have realized all the pellets with the three different clays the mechanical resistance test was performed. The pellets formed using the clays CAN-301 and COL-308 does not pass the test, in fact at the moment to manipulate the pellet it starts to destroy. In the Figure 13 is shown the pellet after the mechanical resistance test.

Figure 13: Pellets during mechanical resistance test, at the left a pellet that does not pass the test and in the right a pellet that support the mechanical test.

The results of the test indicate that just the clay CZP-303 is useful to realize a pellet due to its properties. In fact, all the pellets formed with the clay CZP-303 support the test. For this reason, it was made new pellets with a composition of 20% and 30% m/m of clay and they remain the mechanical resistance properties.

Figure 14: Pellets with a different composition of the two materials.

Figure 14 shows all the pellets formed using the different types of clays before the mechanical resistance test.

Reactivity test results

During the reaction between hydrogen sulfide and the pellets in the hermetic system, it was possible to identify a change in the colour of the pellet after 3 days. At the end of the reactivity test the appearance of the pellet changes completely, Figure 15 shows the colour change from orange to gray

Figure 15: Reactivity test, in the left pellet before the reaction and in the right pellet after the reaction

In order to make the characterization of the reactivity test, it was made the scraping of the pellet surface also; the pellet was cut to middle to identify a non-reacted nucleus.

Scanning Electron Microscopy (SEM) results

The Scanning Electron Microscopy test was used in several parts of the experimental procedure to determine the morphology and composition of the samples.

In the first part was identified the composition and the particle size of the samples SEM-205, SEM-208 and SYM-106 of sand. However, the most relevant result is shown in the Figure 16, which is the image of the sample SEM-208 in a general way the sample shows a regular size distribution due to the sieving. The average value of the particle size is around of 200 um.

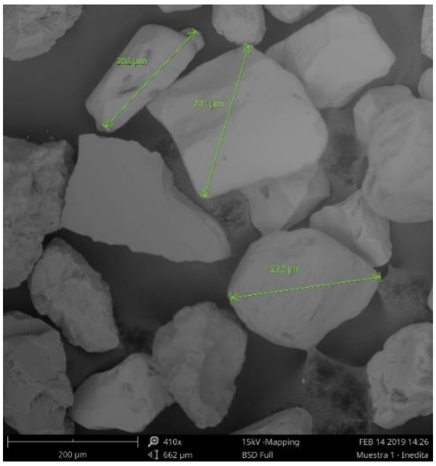

Figure 16: Scanning Electron Microscopy for the sample SEM-208, it shows the average particle size.

Using the Energy Dispersive X-ray spectroscopy (EDX) it was possible to determine the relative quantity of iron and titanium oxides in the sand. In the Figure 17 is shown the elemental map of the sample SEM-208 in which the red and fuchsia colours represent the iron and titanium presence respectively.

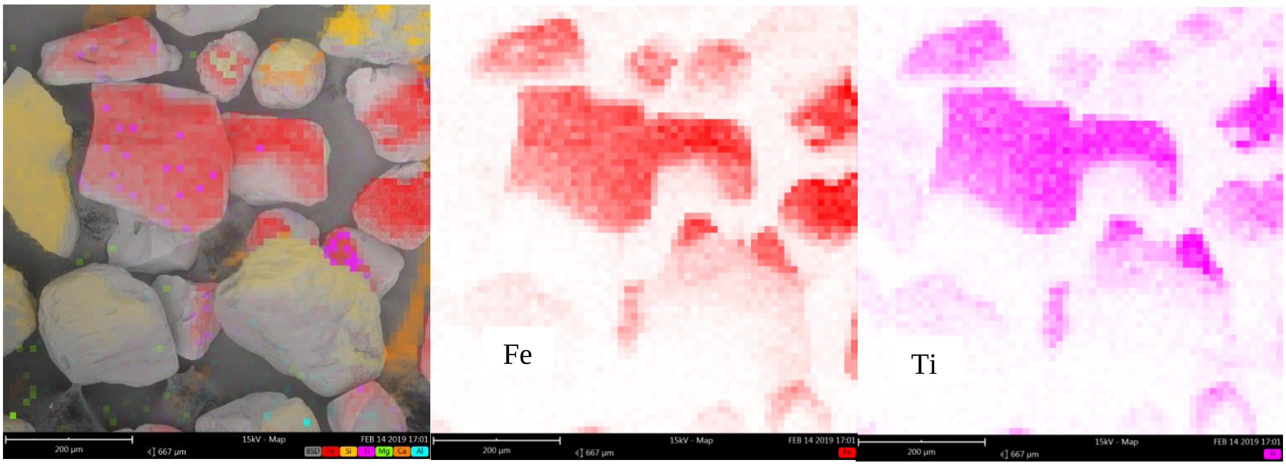

Figure 17: Iron and titanium presence in the sample SEM-206 determined by EDX.

In addition, in the Table 8 is shown the data obtained from the EDX and it confirms that the quantity of iron in the sand collected from the Mompiche coast is higher. Therefore, the sample SEM-208 is the most appropriate to magnetic enrichment for the formation of pellets.

Table 8: Information about element composition of the sample SEM-208 before the magnetic enrichment.

Element	Wt. %	Element	Wt. %
O	45.68	Mg	2.59
Fe	29.44	Ca	1.75
Si	11.76	Al	1.54
Ti	7.25		

In the second part of Scanning Electron Microscopy test it was characterized all the compounds (clay and iron oxide) of the pellets in order to determine that there is not presence of sulfur in their composition.
In the Figure 18 is shown the iron oxide after the treatment step. It is possible to identify a regular morphology of all the particles with a smooth surface and a certain porosity. The average particle size is around 100 um.

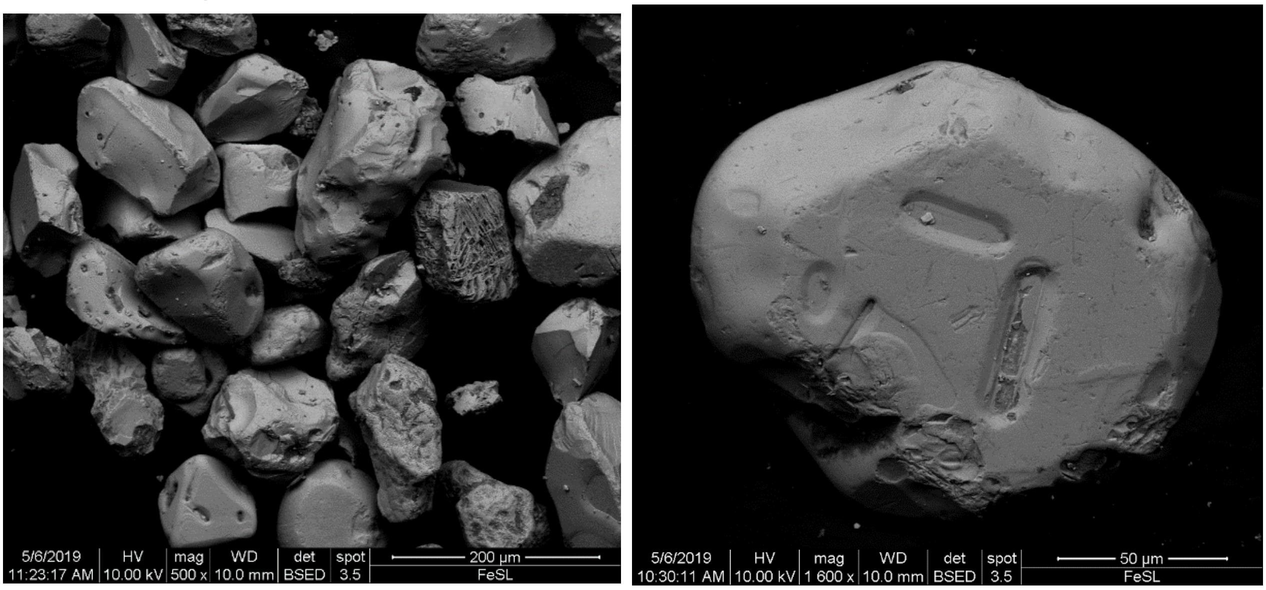

Figure 18: Scanning Electron Microscopy of the iron oxide after treatment step. At the left, an image of 200 um and in the right and image of 50 um.

The Energy Dispersive X-Ray spectroscopy results determine that there is not presence of sulfur element in the composition of the sample. In fact, the Table 9 summarize this analysis and also confirms that the main composition is relating to the iron and titanium oxides.

Table 9: Energy Dispersive X-Ray spectroscopy results of the iron oxide sample SEM-208 after the magnetic enrichment.

Element	Wt.%	Element	Wt. %
O	27.04	Si	1.19
Mg	1.16	Ti	14.69
Al	0.92	Fe	55.00

In addition, in the Figure 19 is evident that does not appear the typical pick of the sulfur. Therefore, the main picks are relating to the iron, titanium and oxygen elements it confirms the presence of iron and titanium oxides.

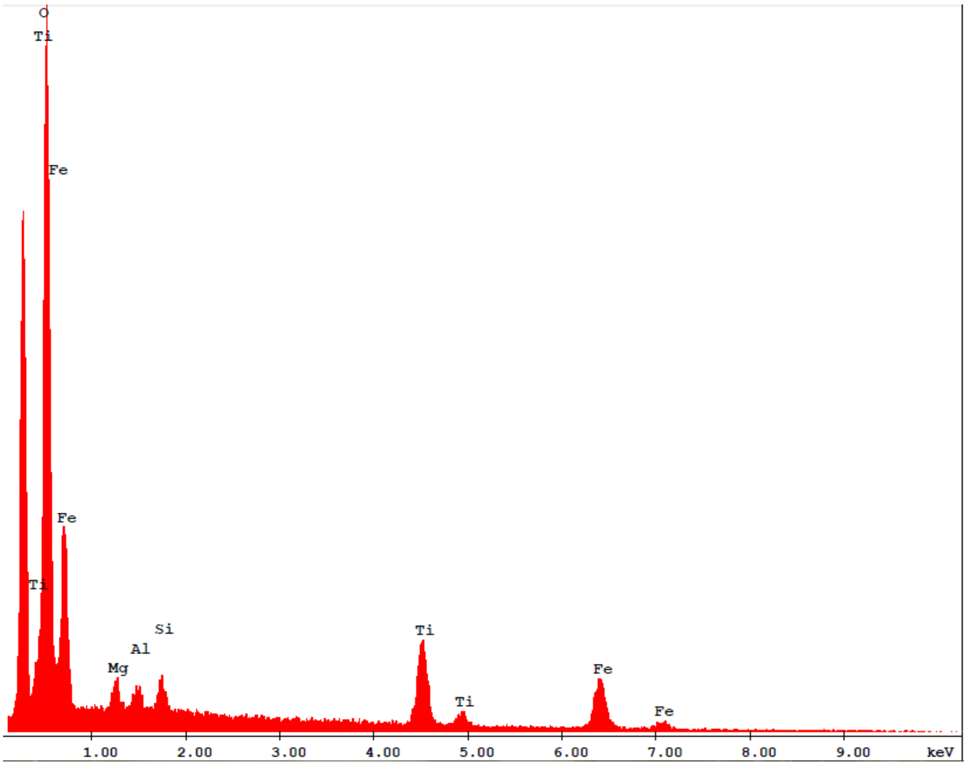

Figure 19: Energy Dispersive X-Ray spectroscopy graphic of iron oxide sample.

On the other hand, it was made the characterization of the clay with the best mechanical resistance property (CZP-303). In the Figure 20 is shown the clay after the concentration step. The particles have an average particle size of 2 um and an irregular morphology due to the milling process.

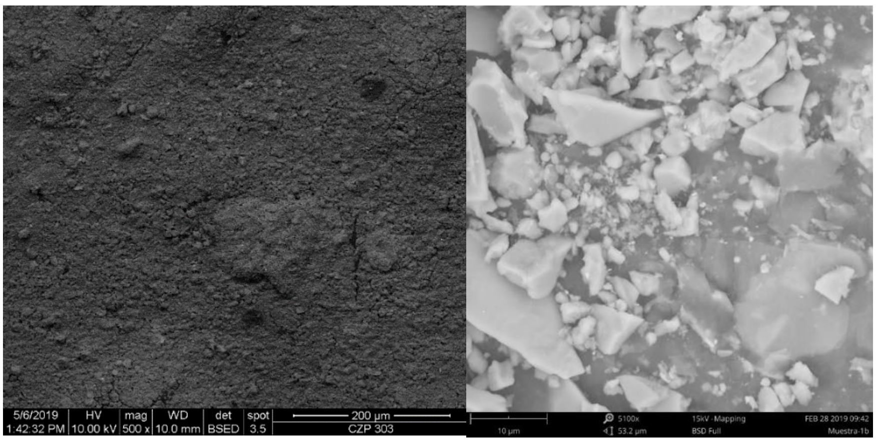

Figure 20: Scanning Electron Microscopy of the clay (CZP-303) after concentration step. At the left, an image of 200 um and in the right and image of 10 um

The Energy Dispersive X-Ray Spectroscopy results determine that there is not presence of the sulfur element in the composition of the clay. In the Table 10 is shown the relative quantities of the elements of the clay CZP-303, an important characteristic of the clay is that exists the presence of iron in their composition

Table 10: Energy Dispersive X-Ray Spectroscopy results of the clay CZP-303

Element	**Wt.%**	**Element**	**Wt. %**
O	41.57	Si	20.05
Mg	0.39	Fe	18.63
Al	19.37		

In addition, in the Figure 21 it is possible to identify that the main picks are relating to the oxygen, aluminum and silicon, it is important to remark the presence of iron in its composition. The reasons could be due to the geographical location.

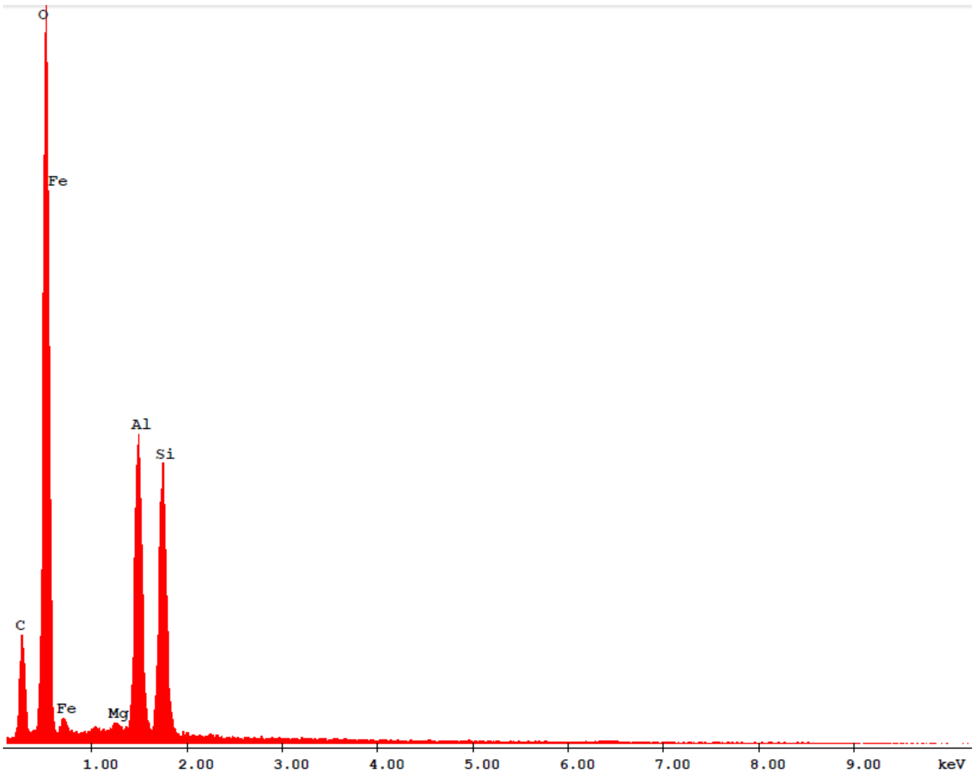

Figure 21: Energy Dispersive X-Ray spectroscopy graphic of clay sample (CZP-303).

The third part of Scanning Electron Microscopy test is relates to the characterization of the pellet after the reactivity test. The sample obtained from the surface of the pellet after made a scrape. The Figure 22 shows the scrapped surface for the pellet with a composition of 65% of clay.

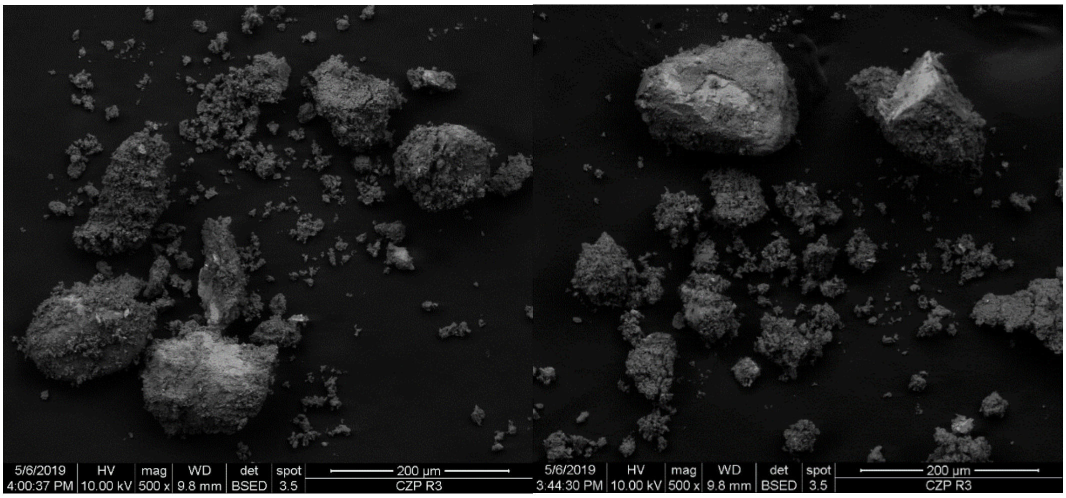

Figure 22: Material obtained from the pellet with a 65% of clay after the reaction

In addition, the Energy Dispersive X-Ray Spectroscopy results for the pellet after the reaction indicates the presence of the sulfur element in the composition of the surface.

Table 11: Energy dispersive X-Ray spectroscopy results of the pellet

Element	Wt.%	Element	Wt. %
C	12.36	S	3.39
O	32.29	Cl	1.33
Na	0.39	Ca	0.25
Mg	4.09	Ti	3.56
Al	8.58	Fe	25.91
Si	7.70		

The carbon element appears due to the presence of the material used for the SEM preparation and the sulfur element appears due to the reaction between the pellet and the hydrogen sulfide.

X-Ray Diffraction results

The X-Ray Diffraction test was performed for the three clays CAN-301, COL-308 and CZP-303. In the Figure 23 is shown the comparison between the three of them, the picks of the diagram are typical for the clay compounds. However, exists a main difference between the clays CAN-301 and COL-308 with the clay CZP-303 because the last one have a peak in the 6 angle and the other clays does not have the peak. It indicates that the clay CZP-303 is a clay of the type of montmorilonites, this maybe the why the pellets formed with this clay pass the mechanical resistance test.

Even after to have made an excellent purification process exists the presence of quartz in the composition of the natural clay. In fact, it is possible that this impurity affect the mechanical resistance properties of the pellets in a good way.

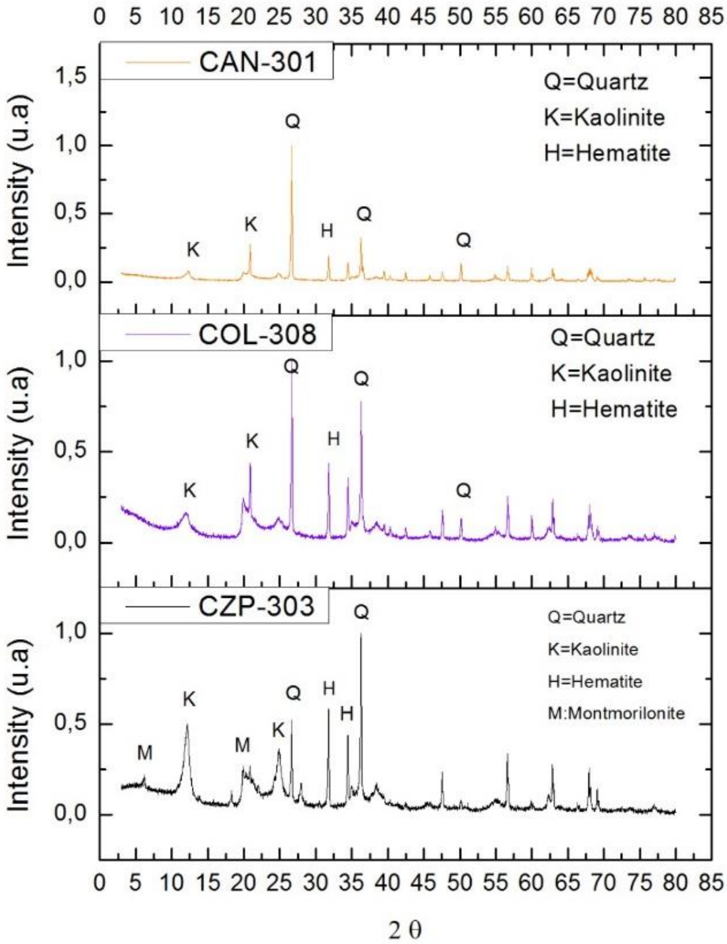

Figure 23: Comparison between the X-Ray diffraction results of the clays CAN-301, COL-308 and CZP-303.

On the other hand, in the Figure 24 is shown the results for the iron oxide after the treatment step in fact, it confirms the presence of the iron and titanium oxides in its composition

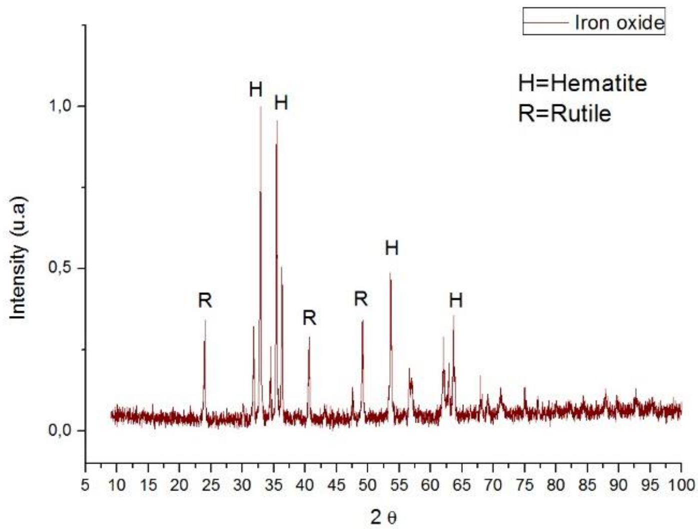

Figure 24: X-Ray diffraction result of the iron oxide after the treatment step

The X-Ray diffraction results of the pellets after the reaction is shown in the Figure 25 and it presents the pattern of the mixture between the iron oxides and clay. In addition, it confirms that the reaction of the pellets works, due to the presence of the variations in the peaks. However, it was not possible to obtain a quantitative analysis from the results of the X-Ray diffraction test, due to the minimum quantity of sample necessary to obtain a pattern or peak should be mayor of 5% m/m of the total amount of the sample (Cruz, 2005).

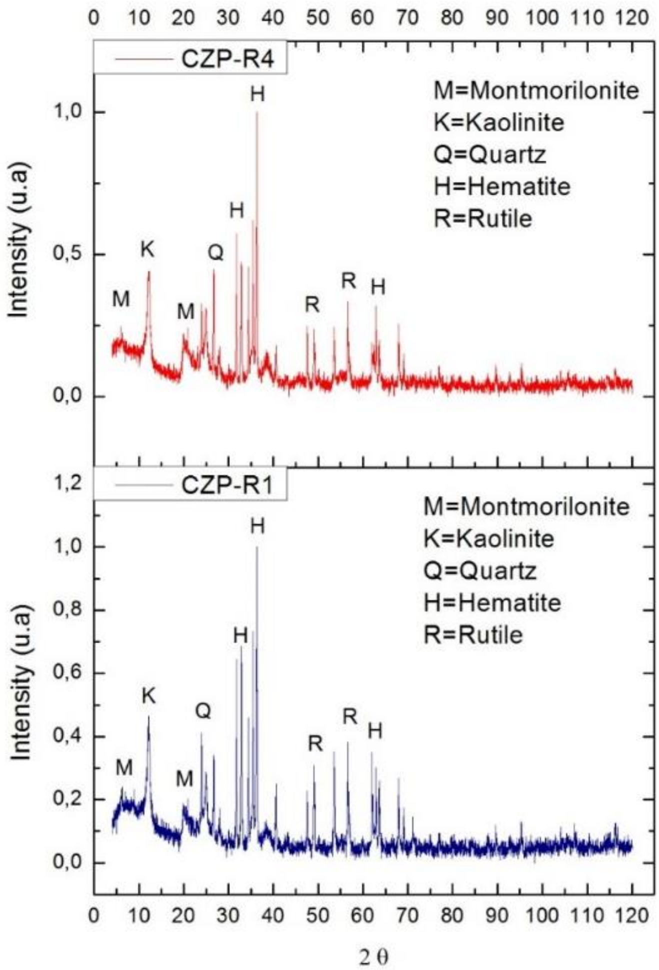

Figure 25: X-Ray diffraction result of the pellets 60% and 65% after the reactivity step

On the other hand, in the Figure 26 is shown the X-Ray diffraction results for the pellets with 20% and 25% of clay and it confirms that the quantity of clay directly affects the reactivity with the H_2S. In addition, it is possible to look that the main peaks of the clay disappear. It could be indicates two conclusions the first one is relates to a change in the internal structure of the clay and the second one is relates to about that the quantity in the mixture to form the pellet is not sufficient to appear in the X-Ray diffraction pattern.

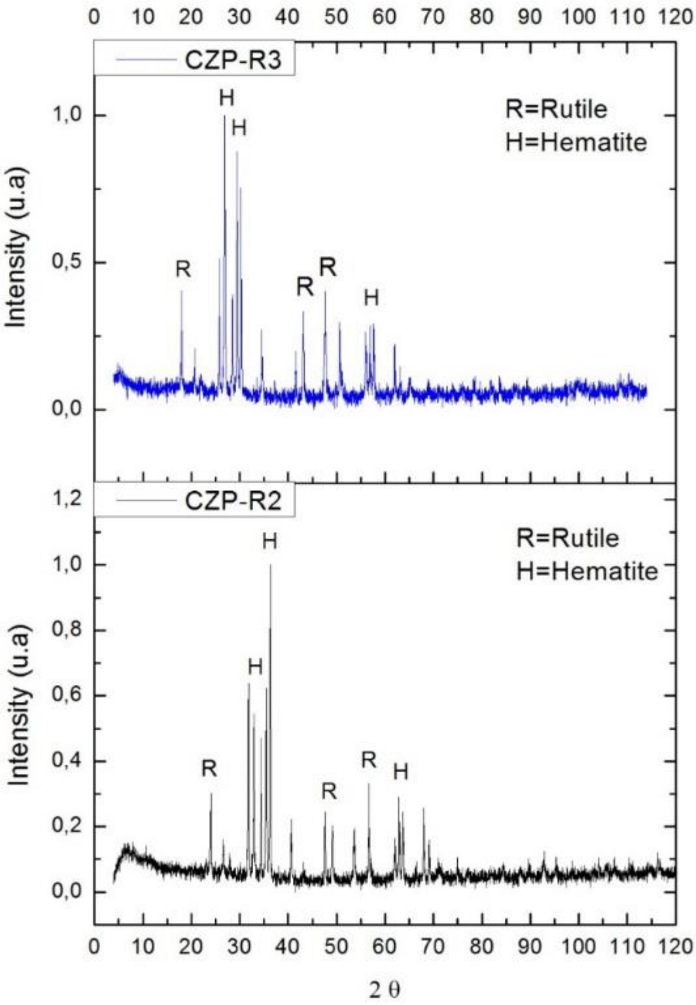

Figure 26: X-Ray diffraction result of the pellets 20% and 25% of clay after the reactivity step

Conclusions

- After to prove several relations of mass composition between the ferruginous sands and clays it was obtained pellets with an excellent mechanical resistance and a certain reactivity with the gaseous H_2S. This provide a new economical technology and the easy access in Ecuador for the sweetening of the natural gas.
- Using the Powder X-Ray Diffraction technique and the Scanning Electron Microscopy it was identified the different phases of each sample obtained from several places of Ecuador.
- The quantity of clay in the pellets directly affects the mechanical resistance properties and the reactivity with the H_2S.
- The best clay with the plastic and agglomerated characteristics that favour the formation of the pellets with a high mechanical resistance and chemical reactivity with the gaseous H_2S was obtained from Zamora Chinchipe (CZP-303).
- The mechanical resistance test results indicate that the best clay for the pellet formation is the kind of clay of the smectites family.
- Such it was mentioned before all the samples presents a chemical reactivity with the gaseous H_2S due to the presence of the different mineral phases of the iron oxides.
- Finally, it was observed that the clay not just has the function of agglomerating also due to in its composition exist iron takes part of the reaction with the gaseous H_2S .

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ANNEX I

No.	Sample		Tray (gr)	Wet Clay (gr)	Tray+ Dry sample (gr)	Dry Clay (gr)	Removal Water (gr)	% Removal Water
1	**180807.6**	**CZY-304**	277.51	2774.77	2300.53	2023.02	751.75	27.09%
			366.23	2718.02	2314.75	1948.52	769.5	28.31%
			275.95	2844.77	2320.76	2044.81	799.96	28.12%
				8337.56		**6016.35**	**2321.21**	**27.84%**
2	**180807.5**	**CZP-303**	277.51	3941.89	3222.17	2944.66	997.23	25.30%
			366.23	3915.48	3261.8	2895.57	1019.91	26.05%
			275.95	4079.63	3437.95	3162	917.63	22.49%
				11937		**9002.23**	**2934.77**	**24.61%**
3	**180808.8b**	**COL-308**	277.55	3299.6	2452.99	2175.44	1124.16	34.07%
			366.22	3426.57	2579.06	2212.84	1213.73	35.42%
			275.96	3623.91	2693.45	2417.49	1206.42	33.29%
				10350.08		**6805.77**	**3544.31**	**34.26%**
4	**180807.6b**	**CZY-305**	365.13	2230.49	2131.11	1765.98	464.51	20.83%
			273.43	2367	2147.54	1874.11	492.89	20.82%
				4597.49		**3640.09**	**957.4**	**20.82%**
5	**180807.1**	**CAN-301**	273.43	2885.7	2899.92	2626.49	259.21	8.98%
			277.55	2490.09	2533.58	2256.03	234.06	9.40%
				5375.79		**4882.52**	493.27	**9.19%**
6	**180807.3**	**CZN-302**	365.13	3304.58	3598.2	3233.07	71.51	2.16%
			275.18	9664.61	8765.92	8490.74	1173.87	12.15%
			275.18	3229.98	3482.63	3207.45	22.53	0.70%
				6534.56		**6440.52**	94.04	**15.01%**
7	**180807.8**	**CZN-306**	365.33	2773.25	2383.68	2018.35	754.9	27.22%
			275.18	2828.06	2335.28	2060.1	767.96	27.16%
			273.48	2884.62	2375.72	2102.24	782.38	27.12%
				8485.93		**6180.69**	**2305.24**	**27.17%**
8	**180808.8a**	**COL-307**	277.51	4216.17	3468.9	3191.39	1024.78	24.31%
			366.23	3201.88	2908.22	2541.99	659.89	20.61%
			275.95	3397.57	2895.03	2619.08	778.49	22.91%
				10815.62		**8352.46**	**2463.16**	**22.61%**

Table 12: Summarizing of calculations of the water percentage in the clays.