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Escuela de Ciencias Químicas e Ingeniería

TÍTULO: Preview of a Small and Medium-sized Enterprises Project for the Adsorption of Acid Gases from Ferrotitaniferous Sands of Ecuador

Trabajo de integración curricular presentado como requisito para la obtención del título de Petroquímica

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A mis padres Jorge Adalberto y Doris Azucena, por hacerme la persona que soy. Todos mis logros en la vida se los debo a ustedes, que siempre confiaron en mis capacidades, me guiaron por el buen camino y me enseñaron a luchar por mis sueños. Espero poder compensar por lo menos un poco de todo lo que me dan.

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RESUMEN

El presente trabajo tiene el objetivo de desarrollar un modelo de Pequeña y Mediana Empresa (PYME) para el tratamiento de arenas ferrotitaníferas utilizadas para la adsorción de sulfuro de hidrógeno. Para la realización del mismo, se recolectaron 13 muestras de arena de la Zona Costera del Ecuador. Luego, mediante un análisis de microscopía electrónica de barrido (SEM), se determinó el contenido de hierro del 29,44% y el contenido de titanio del 7,21% en las arenas negras de la zona de Mompiche-Esmeraldas, por lo que fueron elegidas para el trabajo. Posteriormente, se realizó un análisis de la empresa utilizando el Diamante de Porter, que permitió conocer las fortalezas y debilidades del proyecto. Además, se detallaron los procesos para el tratamiento de las arenas: recolección, separación magnética in-situ, transporte, transferencia y almacenamiento, mediante un diagrama de bloques, y se calculó la capacidad de la planta obteniendo un valor de 574 Ton / año. Finalmente, el análisis de costos de la maquinaria y los equipos necesarios para el tratamiento de las arenas negras determinó que se gastarán aproximadamente $ 48,000.

Palabras clave: Arenas ferrotitaníferas, adsorción de gases ácidos, óxidos de hierro, Pequeña y Mediana Empresa, sulfuro de hidrógeno, Zona Costera del Ecuador.

ABSTRACT

The present work has the objective to develop a Small and Medium-sized Enterprise (SME) model for the treatment of ferrotitaniferous sands used for adsorption of hydrogen sulfide for the accomplishment of the same one, the collection of 13 samples of sand from the Coastal Zone of Ecuador was realized. Later, by means of Scanning Electron Microscopy (SEM), a 29.44 % mass of iron and 7.21 % mass of titanium was determined in the black sands of the zone of Mompiche-Esmeraldas, reason why they were chosen for the work. Subsequently, an SME analysis was carried out using Porter's Diamond, which allowed to know the strengths and weaknesses of the project. Further, the process of collection, in-situ magnetic separation, transport, transfer and storage was detailed by means of a block diagram, and the plant capacity was calculated obtaining a value of 574 Ton/year. Finally, the cost analysis of the machinery and equipment necessary for the treatment of the black sands determined that approximately $ 48,000 will be spent.

Keywords: Ferrotitaniferous sands, adsorption of acid gases, iron oxides, Small and Medium-sized Enterprise, hydrogen sulfide, Coastal Zone of Ecuador

ABBREVIATION INDEX

$(Ni, Fe)_9S_8$:	Pentlandite;
AGV:	Acid Gas Volume;
ARD:	Acid rock drainage;
DEA:	Di-ethanol amine;
DIPA:	Di-isopropyl amine;
DPB:	Diagram Process Block;
ENAMI:	Empresa Nacional Minera del Ecuador;
$Fe_{0.83-1}S_8$:	Pyrrhotite group;
Fe_3O_4:	Magnetite;
Fe_7S_8:	Pyrrhotite;
Fe_8S_8:	Pyrrhotite;
Fe_9S_8:	Kansite;
FeS:	Triolite, from meteorites;
FeS_2:	Pyrite / Marcasite, sulfur employed for extracting sulfuric acid;
$FeTiO_3$:	Ilmenite, known as Manaccanite, a Titanium-Iron oxide mineral;
H_2CO3:	Carbonic acid;
H_2S:	Hydrogen sulfide (Sulfhydric acid);
HC:	Hydrocarbon;
HDS:	Hydrodesulfuration processes;
IIGE:	Instituto de Investigaciones Geológicas del Ecuador;
INÉDITA:	Programa Nacional de Financiamiento para Investigación;
MDEA:	Methyl di-ethanol amine;
MEA:	Mono-etanol amine;
MMSCFD:	Million standard cubic feet per day
NGP:	Natural gas of Petroleum;
PEGDE:	Polyethylene glycol di-methyl ether;

SENESCYT:	Secretaría Nacional de Educación Superior, Ciencia, Tecnología e Innovación;
SiO_2:	Quartz;
SME:	Small and medium-sized enterprise;
SEM:	Scanning Electron Microscopy
XRD:	X-ray diffraction analysis;
γ- Fe_2O_3:	Maghemite;
α- Fe_2O_3:	Hematite.

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CHAPTER 1: INTRODUCTION

1.1. Problem Statement

Processes such as gas sweetening, oil refining, and petrochemical processing are currently carried out in the hydrocarbon (HC) industry. These processes use raw materials that contain unwanted gases known as acid gases. Acid gases are harmful gases because they can cause serious corrosion problems in pipes, infrastructure of facilities and equipment, and also they can cause environmental problems. Therefore, it is necessary to eliminate them, for which different processes are carried out depending on the concentrations and volumes that they are present.

One of the processes highly used is the adsorption on solid beds, through which the gaseous particles are adsorbed on solid sequestrants. The most used adsorbents are iron oxides, due to their great abundance in natural sources. Once the gases are adsorbed, their final disposal is thought of as well as in the regeneration of the solid beds; so that they are friendly processes with the environment.

1.2. Justification

In Ecuador, there are large amounts of black or ferrotitaniferous sands, which are sands that have high contents of minerals rich in iron and titanium oxides. Both iron oxides and titanium oxides, due to their characteristics, are used in different industrial applications associated with hydrocarbons, nanotechnology and the energy industry.

In Ecuador, the black sands are located in volcanic and coastal areas, so they are present in great quantities in our country because it is rich in volcanoes and beaches. Due to their location, they are regenerable resources, so they should be used for different applications. However, in Ecuador the characteristics of the ferrotitaniferous sands are little known, the reason why there have been few investigations regarding their characterization and possible applications.

An application with which these sands can be valorized is by using them as natural sources for obtaining iron and titanium oxides, for their later use as solid beds for the adsorption of acid gases coming from the HC industry. Thus, the existing large quantities are taken advantage of, generating profits and contributing to the care of the environment.

1.3. Context

This work is part of a project called "Ferruginous and Titaniferous sands of Ecuador as Adsorbents of Acid Gases in the Hydrocarbons Industry", which was the winner of a call launched by the Programa Nacional de Financiamiento para Investigación (INEDITA), proposed in 2018 by the Secretaría Nacional de Eduación Superior, Ciencia, Tecnología e Innovación (SENESCYT). This research project, globally, seeks to develop, through activities of a technical-scientific nature, the industrial valorization of the ferrotitaniferous sands of Ecuador in the HC industry. To achieve this objective, the project is based on the principles of sustainable development and the postulates of Green Chemistry.

CHAPTER 2: OBJECTIVES

2.1. General Objective

- Develop an SME model for the removal of hydrogen sulfide, an acid gas associated with the exploitation and refining of hydrocarbons, through the valorization of the ferrotitaniferous sands occurring in the Coastal Zone of Ecuador; that allows the boost of the regional economy and the generation of direct and indirect jobs, for the manufacture, distribution, and use of the products generated in this research project.

2.2. Specific Objectives

- Sample and characterize the ferrotitaniferous sands of Volcanic and Coastal Zones of Ecuador, to determine the presence of iron and titanium oxides, which can be used for the design of solid beds.
- Determine the capacity of the plant and analyze individually each one of the processes of ferrotitaniferous sand treatment processes carried out, detailing volumes and capacities of the machinery and the necessary equipment, taking into account processes used in the country
- Perform an economic analysis of the treatment processes: collecting, in-situ magnetic separation, transfer, transport and storage of ferrotitaniferous sands, for later use as solid beds.
- Define new valuation routes for waste streams from ferrotitaniferous sand treatment processes.

CHAPTER 3: THEORETICAL BACKGROUND

3.1. Acid Gases

Carbon dioxide (CO_2) and hydrogen sulfide (H_2S) are acid gases. These are polluting gases produced by the anaerobic decomposition of organic waste coming from industrial processes (Tacuri, 2015), as well as they are present in nature in natural sources (reservoirs). Acid gases, in the presence of water, can cause serious problems of corrosion due to the formation of carbonic acid and sulfhydric acid. Within the HC industry, they are present in refinery gas streams, natural gas sweetening plants, wastewater treatment, petrochemicals, among others (Viloria, 2014).

Hydrogen sulfide is a colorless, flammable gas with a characteristic unpleasant odor that is naturally generated in crude oil, natural gas, and human and animal waste (OSHA, 2007). When reaching a concentration of 50 ppm, this gas can have a narcotizing effect in the olfactory cells, in such a way that its smell is not felt. It is a very toxic gas because it can cause serious damage to health, so it is necessary to be very careful with its handling (The Linde Group, 2012). Regarding its toxicological information, the daily environmental exposure limit value (VLA-ED), which represents the average concentration of H_2S in the breathing zone of any person on a normal 8-hour workday, is a maximum of 5 ppm so that there is no serious and permanent damage to health. In the same way, the short-term environmental limit value (VLA-EC), which represents the average concentration of H_2S in the breathing zone of any person in a period of 15 minutes, is a maximum of 10 ppm so that there is no serious and permanent damage to human health (Instituto Nacional de Seguridad y Salud en el Trabajo, 2019).

Carbon dioxide is an odorless and colorless gas that is found naturally in the air at concentrations ranging between 300 and 500 ppm. It is important for the development of life and is present in volcanoes, hot springs, glaciers, diluted carbonate rocks, and the human being is capable of producing it. This gas is toxic to humans because it can cause suffocation (Fundación para la Salud Geoambiental, 2018). The VLA-ED for CO_2 is a maximum of 5000 ppm (Instituto Nacional de Seguridad y Salud en el Trabajo, 2019).

3.1.1. Corrosion caused by CO_2

Corrosion caused by CO_2, also known as sweet corrosion, occurs in the production or transportation systems of an oil and gas operation. This corrosion occurs at partial pressures from 21 kPa (Gerus, 1974).

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad (1)$$

$$Fe^{2+} + H_2CO_3 \rightarrow FeCO_3 + 2H^+ \rightarrow Fe^{2+} + HCO_3^- + H^+ \quad (2)$$

As observed in equations 1 and 2, the products obtained from the corrosion process are carbonic acid (H_2CO_3), ferrous carbonate ($FeCO_3$) and hydrogen cation (H^+). Both acid and carbonate are very corrosive compounds. On the other hand, hydrogen generates acidity, and can cause a corrosive phenomenon known as hydrogen permeation. In the HC industry, hydrogen permeation occurs when hydrogen accumulates in areas with high loads, in which critical concentrations are reached that generate different cracks in steel alloys (Metrohm, 2012). To prevent corrosion with these compounds, organic films that act as barriers are usually used, as well as inhibitors that neutralize the acidity of carbonic acid (Asrar, et al., 2016). In addition, in outcrops and in the mining industry, H^+ causes acidification and acid rock drainage (ARD) that is contamination.

3.1.2. Corrosion caused by H_2S

Corrosion caused by hydrogen sulfide, also known as sour corrosion, commonly occurs in natural gas transportation systems. Corrosion only occurs in the presence of water, so if the H_2S is in the gaseous phase at normal pressure and temperature conditions, it is negligible (González, 2004). The mechanism that governs corrosion has two stages:

- In the first stage, the hydrogen sulfide is put in contact with the water and the adsorption of the HS^- ion occurs on the metal surface. This causes the formation of the intermediate Fe $(HS^-)_{ads}$ that favors the anodic dissolution of iron. The ions are chemisorbed on the metal surface forming a monolayer (Viloria & Vera, 1994).

$$H_2S + H_2O \rightarrow H_3O^+ + HS^- \quad (3)$$

$$Fe + HS^- \rightarrow Fe(HS^-)_{ads} \quad (4)$$

$$Fe\,(HS^-)_{ads} + H_3O^+ \rightarrow Fe(H\text{-}S\text{-}H)_{ads} + H_2O \quad (5)$$

- Then, in the second stage, the intermediate ion regenerates and the proton is reduced

$$Fe(H\text{-}S\text{-}H)_{ads} \rightarrow Fe(HS^-)_{ads} + H_{ads} \quad (6)$$

Finally, the net reaction is:

$$Fe + H_2S \rightarrow FeS + H_2 \quad (7)$$

As we can see in equation 7, the reaction products obtained are hydrogen and ferrous sulfide (triolite). However, iron sulfide can exist in several molecular forms such as FeS_2 (pyrite or marcasite), Fe_7S_8 (pyrrhotite), Fe_9S_8 (kansite). Or $(Ni, Fe)_9S_8$ (pentlandite). Therefore, the iron sulfide obtained will depend on the operating conditions to which it is worked (Gerus, 1974). Triolite is a mineral gray-brown or bronze brown that belongs to the pyrrhotite group ($Fe_{0.83\text{-}1}S_8$). Triolite is an Italian mineral that constitutes meteorites. It is stoichiometric FeS, nonmagnetic, without vacancies in its structure. Pyrrhotite is a bronze-red mineral that has a monocyclic crystal system that is found in basic igneous rocks and metamorphic rocks with pentlandite, pyrite, marcasite, and magnetite. It has varying magnetic powers, depending on the number of Fe vacancies in the crystal structure (Mindat, 2017). Kansite is an imperfect compound that allows the diffusion of Fe^{2+} (Fernández, 2011). On the other hand, hydrogen causes corrosion by hydrogen permeation, as happens in the CO_2 corrosion mentioned above.

In this work, only the corrosion caused by H_2S is considered.

3.2. Hydrodesulfurization Processes

Within the refineries, there is a process that becomes very important in recent times, this is the hydrodesulfurization process (HDS). This process consists of reducing the sulfur content found in crude oil. Sulfur is a pollutant that can cause problems of corrosion and poisoning in the engines of vehicles, as well as pollution of the environment. The HDS processes are based on a sulfur hydrogenation process to obtain organic compounds and H_2S (Huitrón, 2013). It is necessary that the hydrogen used in any petrochemical process contains a high purity between 95 and 99 % and that it can be regenerated (Kraus, 1998).

Hydrogen sulfide, which is the main by-product of this process, is recovered to be treated by steam separation, by a combined high and low pressure separator or by an amines wash that generates a concentrated H_2S stream and it is subsequently sent to the sulfur recovery unit (Huitrón, 2013). Because H_2S is highly toxic and difficult to handle gas, it is better to convert it to elemental sulfur. In the sulfur recovery unit, 90 to 97 % of the H_2S is transformed into liquid or solid sulfur, with acceptable quality, which can be marketed later (Tacuri, 2015). On the other hand, the hydrogen sulfide obtained could be captured by different methods, including the adsorption process with some adsorbent, such as ferruginous sands, and then sent for sulfur recovery.

In Ecuador, there are regulations that govern the sulfur content that must be present in the extra gasoline, super gasoline and diesel. The requirements of extra and super gasolines establish that they must have a maximum sulfur content of 0.065 % mass (NTE INEN 935, 2016), and those of premium diesel fuel establish a sulfur content of 5 % mass (NTE INEN

1489, 2012). Refineries must meet these standards by extracting sufficient amounts of sulfur from the treated, concentred H_2S streams.

3.3. Sweetening Processes of natural gas

To eliminate acid gases it is necessary to carry out a sweetening process, after which the gases will meet certain content specifications. The content of H_2S after the natural gas (NGP) sweetening process must reach a maximum of 4 ppm and the CO_2 content must reach a maximum of 2 % (Younger & Eng, 2004). In Ecuador, the content of hydrogen sulfide in natural gas must reach a maximum of 4.38 ppm (NTE INEN 2489, 2009). For this, the acid gases can be subjected to different conditioning processes such as chemical absorption, physical absorption, hybrid processes, direct conversion, permeable membranes and adsorption with solid beds (Kohl & Nielsen, 1997). The use of each one depends on the volume and the characteristics of acid gases, and the final specifications required. Both types of absorption refer to the transfer of AGP to a liquid phase in which it is soluble.

3.3.1. Physical Absorption

Physical solvents are responsible for performing physical absorption without the occurrence of any reaction. It is favored at partial pressures above 200 psi. The decrease of pressure and a small application of heat allow the solvents to regenerate. This type of absorption has high affinity for heavy hydrocarbons. Physical solvents fulfill a better function when acid gases have a high concentration. Its biggest advantage over other processes is that they are not corrosive, so they can use carbon steel equipment. Physical processes include the washing process with water, the use of polyethylene glycol dimethyl ether as a solvent (Selexol process), the use of pyrrolidone (Purisol process), the use of methanol (Rectisol process), among others (Burr & Lyddon, 2008).

3.3.2. Chemical Absorption

Chemical solvents are responsible for performing chemical absorption with the occurrence of a chemical reaction. These allow the elimination of high percentages of acid gases; however, they have serious disadvantages such as a large amount of energy used, a very small acid gas charge size and the corrosion generated by the solutions. The absorption towers carry out the processes of chemical absorption with alkanolamines (regenerable solutions) or by in-line injection with liquid sequestrants (non-regenerable solutions). The most used alkanolamines in the natural gas industry are mono-ethanol amine (MEA), di-ethanol amine (DEA) and methyl di-ethanol amine (MDEA). Taking into account acid gas volumes, if one has 250 million standard cubic feet per day (MMSCFD) and H_2S contents between 20 and 100 ppm, one should use alkanolamines solutions; whereas if one has up to 60 MMSCFD and H_2S contents lower than 100 ppm, one should use liquid sequestrants, mainly triazines (Viloria, 2014).

3.3.3. Hybrid Processes

Hybrid processes are a combination of chemical and physical processes. They take advantage of the high absorption capacity of chemical processes and the low energy levels required by physical processes. The best-known hybrid process is Sulfinol, which uses tetrahydrothiophene dioxide (sulfolane) as a physical solvent, di-iso-propyl-amine (DIPA) as a chemical solvent and water (Estrella, 2010).

3.3.4. Direct Conversion Processes

The direct conversion processes convert H_2S (removed from natural gas by physical or chemical solvents) into elemental sulfur without the need of using a sulfur recovery unit, through oxidation and reduction reactions of hydrogen sulfide into an alkaline solution of iron chelate. The reaction that occurs allows the reduction of iron ions from 3+ to 2+. Then, iron 2+ is reoxidized to iron 3+ by atmospheric oxygen, regenerating the solution. The most used process is the Claus process (Kohl & Nielsen, 1997).

3.3.5. Permeable membranes

The permeable membranes allow the separation by diffusivity differences that present carbon dioxide, hydrogen sulfide, and water. These elements pass through the membrane by the application of a motive force, unlike hydrocarbons that cannot easily pass through it. However, the separation is not total, so certain hydrocarbons will suffer losses by running into the streams of acid gases. On the other hand, slow gases such as nitrogen and aliphatic hydrocarbons remain behind and do not cross the membranes (Ricaurte, 2009).

3.3.6. Adsorption Process

The adsorption process retains molecules, ions or atoms from liquids, solids or dissolved gases (adsorbate) on a solid surface of a material (adsorbent). Solid adsorbents, which are metal oxides of iron, zinc, magnesium, and calcium, are responsible for performing this process. It is necessary to granulate these solids to increase the surface area that will react with hydrogen sulfide. Ceramic and fiberglass are inert materials used as support for solid adsorbents. The most used adsorbents in the HC industry are iron oxides because of its low costs. The set of several particles of adsorbents is a solid bed. In the industries, the adsorption process is carried out through contact or adsorber towers that contain solid beds. The adsorption process is carried out for gas volumes lower than 125 MMSCFD and for concentrations lower than 100 ppm. When the iron oxide traps the H_2S, the surface of the solid retains the gaseous particles, and then the chemical reactions between the acid gas and the adsorbent take place (Ricaurte, 2009):

$$6\ H_2S_{\ (g)} + Fe_3O_{4\ (s)} \rightarrow 4\ H_2O_{\ (l)} + S_{\ (s)} + 3\ FeS_{\ (s)} \qquad (8)$$

$$6\ H_2S_{\ (g)} + Fe_3O_{4\ (s)} \rightarrow 4\ H_2O_{\ (l)} + 2\ H_{2\ (g)} + 3\ FeS_{2\ (s)} \qquad (9)$$

$$3\ H_2S_{\ (g)} + Fe_2O_{3\ (s)} \rightarrow 3\ H_2O_{\ (l)} + Fe_2S_{3\ (s)} \qquad (10)$$

The iron oxides that appear in the previous equations include magnetite (Fe_3O_4), maghemite (γ- Fe_2O_3,) and hematite (α- Fe_2O_3) (Castaño & Arroyave, 1998).

- Magnetite: also known as tri-iron tetraoxide or ferric ferrous oxide. It is black. It has a spinel crystal structure and its general formula is AB_2O_4. It is semiconductor, cubic and ferromagnetic. It appears as an associated mineral in most volcanic and ultramafic rocks. It has high electrical conductivity. Its main applications are the pigmentation of paints and linoleum and in the textile industry.
- Maghemite: Octagonal particles form the maghemite. It is brown. It is cubic, semiconductor and ferromagnetic. It has a spinel crystal structure. It is not abundant in nature and can be obtained by oxidation of magnetite. Its main application is the development of devices for magnetic recording.
- Hematite: Also known as iron oxide (III), specularite or oligisto. It is a trigonal, paramagnetic and electrical insulator. It is reddish-brown to black. Limonite is obtained by hydration of the hematite. In nature, it appears in independent deposits (banded mineralixations) or as an associated mineral in rocks. It is widely used for the pigmentation of paints and varnishes and in cosmetics.

The iron sulfides that appear in the previous equations include iron disulfide (FeS_2), ferrous sulfide (FeS) and ferric sulfide (Fe_2S_3).

- Iron disulfide: This compound has two phases: pyrite and marcasite. Pyrite can easily be altered to iron oxides, but it is more stable than marcasite. It has a crystal shape. It is fragile, paramagnetic, pale yellow, brown and has a metallic shine. Being the most abundant sulfur in the Earth, it is present in an infinity of deposits, mainly in America and Europe. It is associated with igneous and sedimentary rocks and in contact metamorphic deposits. Its main applications are in the manufacture of inks, preservation of wood and elaboration of disinfectants.

Marcasite is usually presented in radiated forms. It is stalactitic, covered by irregular crystals. Marcasite has metallic shine and is pale yellow or whitish in color. It is dimorphic, but it has a constant composition. It decomposes more easily than pyrite, so it is less stable. It is located in deposits of limestone replacement and concretions embedded in clay, marl, and slate. Marcasite is not as abundant as pyrite, but it is found in several deposits mainly in Europe. Its most important application is as a source of sulfur (Klein & Hurlbut, 1996).

- Ferrous sulfide: It can be presented in two phases: troilite and amorphous. The troilite phase is dark brown and has a niccolite structure. At temperatures higher than 137 ° C it decomposes (Rodrigues, 2004).
- Ferric sulfide: It can occur in two forms: amorphous or crystalline. The amorphous shape is greenish-yellow in color and has a spinel-like structure. It decomposes at a temperature between 77 and 177 ° C (Rodrigues, 2004).

The objective of the present work is the use of solid beds, as a technology for the adsorption of H_2S

3.3.6.1. Factors that influence the capture of hydrogen sulfide by solid beds

As mentioned earlier, in Ecuador the maximum allowed content of hydrogen sulfide in natural gas is 4.38 ppm. To meet this specification, it is necessary to remove the remaining hydrogen sulfide. The factors that influence the removal of H_2S from natural gas are the following (Torres, 2001):

- <u>H_2O Content:</u> Solid beds that use iron oxides as adsorbents need that the water saturates the natural gas, as this prevents the deposition of certain unwanted solid products. However, the presence of water in the gas increases the corrosion in the pipelines and equipment. Therefore, it is essential to dehydrate the gas after it is sweetened so that it has a maximum water content of 6 lbH_2O / MMSCFD.

- CO_2 Content: If the adsorbent used has an affinity for both H_2S and CO_2, the CO_2 content present in natural gas is important. The less carbon dioxide content ocurrs, the more hydrogen sulfide content can be removed.
- Temperature: The removal of H_2S is favored at high temperatures, so the efficiency of the capture will decrease if very low temperatures are applied.
- Pressure: The removal of H_2S is difficult at low pressures, due to the decrease in the partial pressure of the gas for a given concentration. Therefore, there is a decrease in the solubility of hydrogen sulfide in the water present in the solid beds.
- Variations in flow velocity: The removal of H_2S is difficult when the speed at which the gas goes is reduced because there are turbulences that hamper mass transfer.
- Regenerability: Solid beds must be able to regenerate, in order to be used more than once to be profitable.

3.3.6.2. Reuse and final disposal of solid adsorbents

After using the solid adsorbents in the fixed beds of the contact towers, one of the following procedures for the disposal of the same one must be followed:

- Reverse the flow direction of the NGP: It is a method that allows the solid bed to be used more effectively, in order to use those parts of the bed that have not been used previously (Rodrigues, 2004).

- Dispose of the bed: Following the environmental standards of the area or in turn use it as raw material for different industries, such as the cement industry or the glass industry.
- Regenerate the solid beds used: Removing acid gases, in order to reuse them in a new stage of sweetening. In addition to separating H_2S and CO_2, it is also possible to separate mercaptans (RSR), carbonyl sulfides (SCO) and carbon disulfide (CS_2) (Tacuri, 2015).

3.3.6.3. Available Technologies

Some of the existing technologies for the adsorption of hydrogen sulfide are:

- Iron sponge: This technology consists of hydrated iron oxide or iron hydroxide supported on wood chips or wood shavings. Its function is to remove hydrogen sulfide and mercaptans from different streams present in the chemical and petrochemical industry. The gas passes through the iron sponge and the hydrated iron oxide reacts with the H_2S forming iron sulfide and eliminating the acid gas. It is used before the dehydration process. Before the gas enters the unit of the iron sponge, it is necessary to remove the liquid hydrocarbons. One of its advantages is that it is biodegradable, while one of its disadvantages is that it is expensive. It can be used in a temperature range of 10 to 50 °C (Cherosky & Li, 2013).
- Sulfatreat®: This technology consists of a synthetic iron oxide of Fe_3O_4 and Fe_2O_3 supported on a surface of inert silicates. It is designed to remove hydrogen sulfide and light mercaptans selectively. It is a non-regenerable product and is available as a solid bed in contact towers. After its reaction with H_2S, it produces pyrite, which can cause ARD. The reagent does not regenerate and must be replaced every so often, which could generate large long-term costs (Hydrocarbon Processing, 2006).

- Puraspec™: It is an adsorbent that uses zinc oxide for the removal of hydrogen sulfide. Different industrial processes use this adsorbent, such as natural gas processing, petroleum refining, petrochemicals, and liquefied petroleum gas production. It was used for the first time in 1984. There are some benefits linked to the use of Puraspec™, for example it has good performance because it reduces large amounts of H_2S, it is relatively inexpensive and it is used for the treatment of dry gases. Puraspec™ works in a temperature range from -6 to 204 °C (Hydrocarbon Processing, 2006).
- Dry bed: This technology occurs through solid materials that can be activated carbon, silica gel and molecular sieves of zeolites or carbon. The H_2S molecules are retained in the solids by weak electrostatic forces, so the reaction may be affected by humidity, selectivity, temperature, pressure and the presence of particles. When the solid is carbon, the process requires lower temperature and pressure, so that the energy required for the process is also lower. The reaction takes place in the pores of the activated carbon and the hydrogen sulfide reacts with the oxygen producing sulfur and water. This method is widely used for the purification of biogas used in power generation (Tacuri, 2015).

3.4. Ferrotitaniferous sands

Ferrotitaniferous sands, also called black sands, are mixtures of heavy minerals constituted by iron and titanium oxides, with traces of metals such as manganese, magnesium, aluminum, calcium, vanadium, chromium and silicon (Loaiza, 2017). The black sands are constituted by: minerals such as magnetite, ilmenite, hematite, rutile, zircon; metals such as nickel, manganese, magnesium; and different silicates. The black color of ferrotitaniferous sands is due to the presence of ilmenite. They originate from eroded mafic and ultramafic volcanic rocks, so they have a rounded structure due to the mechanical action of marine and continental waters. Waves act as concentrating forces of sand along the coasts. The heavier materials are located closer to the sea, while the lighter ones move a greater distance. (Chuquirima & Cortez, 2014).

Within the primary and secondary deposits of ferrotitaniferous sands in countries such as Canada, Norway, the United States and Australia, approximately 60% of titanium oxide (TiO_2) found is mostly come from the ilmenite. In South American countries such as Uruguay, Peru, Chile, and Colombia, there are several deposits of black sands with different concentrations of iron and titanium along the coastal zone. In Ecuador, the primary sources of black sands are the formations of the Andes mountain ranges and the Coastal region. These sands have a high content of hematite (Fe_2O_3) and titanium oxide (TiO_2) (Chuquirima & Cortez, 2014).

Table 1 shows the statistics of non-renewable resources in Ecuador in 2009. It can be seen that there is an amount of 12.3 billion tons of ferrotitaniferous sands, which would represents a large amount of resources that can be used.

Table 1. Statistics of renewable resources in Ecuador in 2009 (Source: Varela, 2010).

Metallic Minerals	Tons
Gold	2 000
Silver	4 000
Copper	30 000 000
Non-metallic Minerals	Tons
Gold gravel	4 536 000
Polymetallic	32 000
Limestone	105 691 000 000
Clay	13 000 000
Feldspar	57 000
Kaolin	11 945 000 000
Silica	1 293 000 000
Cast	2 606 000 000
Ferrotitaniferous sands	12 300 000 000

These deposits present mineralogical resources that have not been fully exploited (Soledispa & Villacres, 1990). Therefore, in recent years, projects have been carried out to take advantage of these resources. Some of them took place in Mompiche, which is an enclosure located in the Bolivar parish, Muisne canton, south of the province of Esmeraldas. Mompiche is a small place with beaches that stand out for their warm waters and for the presence of black sands (Gobierno Autónomo Descentralizado Municipal de Muisne, 2014).

One of the projects developed was the geological and geophysical characterization of the western area of Mompiche, which obtained deposits of ferrotitaniferous sands with a high content of Fe and Ti (Díaz, 2013).

Another project attempted to recover metallic iron from the ferrotitaniferous sands of Suspiro´s beach, in the Mompiche area, by direct reduction in a cubilote furnace. The results obtained were not so good, since only a recovery of 15 % of iron was achieved (Chuquirima & Cortez, 2014).

Then, a paper proposed the development of a recovery process of titanium dioxide from the ilmenite present in the Mompiche area. The magnetic concentration of the ilmenite, the combination of thermal oxidation and carbothermal reduction treatments, and leaching with hydrochloric acid were used for this. The results showed that it is feasible to recover TiO_2 by leaching since it recovered 43 % with 90 % of purity (Trujillo, 2015).

Finally, the National Mining Company (ENAMI) created a project called Tola Norte, located in the canton of Eloy Alfaro, in the Esmeraldas province. This project aims to recover iron and titanium by drilling. In 2014, 2800 m were drilled, 719 samples were collected and a total of 5 % iron was determined (Empresa Nacional Minera del Ecuador, 2016).

3.4.1. Ferrotitaniferous sands from Mompiche

The Ostional Block 1 mining concession is located in the Mompiche Campus in Esmeraldas Province. There are activities of exploitation of black sand, taken from

Negra or Suspiro´s beach, with low environmental impact. The sands that are collected originate by the erosion of ancient conglomeratic rocks with small amounts of black sediments. These sands are very-fine grain, so they can be transported easily and are automatically recovered by the movement of the sea, in such a way that the extraction of them is imperceptible (Chuquirima & Cortez, 2014).

There are previous studies in which a sample of 5 kg of black sands, taken along Suspiro's beach was analyzed. The composition analyses were carried out by the FUNGEOMINE company in the Bondar Clegg laboratories, in Lima-Peru; and obtain the following summary results reported in Table 2:

Table 2. Results of the compositional analyzes of ferrotitaniferous sands taken from Suspiro´s beach (Source: Bondar Clegg laboratories, in: Chuquirima & Cortez, 2014).

Oxides	Abundance (%)
Fe_2O_3	69.23
TiO_2	28.37
MgO	1.45
SiO_2	1.32
Al_2O_3	0.60
CaO	0.49
Na_2O	0.33
P_2O_5	0.24
MnO	0.20
Cr_2O_3	0.13
K_2O	0.07

Note. The results of the standard deviation analysis and statistical errors can be found in the original Laboratory Report.

Figure 1 evidences that majority of the mineral composition of these beach sands are mainly composed by Fe_2O_3 (69.23 %) and TiO_2 (28.37 %), that is a 97.60 % of samples are composed by Fe-Ti minerals.

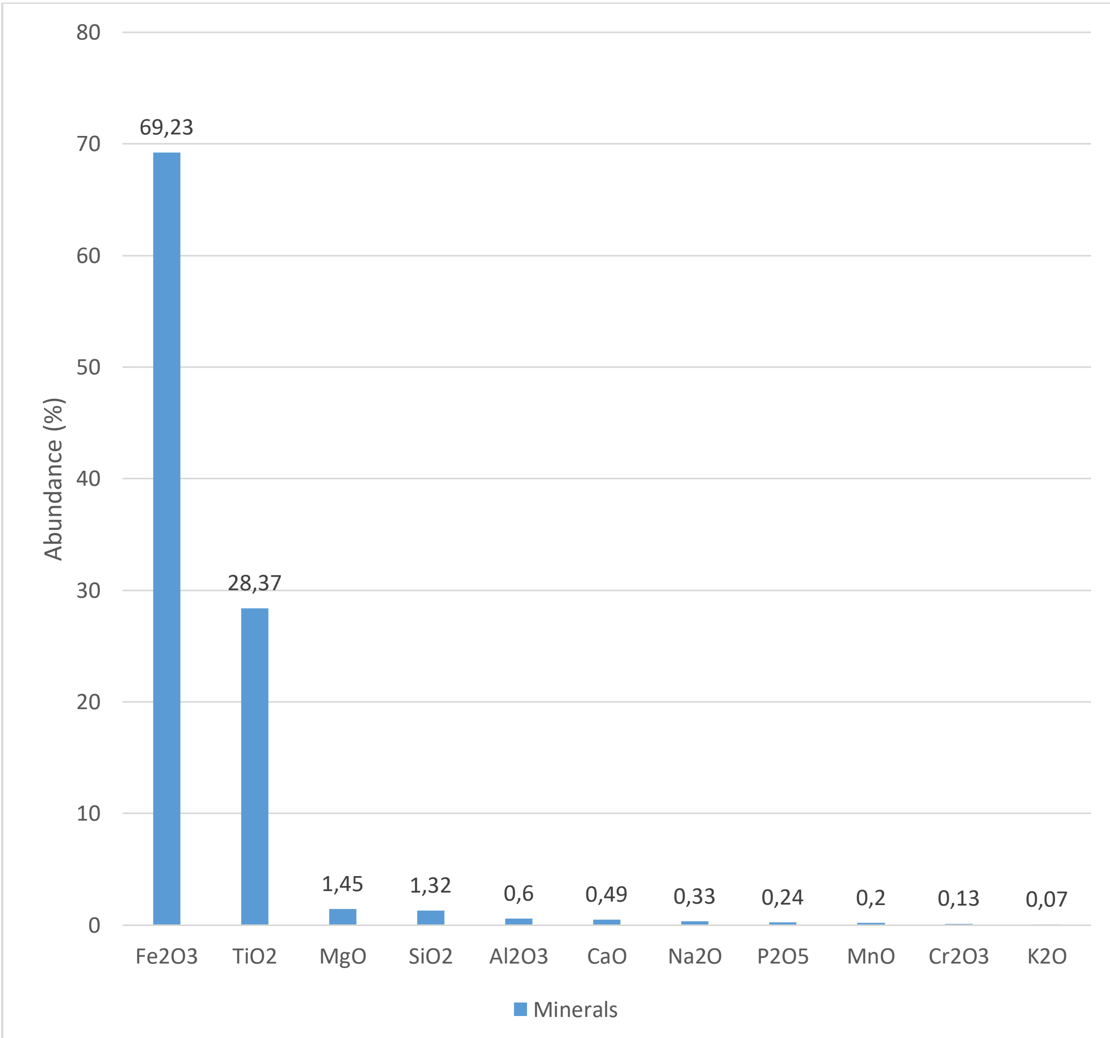

Figure 1. Relative abundance of minerals at Suspiro's beach, Mompiche-Esmeraldas (Source: Bondar Clegg laboratories, in: Chuquirima & Cortez, 2014).

Subsequently, x-ray diffraction analysis (XRD) was carried out for the qualification and quantification of the different minerals present in the sands, and the following results reported in Table 3 were obtained:

Table 3. Results of X-ray diffraction analysis of ferrotitaniferous sands taken from Suspiro´s beach, Mompiche-Esmeraldas (Source: Chuquirima & Cortez, 2014).

Mineral	Formula	Content (%)
Ilmenite	$FeTiO_3$	52
Hematite	Fe_2O_3	38
Magnetite	Fe_3O_4	10
Quartz	SiO_2	-

Observing the results obtained in Table 2 and Table 3, it can be concluded that in Suspiro´s beach there is a majority amount of ferrous oxide and titanium oxide, from which metals (Fe, Ti) can be extracted for different applications.

CHAPTER 4: METHODOLOGY

4.1. Collecting sand's samples

To carry out the study, as part of the INÉDITA research project, thirteen samples of black sands from different parts of Ecuador were collected. The samples of the volcanic zones were taken from the province of Cotopaxi, on the slopes of the Quilotoa Volcano. On the other hand, samples from the Coastal Zones were taken from Esmeraldas, Santa Elena, and Manabí provinces, from the beaches of Anconcito, Olón, Montañita, Pedernales, Mompiche, Punta Galera, Tonsupa and Rio Verde parish (See Figure 2). All samples were collected on four different days and they were identified according to the collection area, the sample number, and each field trip. Table 4 shows detailed information of each collected sample.

Figure 2. Map of Ecuador with the location of areas where sand's samples were collected

Table 4. Identification and description of sand's samples taken from Coastal and volcanic zones of Ecuador

N°	ID	Date	Description	Place
1	SXQ-101	16/07/2018	Sands settled by volcanic eruptions, rich in iron.	Cotopaxi, Southeast of the Quilotoa Volcano.
2	SXQ-102	16/07/2018	Sands settled by volcanic eruptions, intermittent fluvial environment, rich in iron.	Cotopaxi, Southeast of the Quilotoa Volcano.
3	SYA-103	17/07/2018	Beach sands collected in the high tide[1] zone.	Santa Elena, Anconcito Beach.
4	SYA-104	17/07/2018	Beach sands collected on the boundary between the high tide zone and the backshore[2].	Santa Elena, Anconcito Beach.
5	SYO-105	18/07/2018	Beach sands took from the high tide zone.	Santa Elena, Olón Beach.
6	SYM-106	18/07/2018	Beach sands took from the high tide zone.	Santa Elena, North of Montañita Beach.
7	SEV-201	30/07/2018	Crayfish silty sand collected in the high tide zone.	Esmeraldas, Río Verde parish. Top of the beach area.
8	SET-202	30/07/2018	Quartz sand collected in the high tide zone.	Esmeraldas, Tonsupa. Top of the beach area.
9	SET-203	30/7/2018	Quartz sand collected in the low tide[3] zone.	Esmeraldas, Tonsupa. Bottom of the beach area.
10	SMP-204	31/07/2018	Micro-conglomerate sandy of Quartz and Lithic took from the high tide zone.	Manabí, Pedernales. Top of the beach area.
11	SEM-205	31/07/2018	Quartz sand collected in the high tide zone.	Esmeraldas, Mompiche. Top of the beach area.
12	SEM-206	31/07/2018	Quartz sand collected in the high tide zone.	Esmeraldas, Mompiche. Near the mouth of a mini sandy estuary.
13	SEG-207	31/07/2018	Quartz sand collected in the high tide zone.	Esmeraldas, Punta Galera. Near a bay.

Note. [1]High tide: Moment when the seawater floods cover the shore of the coast. [2]Backshore: Beach area between the boundary of the seafoam lines to the outer inner boundary of the beach. [3]Low tide: Time when seawater registers its lowest height.

Within the Ferruginous and Titaniferous sands of Ecuador as Adsorbents of Acid Gases in the Hydrocarbons Industry project, clays were also sampled in different areas of Ecuador.

This in order to use them as a coating of black sands and provide support. However, this sampling is not detailed because this work is based on processes to treat only black sands.

4.2. Scanning Electron Microscopy

In order to analyze the composition of the collected ferrotitaniferous sand's samples, analyses were carried out using a scanning electron microscope. The scanning electron microscopy (SEM) technique generates high-resolution electronic images, by scanning with an electron beam on surfaces of different materials. These microscopes provide information on the composition of the materials because each element composing the sample emits different amounts of electrons (Arenas-Lago, et al., 2017).

SEM analysis was performed only for SYM-106, SEM-205, and SEM-206 samples. This because these samples presented the darkest colors. As mentioned earlier, the darker the color of the ferrotitaniferous sands, the greater the content of ilmenite.

Before performing the SEM analysis some samples were sifted in order to separate the different particle sizes. Table 5 details the results obtained in the global SEM analysis of the SEM-205 sample. Table 6 shows the results obtained in the global SEM analysis of the SEM-206 sample. Table 7 reports the results of the SEM analysis at different spots of the last sieve fraction of the SEM-206 sample. Table 8 shows the results of the global SEM analysis of the last sieve fraction of the SYM-106 sample. Finally, Table 9 reports the results obtained from the SYM-106 sample recovered from sieve # 100.

Table 5.Element composition of the SEM-205 sample

Element Symbol	Weight Concentration (%)
O	38.59
C	26.12
Fe	21.02
Si	5.20
Ti	4.45
Te	2.58
Mg	2.04
Total	100

Table 6. Element composition of the SEM-206 sample

Element Symbol	Weight Concentration (%)
O	45.68
Fe	29.44
Si	11.76
Ti	7.25
Mg	2.59
Ca	1.75
Al	1.54
Total	100

Table 7. Element composition at different spots of the last sieve fraction of the SEM-206 sample

Element Symbol	Weight Concentration (%)							
	Spot 1	Spot 2	Spot 3	Spot 4	Spot 5	Spot 6	Spot 7	Spot 8
O	62.30	57.79	65.33	53.67	62.92	54.17	44.76	52.35
C	-	-	-	17.73	-	15.24	-	-
Si	18.00	17.78	34.67	16.44	16.06	10.95	24.42	22.92
Al	11.73	8.59	-	6.92	5.84	4.51	7.83	8.71
N	-	7.94	-	-	9.59	10.11	-	7.48
Na	4.28	5.62	-	2.59	2.98	2.33	2.55	5.01
Fe	-	-	-	-	-	1.59	12.62	1.63
Ca	3.69	2.04	-	2.66	2.19	1.10	1.94	-
Ti	-	-	-	-	-	-	1.92	-
K	-	0.24	-	-	-	-	2.85	0.96
Mg	-	-	-	-	0.43	-	1.10	0.96
Total	100	100	100	100	100	100	100	100

Table 8. Element composition of the last sieve fraction of the SYM-106 sample

Element Symbol	Weight Concentration (%)
O	59.45
Ca	12.89
Si	10.81
Fe	7.88
Mg	4.39
Al	2.30
P	1.78
Total	100

Table 9. Element composition of the SYM-106 sample recovered from sieve # 100

Element Symbol	Weight Concentration (%)
O	51.33
Si	16.52
Fe	10.83
Mg	9.13
Ca	5.49
Al	3.86
Na	1.21
P	0.84
Ti	0.80
Total	100

To choose the most appropriated sand's sample to be used in acid gas adsorption, it was necessary to interpret the results obtained from the analysis performed. According to the observations made, the titanium oxides are found in the smaller diameter particles, and the iron oxides are distributed in different sieving fractions. The sample that presents greater compositions of iron and titanium, will be the sample that allows obtaining better results to be used as a solid bed. Of the three samples analyzed, the results obtained from the SEM-206 sample show a greater presence of iron and titanium, with contents of 29.44 and 7.25 % mass respectively (see Table 9). In addition, it was the sample that had the darkest black color (Figure 3). Therefore, the sands that will be used to obtain solid beds are those belonging to Mompiche beach.

Figure 3. Images of the SEM-206 sample taken in Mompiche beach-Esmeraldas

4.3. Small and Medium Enterprise Analysis

Small and medium-sized enterprises (SMEs) are a group of companies that according to their sales volume, social capital, number of workers, and their level of production or assets present characteristics of this type of economic entities (SRI, 2012).

SMEs owe their name to the number of workers they own, the sales they make, the present time in the market and their economic growth. The consultants and advisors of the SMEs consider that the group includes those companies that obtain sales volumes that vary between $ 15 000 and $ 20 000 000 annually. However, according to the experience of some SMEs in Ecuador, this group has sales volumes that are between $ 1 and $ 5 million per year (Grupo Enroke, 2014).

SMEs are considered as the axis that guides the economy of most countries since they allow generating more jobs within a nation. In Latin America, small and medium enterprises (SMEs) represent 99 % of all companies and generate jobs for approximately 67 % of the total workforce (CEPAL, 2013).

Small and medium enterprises in the Ecuadorian business sector have a significant contribution. According to the last Censo Nacional Económico, of the 843,745 companies registered in 2016, 90.5 % are companies with annual sales of less than $ 100 000 with between one and nine employees; 7.5 % are companies with annual sales of $ 100 000 to $ 1 000 000 with between ten and forty-nine employees (Delgado & Chávez, 2018). In Ecuador, 39 % of jobs are generated by microenterprises, while 17 % are small and 14 % medium (Jácome & King, 2013).

Taking into account that this project arises as part of an innovative idea, it is taken as a project belonging to the small and medium enterprises of Ecuador. To begin with the SME analysis of the project aimed at the adsorption of acid gases from ferrotitaniferous sands, it is necessary to develop a Diagram of Porter's Diamond (Figure 4), in order to visualize strengths, opportunities, weaknesses, and threats that may occur within the chain of value. This classical diagram allows us to recognize factors such as the allocation of resources, labor regulations, specialized infrastructure and the scientific basis that supports the commercial idea; as well as the competitive sectors, the strategy, the rivalry of other companies, the management model and the market (Figure 5). Subsequently, this SME analysis will be used in order to carry out an economic analysis of the project (OBS Business School, n. d.).

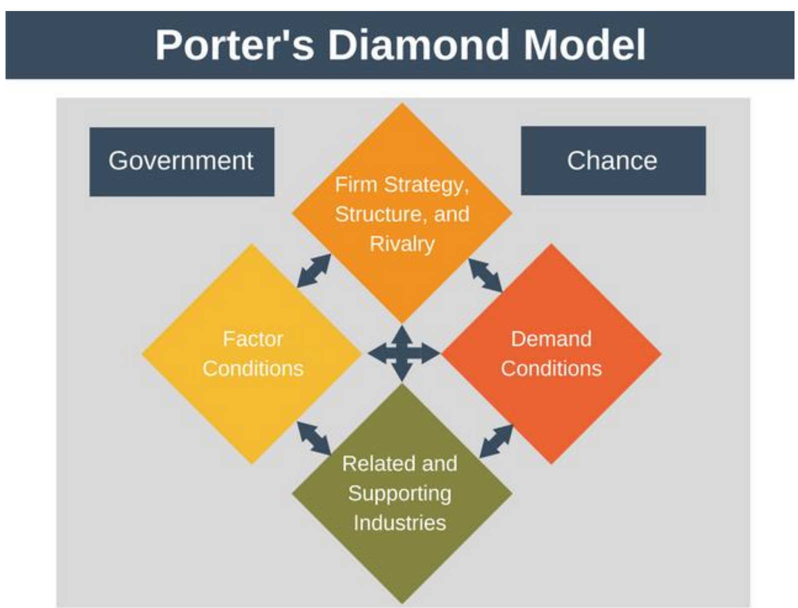

Figure 4. Porter's Diamond Model (Source: Expert Program Management, 2018. Retrieved from https://expertprogrammanagement.com/2018/04/porter-diamond-model/)

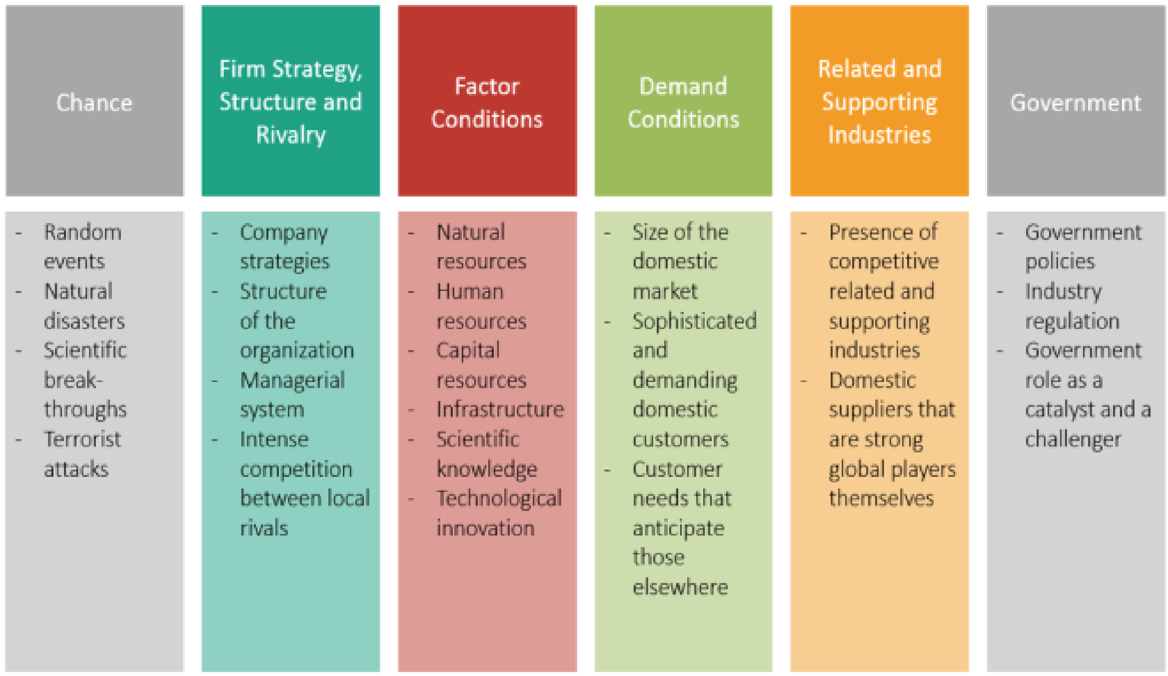

Figure 5. Specifications of each area of Diagram of Porter's Diamond (Source: Business to you, 2018. Retrieved from https://www.business-to-you.com/porter-diamond-model/)

An important tool that can help to generate better SME analysis is the diagram process block. Diagram process block is a figure used to detail a process, allowing a clearer view of the value chain. They are formed by a series of blocks that are connected by arrows (flows) that represent the inputs and outputs. Each block represents a process or a set of processes that are related. The flows must go in one direction, from left to right. As for the flows that pass vertically, the gases must exit through the upper part of the blocks and the liquids and solids must exit through the lower part of the blocks. These diagrams help in the writing of the process that is being carried out (Supervisar Variables, 2018).

4.4. Economic Analysis

Through economic analysis, one can know if a company belonging to SMEs is viable in the future, reducing labor uncertainties. The economic analysis depends on the amount of information that is available about the process that is going to be carried out, the sector of the activity of the company and the objective to be achieved. The analysis begins with the study of the fundamental principles of the company, that is, its mission, vision, and values, as well as its general objectives. In order to clarify the activity that will be carried out by the company must be established an action plan that allows obtaining the best results (Moreno, 2012).

The industrial processes are started as long as they present a favorable economic aspect. For which people must review the expenses and the profits that are going to be obtained when carrying out the process. There are two types of expenses, direct and indirect. Direct expenses correspond to raw materials, labor, equipment, and machinery. The indirect costs correspond to the salaries of the administrative staff and the costs of distributing the product. The net earnings correspond to the total income obtained minus all the expenses incurred during the process. Chemical Engineering magazine publishes one of the best-known chemical plant cost indices, which is based on four specifications with the following percentages for each one (Figure 6): Equipment and Machinery: 61%, Workforce for construction: 22%, Engineering and Supervision: 10 %, Buildings: 7 %, (Jiménez, 2003).

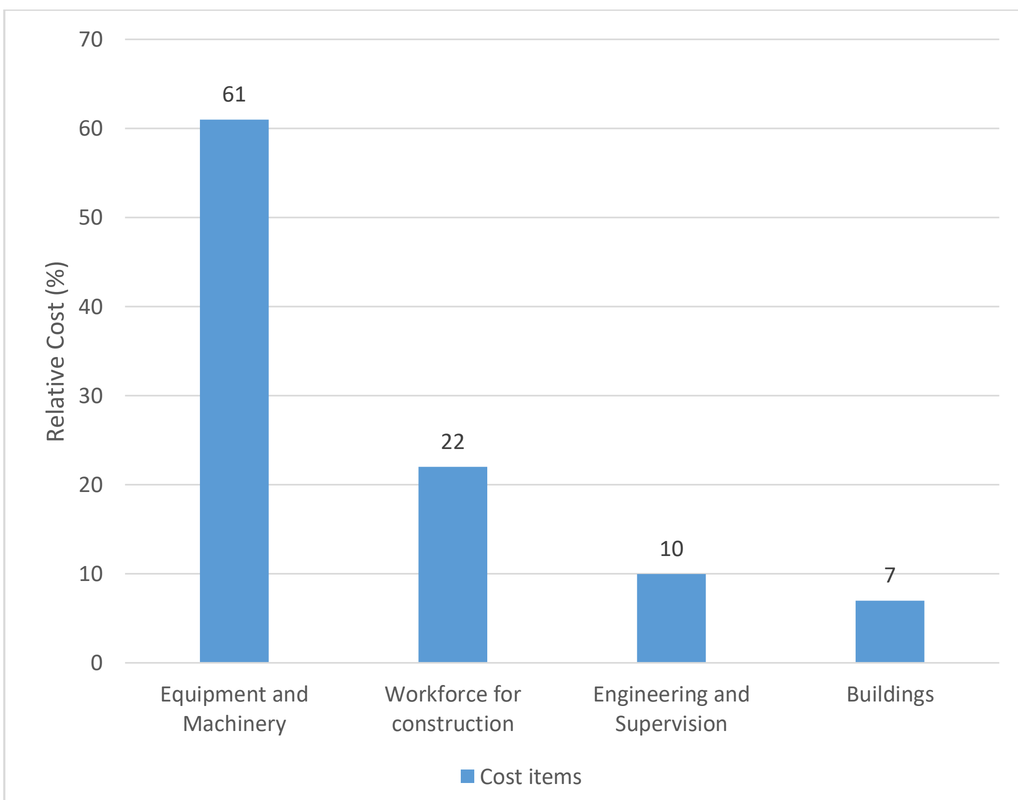

Figure 6. Relative costs of installing a chemical plat (Source: Jiménez, 2003).

In this work, only the black sand's treatment processes are taken into account: collection, in-situ magnetic separation, transfer, transport and storage excluding subsequent processes for obtaining solid beds, because these processes represent the content of subsequent works. Therefore, the gains that will be obtained with the whole process cannot yet be determined, only those costs related to the treatment processes of the ferrotitaniferous sands mentioned above are anticipated.

CHAPTER 5: RESULTS, INTERPRETATION, AND DISCUSSION

5.1. Porter's Diamond Model

In Figure 7 there is a Diagram of Porter's Diamond, which consists of 6 zones mentioned above.

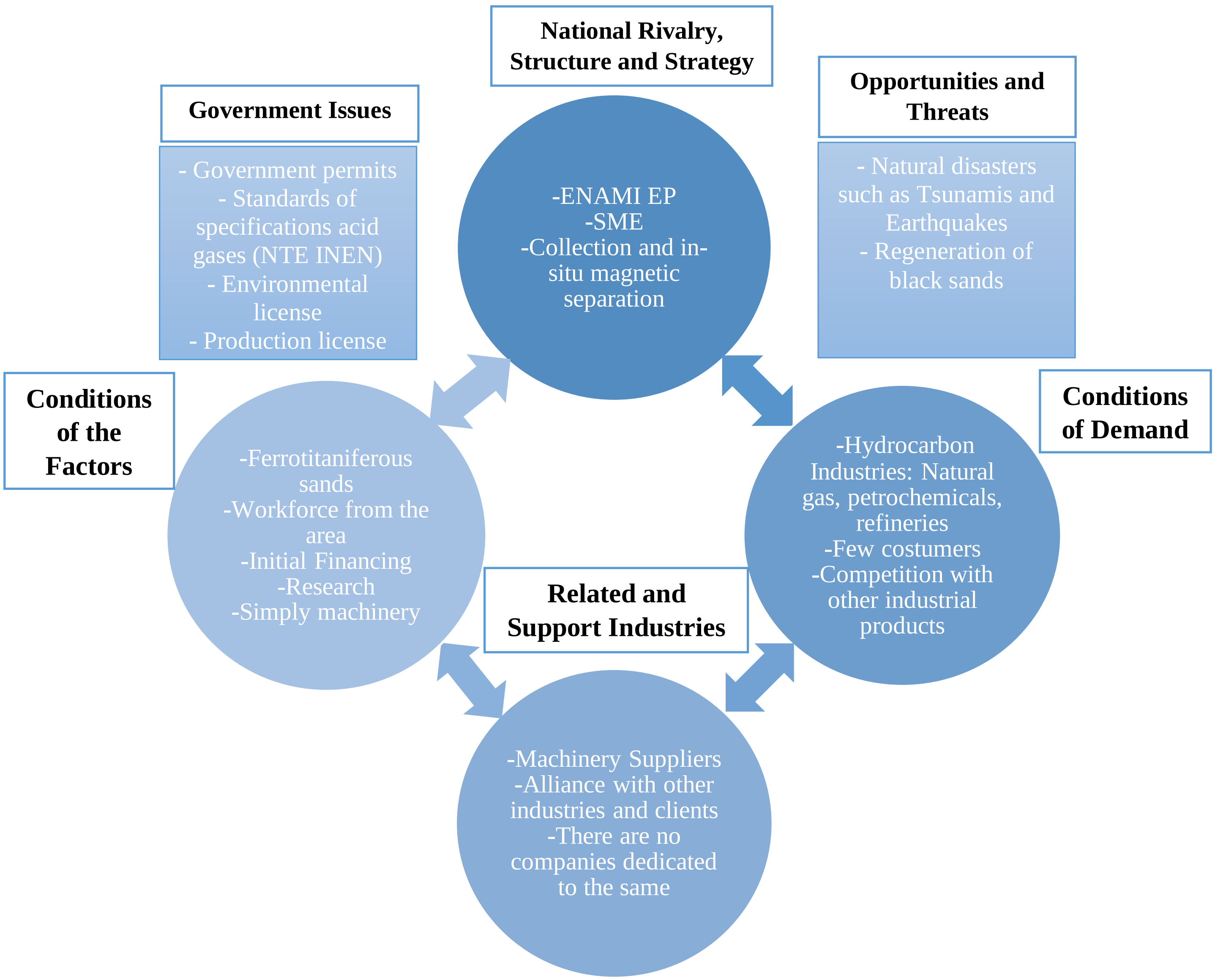

Figure 7. Diagram of Porter's Diamond for the Project of acid gas adsorption processes employing ferrotitaniferous sands

The first zone (represented by the upper circle) consists of the national rivalry, structure, and strategy of the company. The only rivalry that the project presents is with ENAMI EP since both activities are related to the extraction of minerals in the same area. However, the project focuses on the adsorption of acid gases, while ENAMI EP performs mining activities. The structure of the project is based on an activity directed towards the construction of a small or medium-sized company, which seeks to contribute to the country's problems. Finally, the company's strategy is based on minimizing costs because the magnetic separation will be carried out in the same area where the sands are collected, without the need to be transported first.

The second zone (represented by the left circle) consists of the conditions of the factors. This includes natural resources, human resources, capital resources, scientific knowledge and technological innovation. The raw material of the process is ferrotitaniferous sands, which represent a natural resource, so they are present in large quantities. The project will be established in the area of Mompiche-Esmeraldas, in such a way that several jobs will be generated for the local population, improving the labor and economic stability of many people. In addition, the project, which is part of INÉDITA, has initial funding for research (which is being carried out) and its possible development. And, on the other hand, the machinery necessary to complete the first five processes of the project is a simple machinery that is generally used for the construction industry, so it has a large offer. Finally, technological innovation is also present within the project because it seeks to modify machinery, allowing magnetic separation while collecting black sands.

The third zone (represented by the right circle) consists of the demand conditions. This includes the size of the national market, potential buyers and competition. The national market for acid gas adsorbents covers the HC industry, which is mainly composed of refineries and small amounts of NGP sweetening. Solid beds from iron and titanium oxides are products that can be used both nationally and internationally through exports to different countries, inside and outside the continent. Although the market is relatively broad, many of the industries use imported technologies for the adsorption of acid gases (iron sponge, Sulfatreat®, Puraspec ™, dry bed). Therefore, there is a great competition in terms of technologies, which could be overcome with lower sales prices and higher profits.

The fourth zone (represented by the lower circle) consists of the related and support industries. As mentioned above, there are currently no industries dedicated to developing solid beds from ferrotitaniferous sands; however, there are some industries in which industrial wastes contain high proportions of iron and titanium oxides, such as the aluminum industry. In addition, there are also industries dedicated to the iron and steel industry, whose purpose is to extract iron from minerals and work it; as well as industries that use certain elements and compounds founded in large quantities in black sands as raw materials, as is the case of the glass manufacturing industry and the textile industry. Although all these industries do not represent direct competition, they are directly related to the raw material of this project. In this way, the project could be extended to generate alliances by providing raw materials to some industries by selling waste generated within industrial processes, or by taking advantage of waste or products generated by other industries. On the other hand, the project must have machinery suppliers that offer low and accessible rates.

The fifth zone (represented by the rectangle on the left side) includes the terms related to the government. The project needs to have government permits on a legal basis, in order to carry out extraction activities. All this in order to protect national resources and the environment. On the other hand, it is also necessary to follow the NTE INEN standards, created in order to meet the specifications that acid gases must present in the HC industry.

Finally, the sixth zone (represented by the rectangle on the right side) includes opportunities and threats against certain events. Natural disasters that would be extremely dangerous for the acid gas adsorption industry are tsunamis and earthquakes. This is due to the location of the industry (near to the shore). Tsunamis would cause irreparable damage and incredible losses of both human and material resources. Another risk is the high seismic activity that characterizes the Coastal Zone of Ecuador and generates recurrent high-magnitude earthquakes, as the last one registered in April 16, 2016, of Mw: 7.8, whose epicenter was located off the Coastal Zone of Muisne *(Instituto Geofíico de la Escuela Politécnica Nacional, 2016)*. On the other hand, one of the greatest opportunities for the project is the use of black sands as a fully regenerable resource, because tides increases, large amounts of sands reworking and return to the beach zone.

5.2. Diagram Process Block

Figure 8 shows the Diagram Process Block (DPB) of the Ferruginous and Titaniferous sands of Ecuador as Adsorbents of Acid Gases in the Hydrocarbons Industry project.

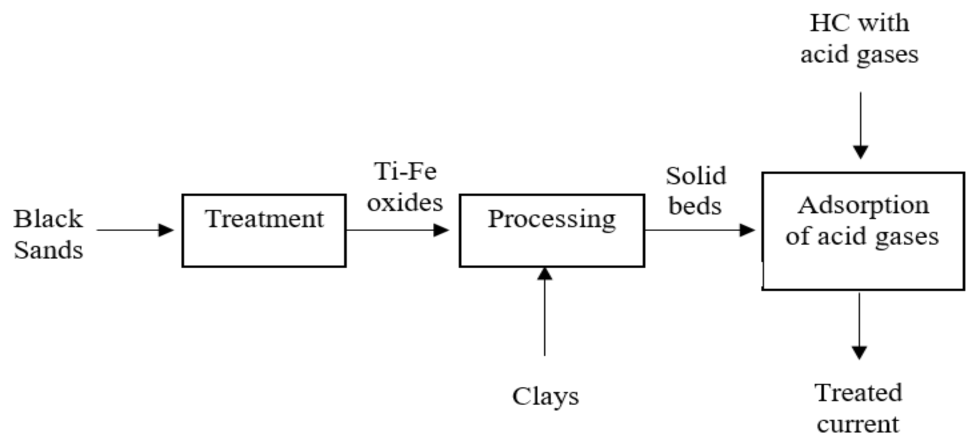

Figure 8. General DBP of the winner project of a call launched by INÉDITA.

The diagram in Figure 8 is a general scheme of all the processes that will be carried out within the project for the adsorption of acid gases from ferrotitaniferous sands, however this work is based solely on the process of treatment of black sands to obtain titanium oxides and iron oxides.

Next, the specific Diagram Process Block for the treatment of black sands is shown in Figure 9.

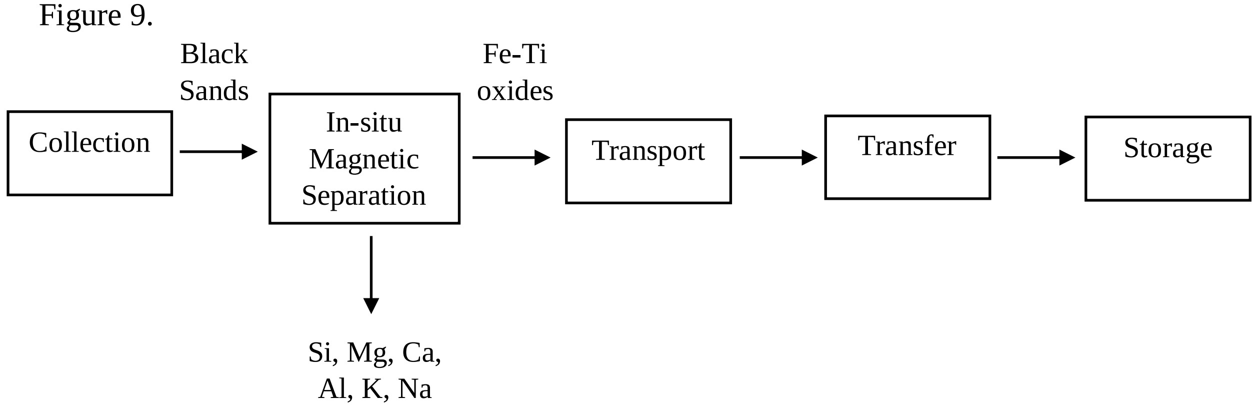

Figure 9. Diagram Process Block for the five processes for the treatment of ferrotitaniferous sands.

5.3. Plant Capacity

The following design bases were taken into account to calculate the capacity of the plant:

- The overdesign factor: It refers to the excess in the size of the equipment considering production increases in the plant with the same infrastructure. This factor is 10 %.
- The percentage of magnetic fraction of the ferrotitaniferous sands from Mompiche: It was determined from the extraction of Fe / Ti oxides with a magnet of 0.1 tesla. From a sample of 250 g of black sands, 66.2 g of Fe / Ti oxides were extracted. Calculating the ratio between these two values, it is obtained a yield of Fe / Ti oxides equals to 26.48 % m/m (Luna, 2019).
- Composition of solid beds: The solid beds are composed of both Fe / Ti oxides and clays, for the calculations a composition of Fe / Ti oxides of 30% and clays of 70% is estimated
- Capacity of the Shushufindi Refinery gas plant: The Shushufindi Refinery, located in the province of Sucumbíos, has a natural gas plant that processes 25 MMSCFD (EP PRETROECUADOR, 2016).
- Amount of commercial product used for H_2S adsorption: An amount of 200 000 pounds of a certain commercial product (oxides + support structure) is used for the adsorption of H_2S into a reactor (Tacuri, 2015).
- Duration time of the commercial product: The amount of 200 000 pounds of a certain commercial product has a duration of 72 days (Tacuri, 2015).

The calculations for obtaining the capacity of the plant are detailed below:

$$Daily\ mass\ flow\ of\ solid = \frac{200\ 000\ pounds}{72\ days} = 2778\ \ pounds/day$$

$$Anual\ mass\ flow\ of\ solid = 2777.78\ \frac{pounds}{day} * \frac{365\ days}{1\ year} = 1013889\ pounds/year$$

$$Anual\ mass\ flow\ of\ solid = 1013889 \frac{pounds}{year} * \frac{1\ Ton}{2200\ pounds} = 461\ Tons/year$$

$$Anual\ mass\ flow\ of Fe - Ti\ oxides = \frac{30}{100} * 461 \frac{Tons}{year} = 138\ \frac{Tons}{year}$$

$$Anual\ mass\ flow\ of black\ sands(x) = \frac{138 * 100}{26.48} = 522\ \frac{Tons}{year}$$

$$138.3 \frac{Tons}{year} - 26.48\ \%$$

$$x \frac{Tons}{year} - 100\ \%$$

Applying the overdesign factor of 10%:

$$Capacity\ of\ plant = 522 + \left(\frac{10}{100} * 522\right) = 574\ \frac{Tons}{year}$$

5.4. Process for the treatment of black sands

For the elaboration of process for the treatment of black sands, information about the process for the extraction of iron and steel was used as the basis. The initial processes that are carried out for the extraction of iron and steel are the processes of prospecting and exploitation, which are very similar to the five processes for the treatment of ferrotitaniferous sands. Lengths and volumes were determined based on the size of existing machinery and equipment, and the amount of machinery was found based on the capacity of the plant and the density of black sands. The capacity of the plant is 574 tons / year and the density of the black sands is approximately 1900 kg / m^3.

- <u>Collection:</u> The backhoes are responsible for removing and collecting the sands of the beach. These have an excavator shovel in the front that is responsible for digging at a certain depth, and a bucket in the back that is responsible for collecting black sands. Excavator shovels can dig at depths of 4.83 m. The bucket has a volume of 0.80 m^3 approximately. For sand collection, only one daily backhoe will be needed.

- <u>In-situ Magnetic Separation:</u> In the second step, the sands are emptied from the backhoe bucket in a magnetized concrete mixer with a capacity of approximately 0.4 m^3 each one and a yield of 2.5 m^3 / h. These mixers work with motor and are small in size, however, they are less expensive and more practical than using a large concrete mixer because they will not transport material. Concrete mixers are machines equipped with a rotating vessel that is used to mix substances, especially cement with water. But in this case, the concrete mixer will be covered with magnets and will have the function of separating iron and titanium oxides from the rest of the black sand, by means of its constant movement. The concrete mixer can be magnetized with large magnetic bars or metal wire coatings such as Co, Fe, Ni (ferromagnetic metals) connected to an electric generator. For the magnetic separation two concrete mixers will be used.

- Transport: The next step is to transport the sands to the treatment plant where the subsequent processes will take place. For this purpose, dump trucks are used and they have an approximate volumetric capacity of 7.5 m^3. Dump trucks are vehicles that have a mechanical device on the chassis that automatically unloads the content. Only one dump truck will be used daily.

- Transfer: Dump trucks arrive at the plant and empty their contents. The emptying operation consists of dislodging the sands from the dump trucks. The sands fall on mechanical conveyor belts of solids. For transporting solid material in bulk, it is necessary to configure the system with rollers that make up a transport gutter. The rollers meet repeatedly along the line to prevent the tape from deforming and touching the base of the transport structure. The belt works thanks to an engine located in the final part and contains loading and unloading devices such as hoppers *(Quiminet, 2012)*. The grains of sand are transported horizontally and then elevated to be placed in storage silos.

- Storage: The sand is stored in silos, which are tanks designed for the collection of bulk solids. These tanks are generally cylindrical, made of plates of smooth or corrugated iron, galvanized, of different thicknesses. The most used silos have a capacity of 70 tons. The base of the silos can be flat or conical to facilitate the exit of the grain. The roof is conical, usually with a drop angle of 25 °. They are usually equipped with ventilation systems based on motor fans *(Trecco, 2013)*. As it is necessary to store 138 tons of Fe/Ti oxides, only two silos will be needed.

Table 10 summarizes the necessary quantities of each equipment, the volumes they will have in each load, the performance of the machine (if they have one) and the time it will take to perform each process.

Table 10. Quantities and time used of each machinery

Machinery	Quantity	Volume (m^3)	Yield (m^3/h)	Time (h)
Blackhoe	1	0.80	-	0.5
Concrete mixer	2	0.80	5	2
Dump truck	1	7.5	-	1.5
TOTAL				4

At the end of table 10, the total hours that the collection, in-situ, magnetic separation and transport processes will take are shown. This time represents a half of a working day, therefore two daily trips can be made transporting a total of 15 m^3 of black sand.

As the density of the black sand is known, the amount of black sand that will enter the plant daily can be calculated:

$$15\,\frac{m^{\,3}}{day} * \frac{1900\,kg}{m^3} * \frac{1\,Ton}{1000\,kg} = 28.5\,Ton/day$$

As a quantity of black sands required is 574 Ton / year, machinery must be rented for approximately 20 days.

5.5. Cost Analysis

Table 11 shows the daily rental cost of each machinery, and the total value to be paid.

Table 11. Cost of rental of machinery per day (Source: The base rental prices recovered from https://www.manualdeobra.com/blog/2016/7/18/magazine-de-construccion)

Machinery	Quantity	$/day (unit cost)	$/day (total cost)
Backhoe	1	230	230
Electric Generator	2	90	180
Concrete mixer	2	30	60
Dump trucks	1	150	150
Total			1220

As one can see in Table 11, the rental prices of construction machinery are relatively low, reaching $ 1200 / day, so the amount of $ 24 000 would be spent in 20 work days. As it takes a few days a year to cover the annual capacity of the plant, it is not feasible to acquire own machinery.

On the other hand, the mechanical conveyor is an industrial equipment and must be purchased. Its price varies by capacity and manufacturing material, but it costs approximately $ 4 000.

The silo, which can have the same structure as a corn silo, is a team that needs a stronger investment since its price is approximately $ 10 000. In addition, as mentioned earlier, two silos will be needed, so the cost will be $ 20 000.

The total value to be paid for the necessary machinery for the treatment of ferrotitaniferous sands is $ 48 000.

CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

- From the Scanning Electron Microscopy performed on the thirteen samples taken from the ferrotitaniferous sands, it was determined that the most suitable sample to be used as an adsorbent of acid gases is the SEM-206 since it has 29.44 % mass of iron and 7.21 % mass of titanium. This sand belongs to the area of Mompiche, Esmeraldas.
- The collection process and the in-situ magnetic separation process take place together by means of a magnetized concrete mixer. The magnetization can be done with large magnetic bars or metal wire coatings such as Co, Fe, Ni (ferromagnetic metals) connected to an electric generator.
- Taking into account certain design bases, the capacity of the plant is 574 Tons / year.
- Processes of collection, in-situ magnetic separation en transport require the use of simple construction machinery, which can be easily found in the market. Rental prices vary between $ 30 and $ 230 per day depending on the machinery.
- The equipments used for the processes of transport and storage of Fe/Ti oxides are most expensice. These need an investment of $ 24 000.
- The cost analysis determined that it is neccesary approximately $ 48,000 to purchase the machinery and equipment for the treatment of the black sands.
- The waste generated in the magnetic separation process, specifically the compounds with silicon and aluminum, can be used as raw material for the recovery of the glass industry.
- The process illustrated by the way of the proposed SME Analysis will allow us to valorize natural resources that are found in large quantities in Ecuador. The business is profitable and has a broad market that must be exploited with low prices, sales strategies, and guaranteed product performance.
- The SME project must continue from the storage process, in the next works, taking advantage of Fe-Ti oxides recovered form Mompiche-Esmeraldas.

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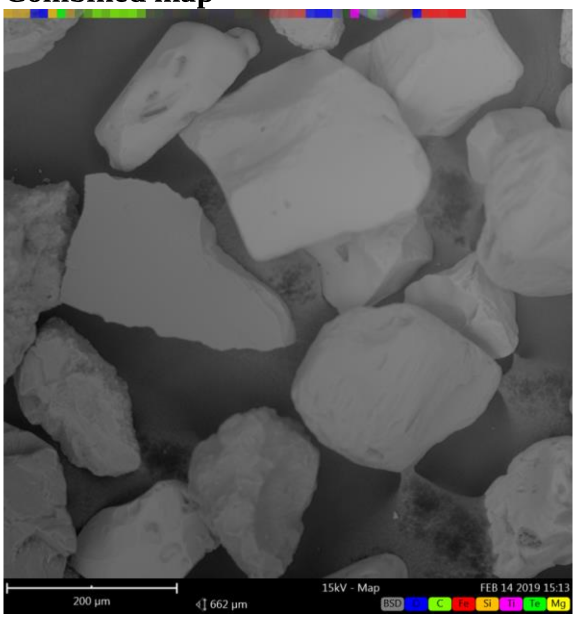
ANNEXES

Annexe 1: SEM Analysis of SEM-205 sample

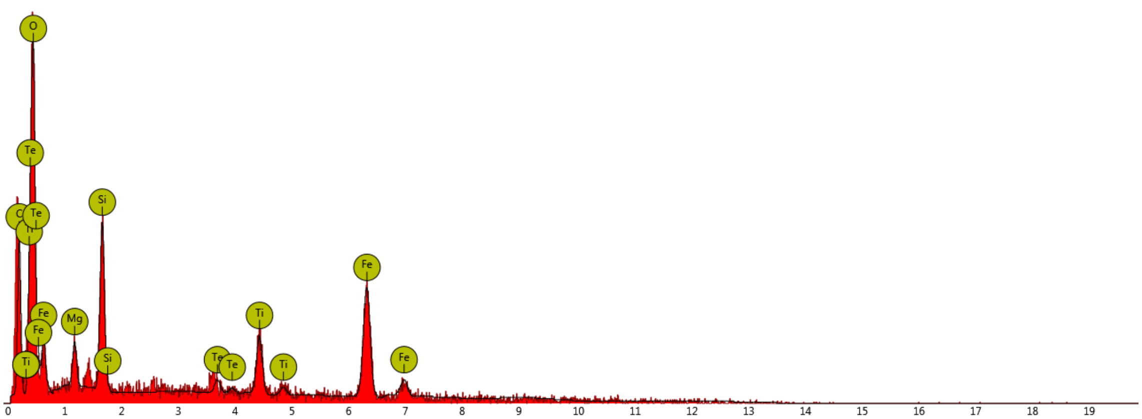
Map

Combined map



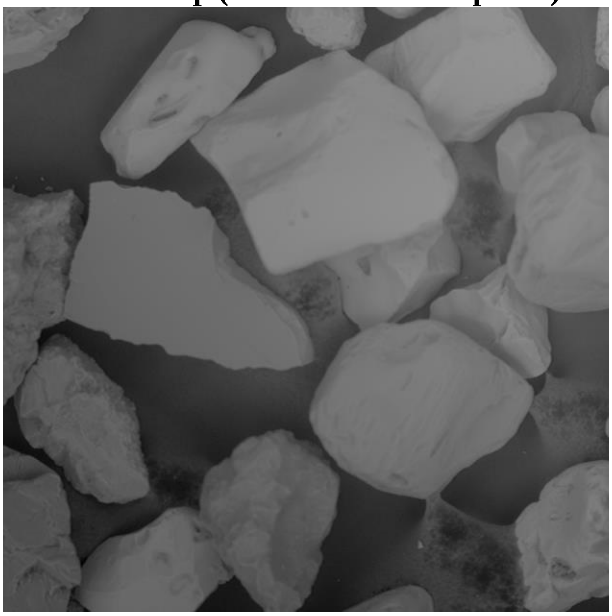
Element Symbol	Atomic Conc.	Weight Conc.	Oxide Symbol	Stoich. Conc.
O	45.13	38.59		
C	40.69	26.12	C	74.14
Fe	7.04	21.02	Fe	12.83
Si	3.46	5.20	Si	6.31
Ti	1.74	4.45	Ti	3.17
Te	0.38	2.58	Te	0.69
Mg	1.57	2.04	Mg	2.86

FOV: 662 µm, Mode: 15kV - Map, Detector: BSD Full, Time: FEB 14 2019 15:13



Disabled elements: B

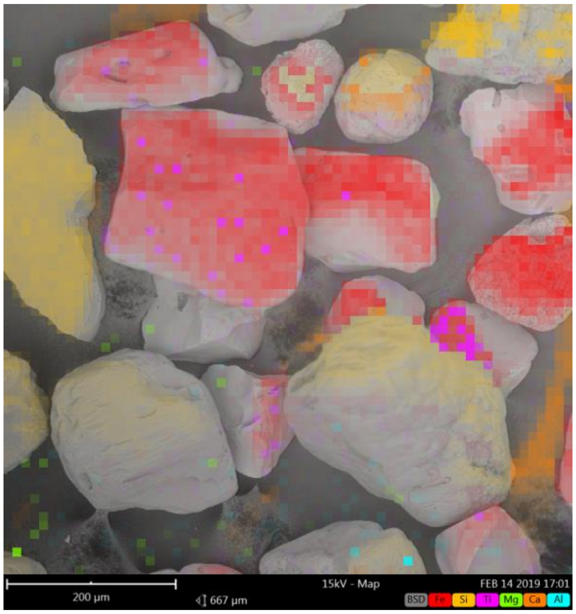
Cut out of map (resolution: 64x64 pixels)



Annexe 2: SEM Analysis of SEM-206 sample

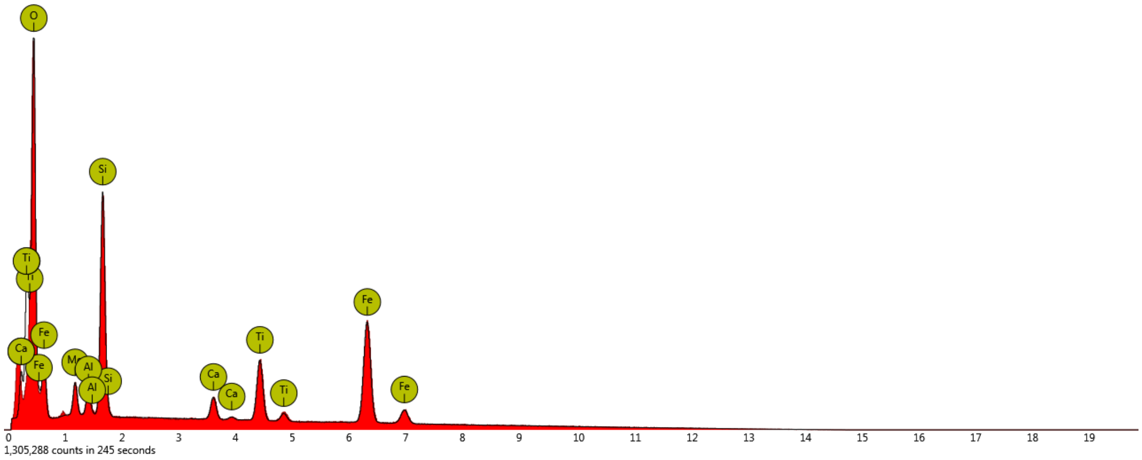
Map

Combined map



Element Symbol	Atomic Conc.	Weight Conc.	Oxide Symbol	Stoich. Conc.
O	68.64	45.68		
Fe	12.67	29.44	Fe	40.40
Si	10.06	11.76	Si	32.09
Ti	3.64	7.25	Ti	11.61
Mg	2.56	2.59	Mg	8.18
Ca	1.05	1.75	Ca	3.35
Al	1.37	1.54	Al	4.37

FOV: 667 µm, Mode: 15kV - Map, Detector: BSD Full, Time: FEB 14 2019 17:01



Disabled elements: B, C, Te

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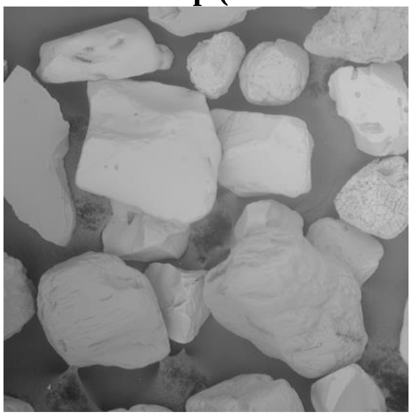
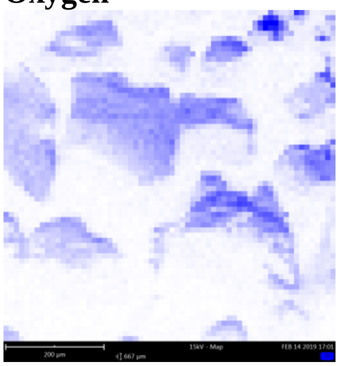
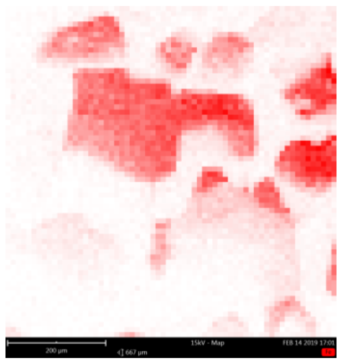


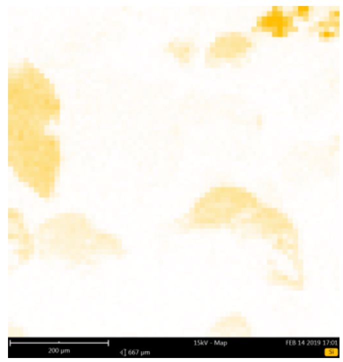
Oxygen



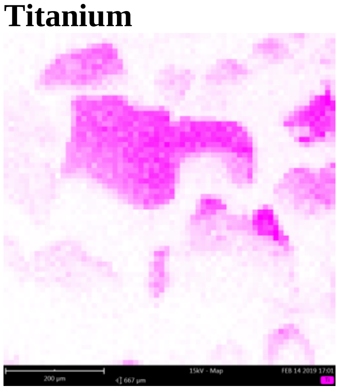
Iron



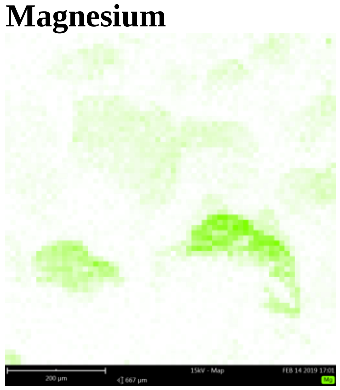
Silicon



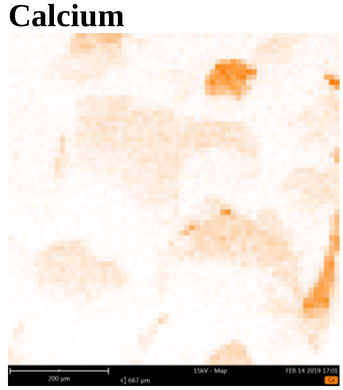
Titanium



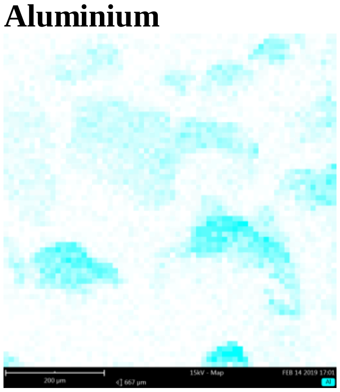
Magnesium



Calcium

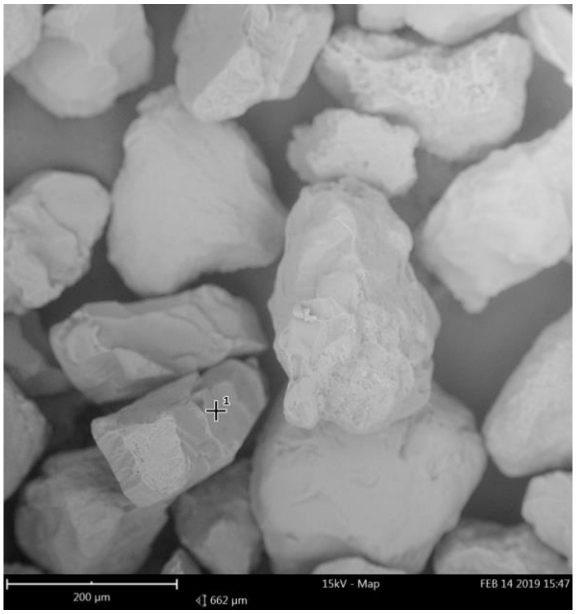


Aluminium



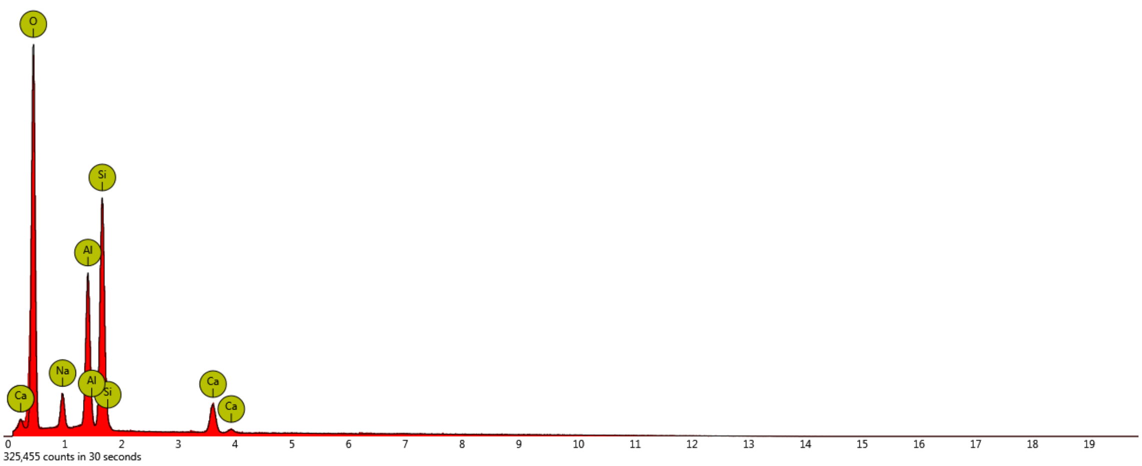
Annexe 3: SEM Analysis of the last sieve fraction of SEM-206 sample

Spot 1



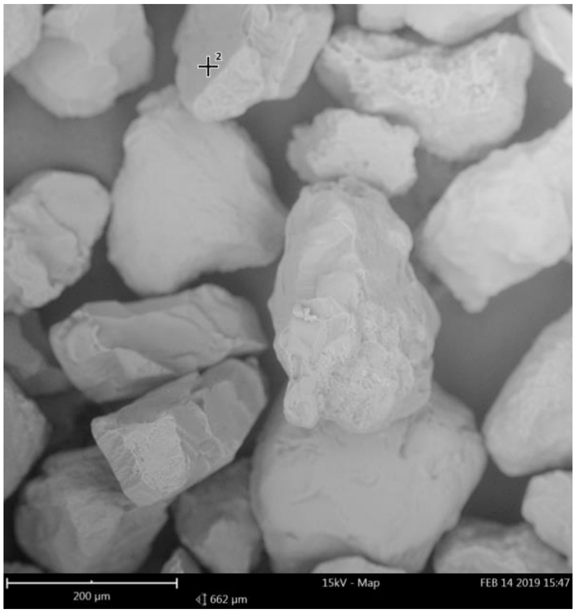
Element Symbol	Atomic Conc.	Weight Conc.	Oxide Symbol	Stoich. Conc.
O	74.20	62.30		
Si	12.21	18.00	Si	47.34
Al	8.28	11.73	Al	32.10
Na	3.55	4.28	Na	13.75
Ca	1.75	3.69	Ca	6.80

FOV: 662 µm, Mode: 15kV - Map, Detector: BSD Full, Time: FEB 14 2019 15:47



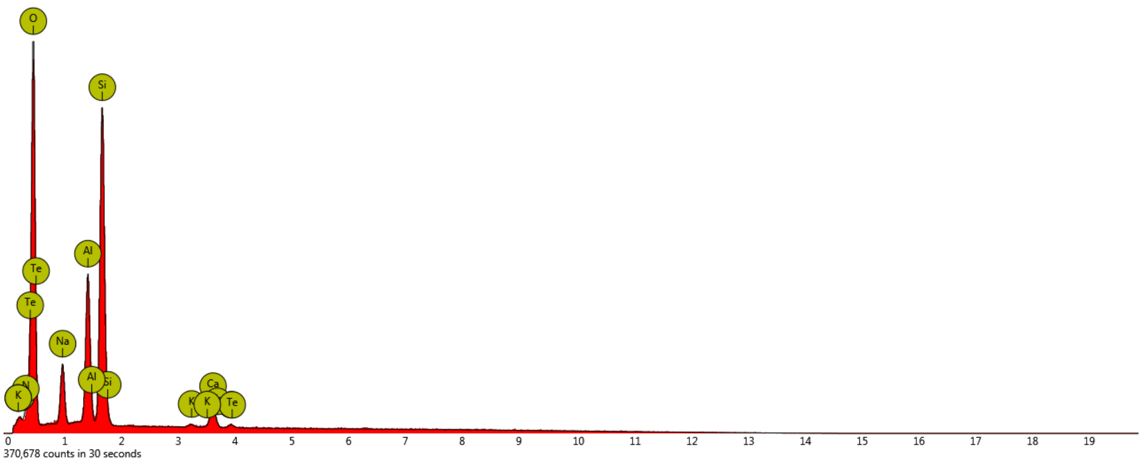
Disabled elements: B, N, Sb, Te

Spot 2



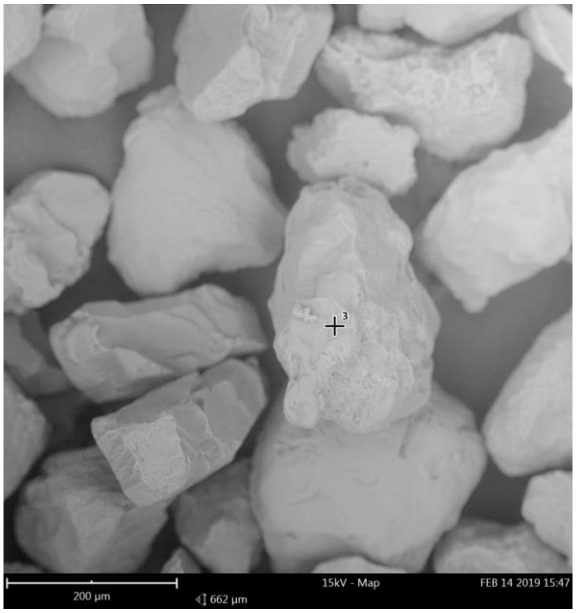
Element Symbol	Atomic Conc.	Weight Conc.	Oxide Symbol	Stoich. Conc.
O	66.50	57.79		
Si	11.65	17.78	Si	34.78
Al	5.86	8.59	Al	17.50
N	10.44	7.94	N	31.17
Na	4.50	5.62	Na	13.43
Ca	0.94	2.04	Ca	2.80
K	0.11	0.24	K	0.33

FOV: 662 µm, Mode: 15kV - Map, Detector: BSD Full, Time: FEB 14 2019 15:47



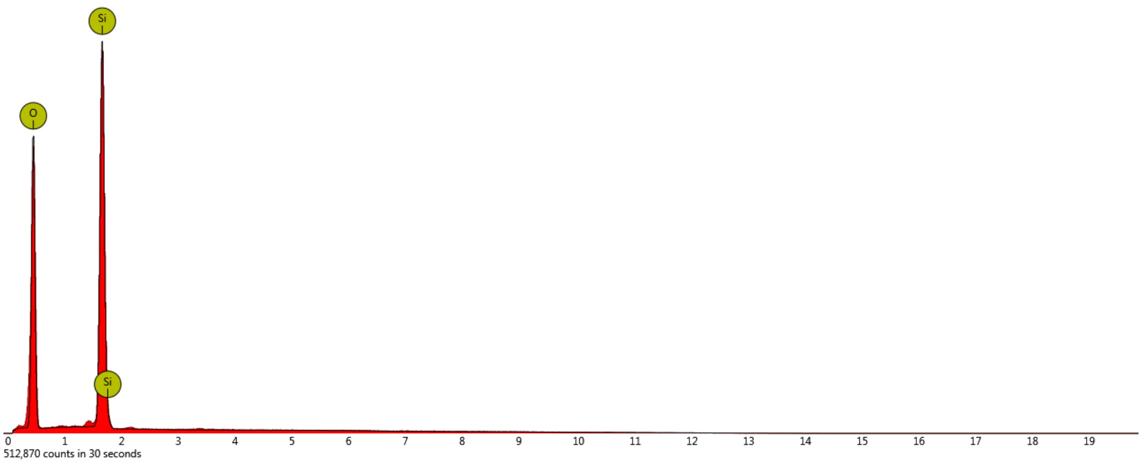
Disabled elements: B

Spot 3



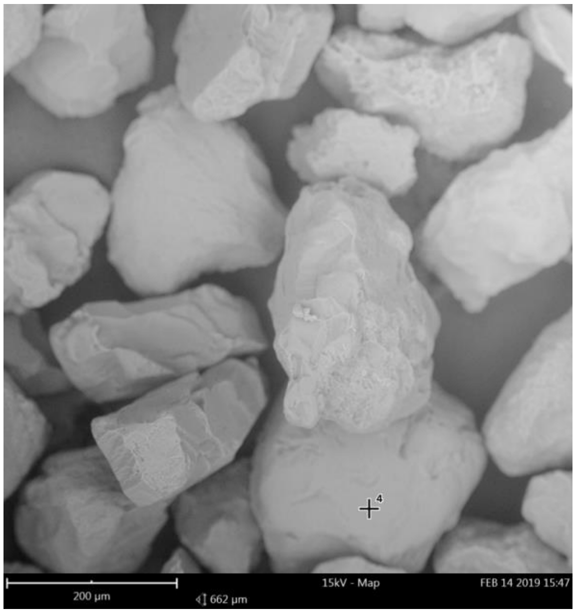
Element Symbol	Atomic Conc.	Weight Conc.	Oxide Symbol	Stoich. Conc.
O	76.79	65.33		
Si	23.21	34.67	Si	100.00

FOV: 662 µm, Mode: 15kV - Map, Detector: BSD Full, Time: FEB 14 2019 15:47



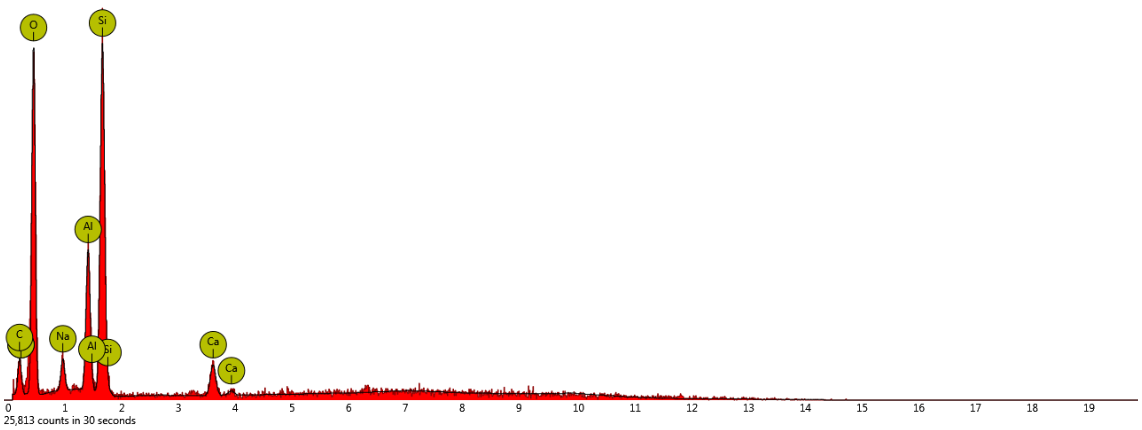
Disabled elements: B, N

Spot 4



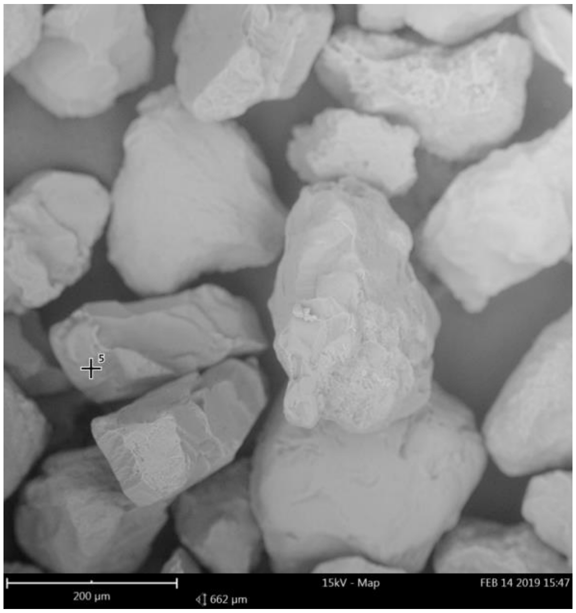
Element Symbol	Atomic Conc.	Weight Conc.	Oxide Symbol	Stoich. Conc.
O	57.33	53.67		
C	25.23	17.73	C	59.13
Si	10.00	16.44	Si	23.44
Al	4.38	6.92	Al	10.27
Ca	1.13	2.66	Ca	2.66
Na	1.92	2.59	Na	4.51

FOV: 662 µm, Mode: 15kV - Map, Detector: BSD Full, Time: FEB 14 2019 15:47



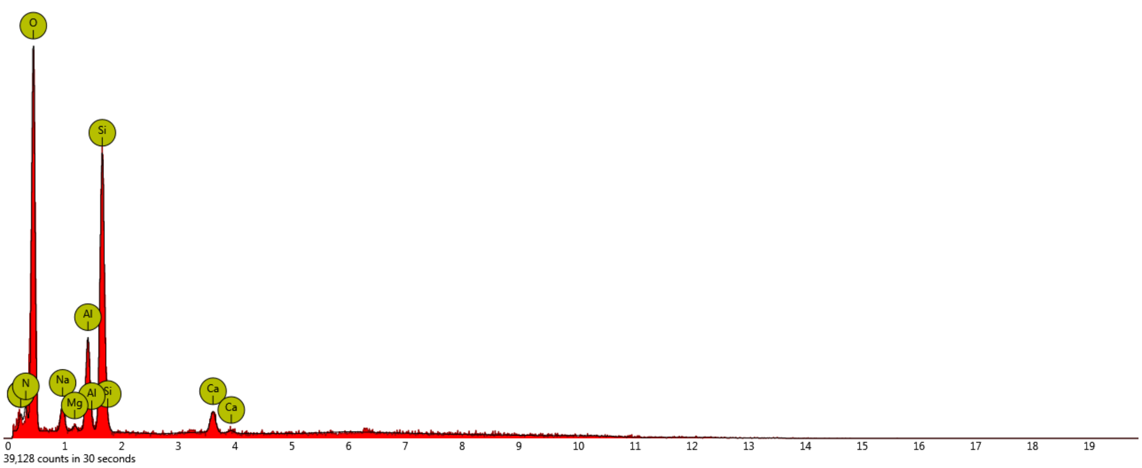
Disabled elements: B, Br, Gd, In, N, Sb, Te

Spot 5



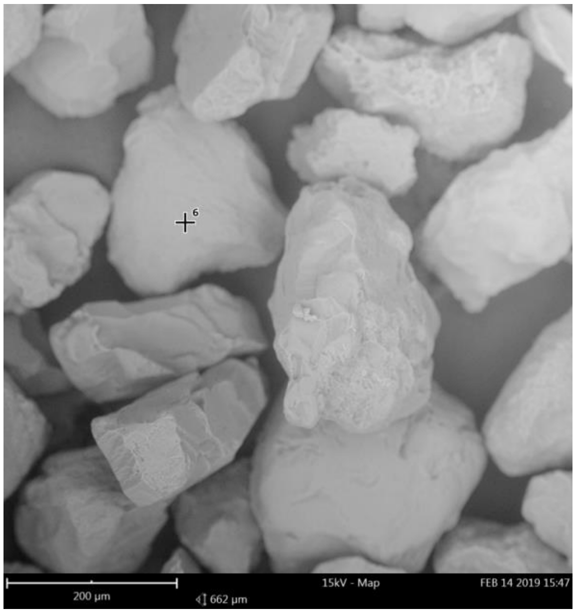
Element Symbol	Atomic Conc.	Weight Conc.	Oxide Symbol	Stoich. Conc.
O	70.13	62.92		
Si	10.20	16.06	Si	34.14
N	12.21	9.59	N	40.89
Al	3.86	5.84	Al	12.92
Na	2.31	2.98	Na	7.74
Ca	0.97	2.19	Ca	3.26
Mg	0.31	0.43	Mg	1.05

FOV: 662 μm, Mode: 15kV - Map, Detector: BSD Full, Time: FEB 14 2019 15:47



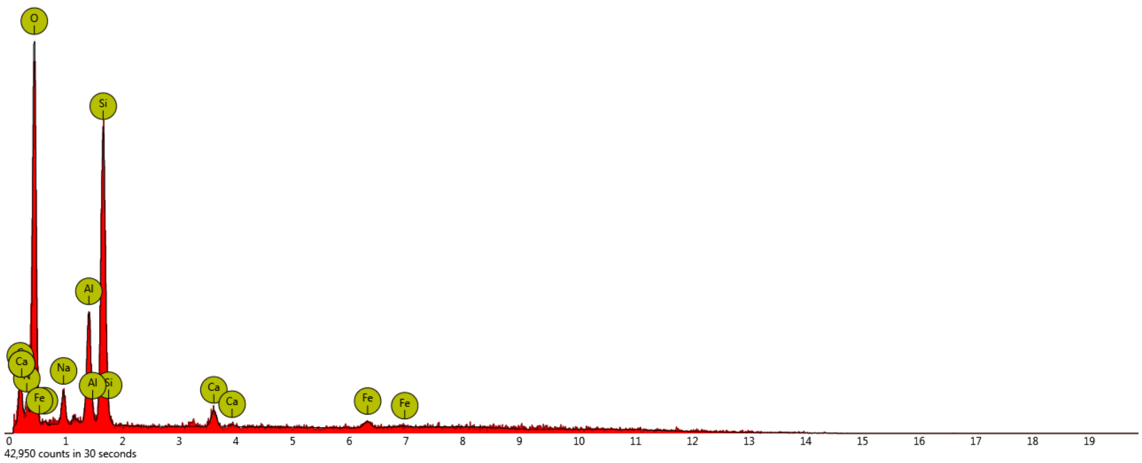
Disabled elements: B, Br, Cs, Sb, Te

Spot 6



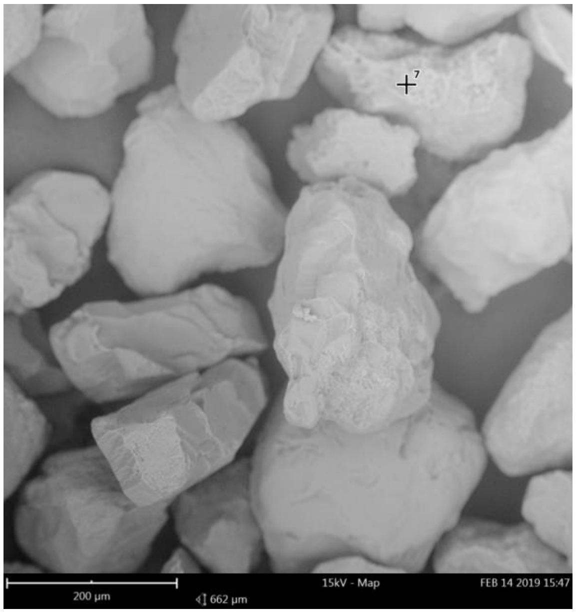
Element Symbol	Atomic Conc.	Weight Conc.	Oxide Symbol	Stoich. Conc.
O	55.59	54.17		
C	20.83	15.24	C	46.91
Si	6.40	10.95	Si	14.41
N	11.85	10.11	N	26.68
Al	2.74	4.51	Al	6.18
Na	1.67	2.33	Na	3.75
Fe	0.47	1.59	Fe	1.05
Ca	0.45	1.10	Ca	1.02

FOV: 662 µm, Mode: 15kV - Map, Detector: BSD Full, Time: FEB 14 2019 15:47



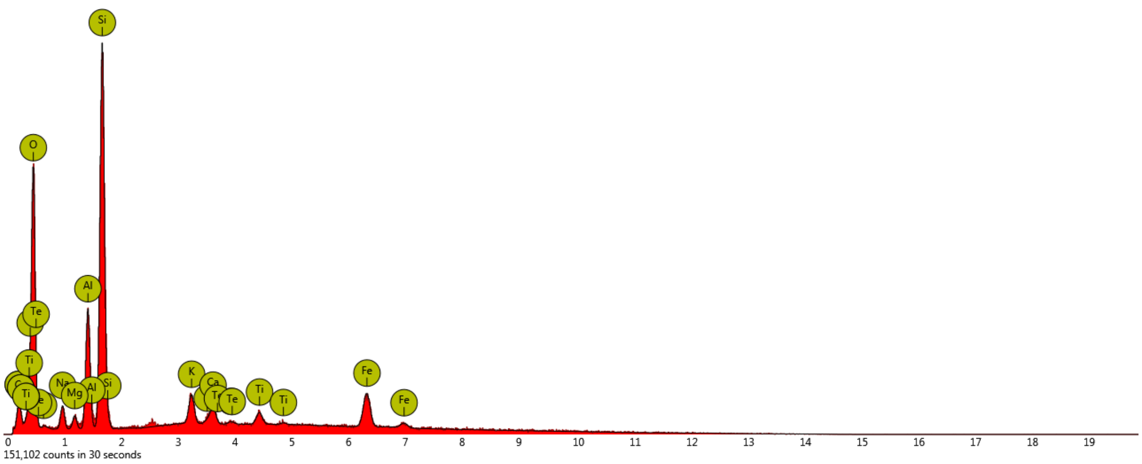
Disabled elements: B, Cs, Sb, Sn, Te

Spot 7



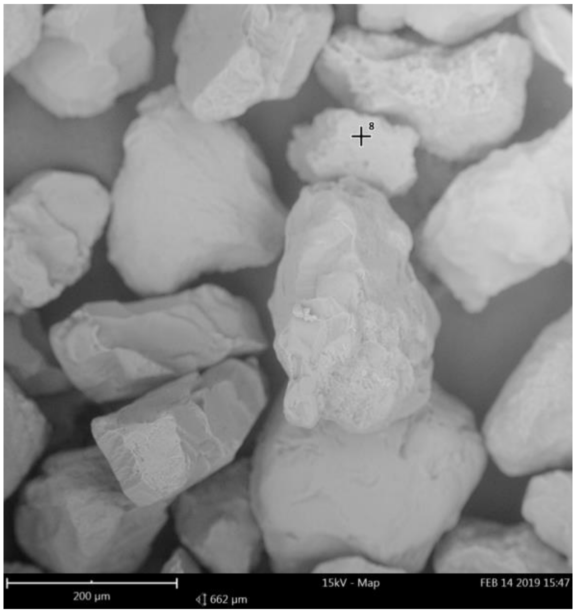
Element Symbol	Atomic Conc.	Weight Conc.	Oxide Symbol	Stoich. Conc.
O	62.15	44.76		
Si	19.32	24.42	Si	51.05
Fe	5.02	12.62	Fe	13.27
Al	6.45	7.83	Al	17.04
K	1.62	2.85	K	4.28
Na	2.47	2.55	Na	6.52
Ca	1.08	1.94	Ca	2.84
Ti	0.89	1.92	Ti	2.35
Mg	1.00	1.10	Mg	2.65

FOV: 662 µm, Mode: 15kV - Map, Detector: BSD Full, Time: FEB 14 2019 15:47



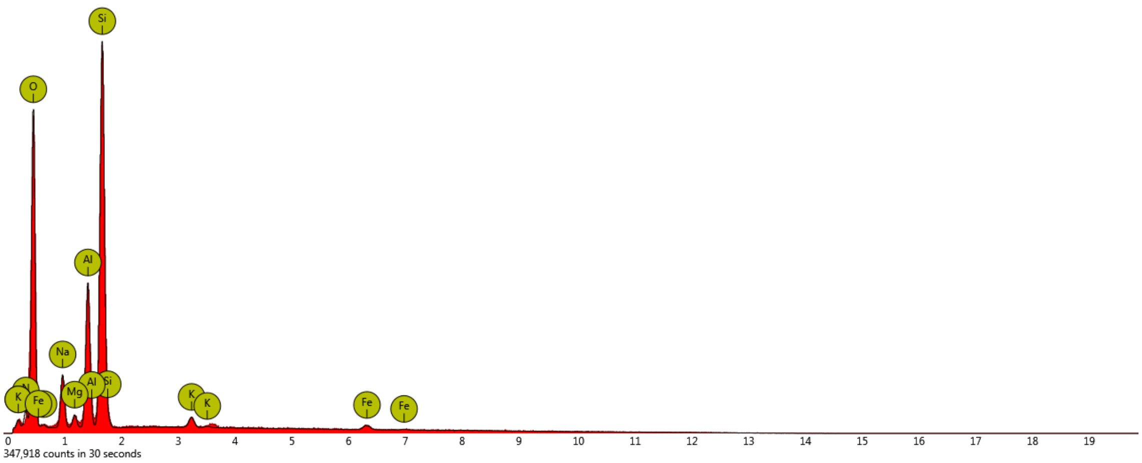
Disabled elements: As, B, Ba, Br, Sb, W

Spot 8



Element Symbol	Atomic Conc.	Weight Conc.	Oxide Symbol	Stoich. Conc.
O	62.26	52.35		
Si	15.53	22.92	Si	41.14
Al	6.14	8.71	Al	16.27
N	10.16	7.48	N	26.91
Na	4.15	5.01	Na	10.99
Fe	0.55	1.63	Fe	1.47
Mg	0.75	0.96	Mg	1.99
K	0.47	0.96	K	1.23

FOV: 662 µm, Mode: 15kV - Map, Detector: BSD Full, Time: FEB 14 2019 15:47

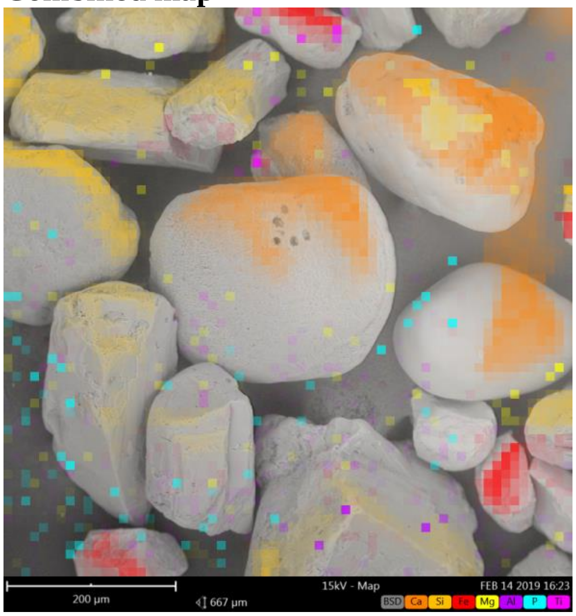


Disabled elements: B, Br, Sb

Annexe 4: SEM Analysis of the last sieve fraction of SYM-106 sample

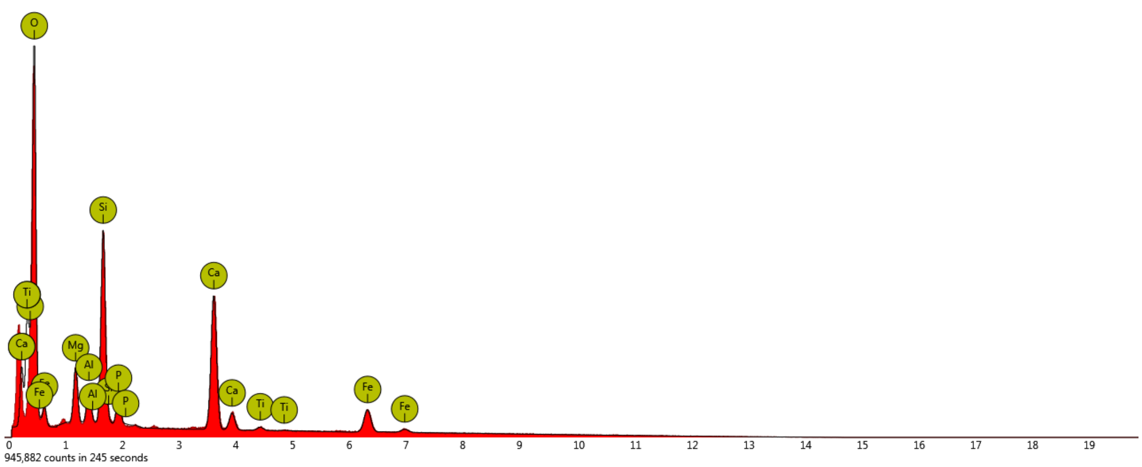
Map

Combined map



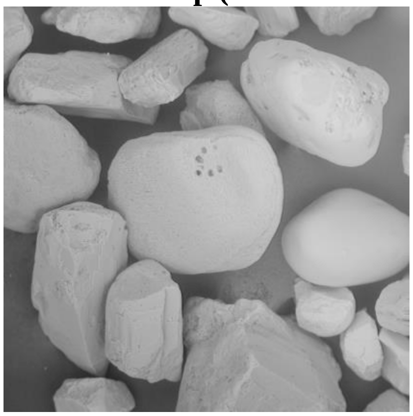
Element Symbol	Atomic Conc.	Weight Conc.	Oxide Symbol	Stoich. Conc.
O	75.88	59.45		
Ca	6.56	12.89	Ca	27.21
Si	7.86	10.81	Si	32.59
Fe	2.88	7.88	Fe	11.95
Mg	3.69	4.39	Mg	15.29
Al	1.74	2.30	Al	7.22
P	1.17	1.78	P	4.86

FOV: 667 µm, Mode: 15kV - Map, Detector: BSD Full, Time: FEB 14 2019 16:23

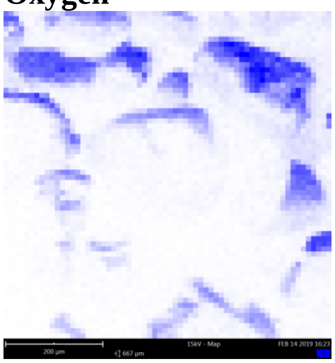


Disabled elements: B, C, N, Tb, Te

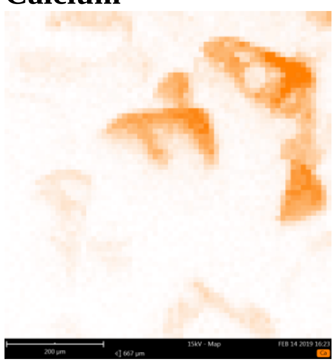
Cut out of map (resolution: 64x64 pixels)



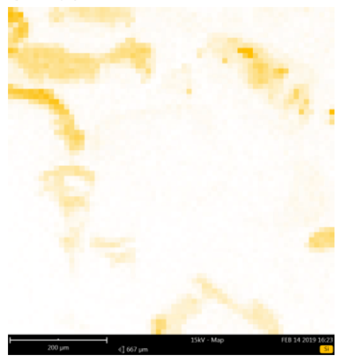
Oxygen



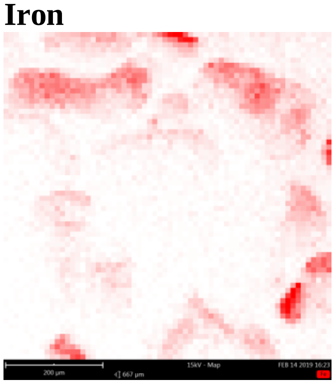
Calcium



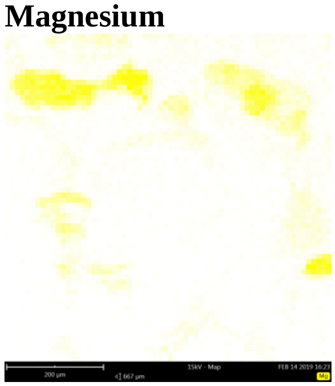
Silicon



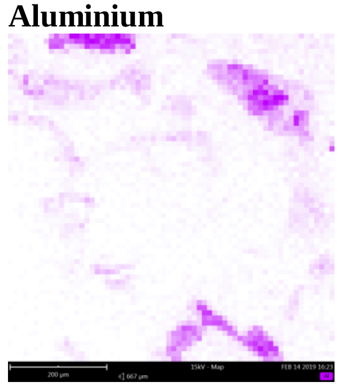
Iron



Magnesium



Aluminium



Phosphorus

Titanium

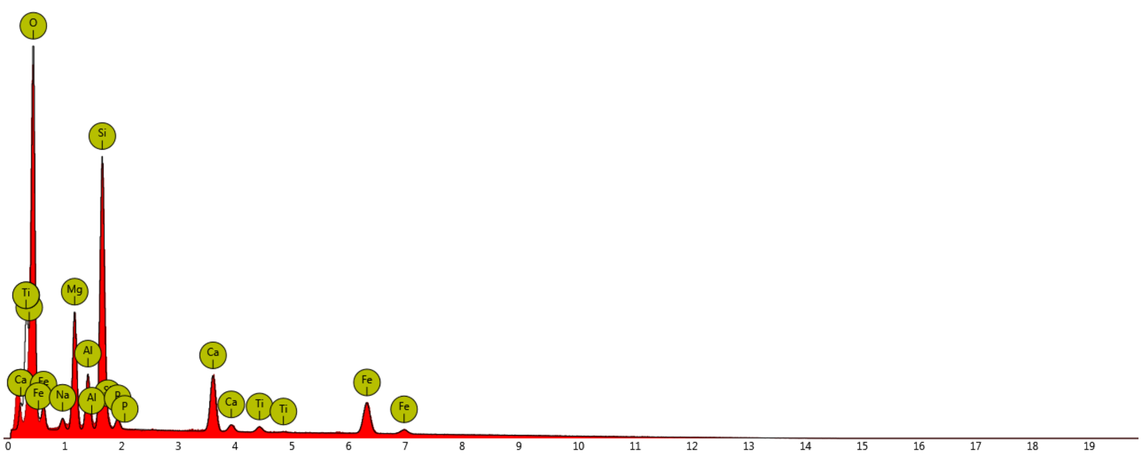
Annexe 5: SEM Analysis of SYM-106 sample recovered from sieve # 100

Map

Combined map

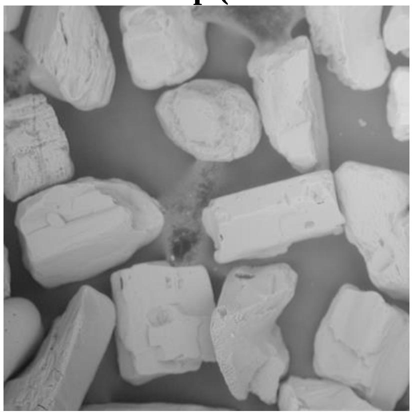
Element Symbol	Atomic Conc.	Weight Conc.	Oxide Symbol	Stoich. Conc.
O	67.65	51.33		
Si	12.40	16.52	Si	38.34
Fe	4.09	10.83	Fe	12.64
Mg	7.92	9.13	Mg	24.49
Ca	2.89	5.49	Ca	8.92
Al	3.01	3.86	Al	9.32
Na	1.11	1.21	Na	3.42
P	0.57	0.84	P	1.78
Ti	0.35	0.80	Ti	1.09

FOV: 667 µm, Mode: 15kV - Map, Detector: BSD Full, Time: FEB 14 2019 16:48

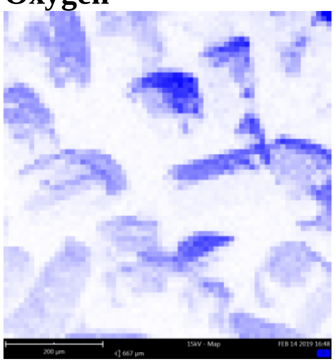


Disabled elements: B, C, Te

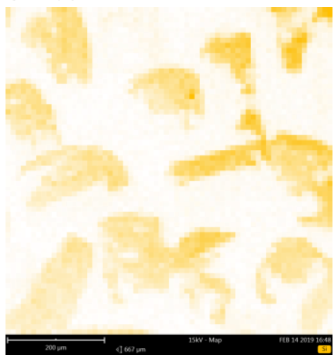
Cut out of map (resolution: 64x64 pixels)



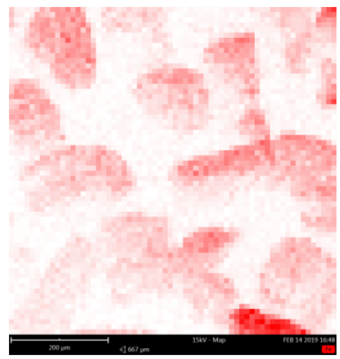
Oxygen



Silicon

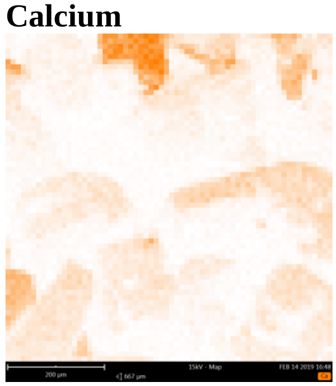


Iron

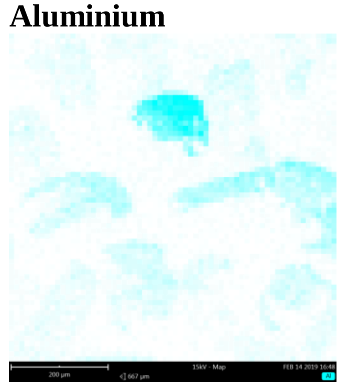


Magnesium

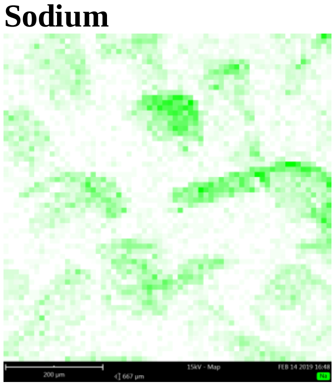
Calcium



Aluminium



Sodium



Phosphorus

Titanium