MINING LAB BEGINNINGS

IV Edition

CHALLENGES

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nexa

Theme: Circular Economy

CHALLENGE 1 New Applications for Aripuanã Tailings

Nexa has Circular Economy in its DNA, as evidenced by the projects developed at the Juiz de Fora unit, where waste recycling from other companies is carried out in the Waelz process for zinc recovery. In Vazante/Morro Agudo, where zinc concentrate is obtained, the co-products are Pb/Ag concentrates and zincal for soil acidity correction.

For this challenge, a solution is sought for the unit located in Aripuanã, where the focus is on mining, which transforms ore into zinc, copper, and lead concentrate. The ROM – "Run of mine," ore before beneficiation – has characteristics of a Volcanogenic Massive Sulfide (VMS) deposit, with a recurrence of carbonates and cherts (silica microcrystalline sedimentary rock, mainly formed by quartz).

The beneficiation of the ROM extracted from the mine must go through the following stages: comminution, flotation, thickening, and filtering. The following stages demonstrated in **Figure 1** will be described in a simplified manner.

I - The material is comminuted to achieve homogeneous particle size, preparing for the flotation stages where particle diameter is a relevant factor for the separation process of the desired metals. First, the ROM goes through a crusher, then through a SAG mill, and finally through a ball mill, where water is added to the process.

II - The first flotation aims to separate the part of the ROM containing talc (OF - overflow) from the part containing heavy metals (UF - underflow). The OF is directly taken to the thickener and then to the filter press. These two processes are responsible for the dry deposit of waste. The UF, rich in heavy metals, is directed to stage III.

III - In the second flotation, the material of interest is copper, which exits in the OF of the floatation present in stage III. To concentrate it, a thickener and a filter press are used. The UF generated in the floatation, containing other metals, is directed to stage IV.

IV - Here, the third flotation occurs, with the OF containing a higher concentration of lead, which also goes through the thickener and filter press to remove excess moisture from the material. The remaining UF goes to the third floatation, which will select zinc in stage V.

V - Finally, the material from the UF of the previous stage is also floated. In the floatation shown in V, the OF with a higher concentration of zinc is obtained, which is led to the next equipment that, as before, removes the moisture. The UF of this stage is the reject of heavy metals mixed in the thickener (VI) and containing the OF of talc. Thus, the UF of this thickener (VI) is taken to the filter press for the dry deposition of the reject.

It should be noted that the effluents generated in the overflow of all thickeners are directed to the treatment station, where part of the treated water is reused in the process or for other activities at the unit.

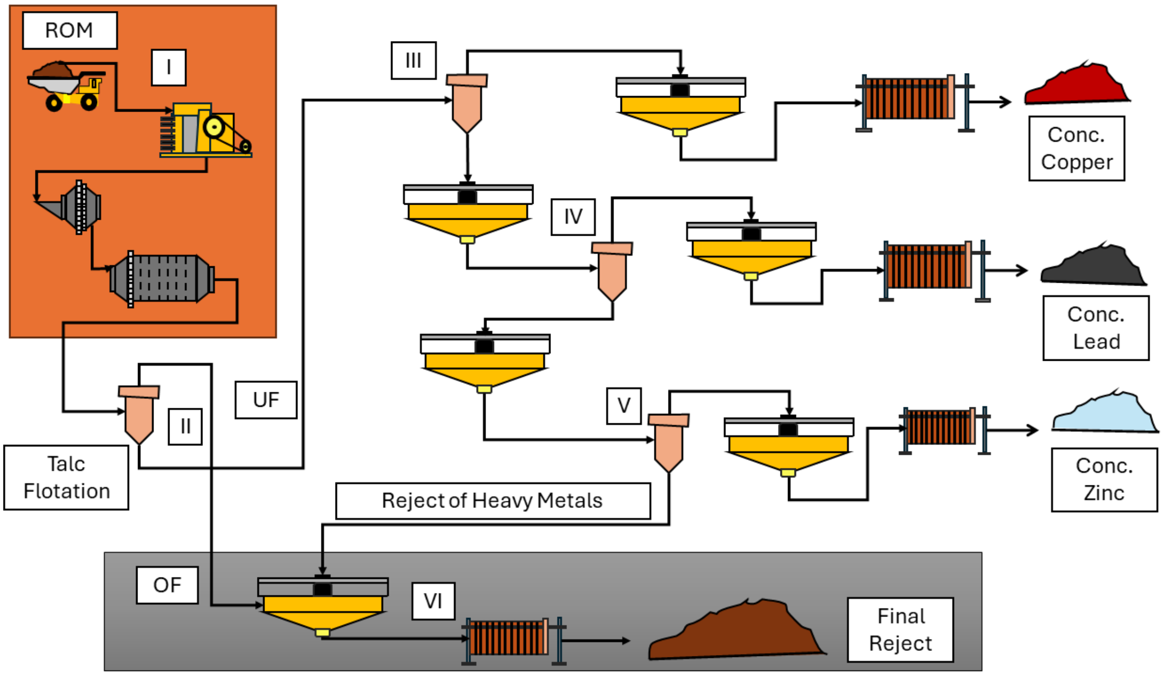

Figure 1: Simplified flowchart of Aripuanã.

The final residue generates approximately 1.9 Mt/year, with 90% of its mass composition coming from heavy metal rejects, and it has a moisture content between 15-20%. The mineralogical characterization of the talc flotation reject demonstrates that it is mainly composed of talc, galena, calcite, chlorite, tremolite-actinolite, and pyrrhotite. On the other hand, the heavy metal reject is predominantly composed of quartz, mica, calcite, chlorite, tremolite-actinolite, pyrrhotite, and dolomite. **Tables 1, 2,** and **3** show the approximate mineralogical and chemical composition of the residue generated in Aripuanã.

Table 1: Tailings from talc flotation overflow

Talc tailings	
Mineral	Approximate mass composition (%)
Talc	70
Galena	5
Calcite	2
Chlorite	2
Tremolite-actinolite	10
Pyrrhotite	2

Table 2: Tailings from the zinc flotation underflow

Reject of heavy metals	
Mineral	Approximate mass composition (%)
Quartz	40
Chlorite	14
Mica	10
Dolomite	10
Tremolite-actinolite	5
Pyrrhotite	2

Table 3: chemical composition of the final tailings

Chemical elements	Quantities
SiO_2 (%)	40-45
Fe (%)	10-14
Al_2O_3 (%)	7-10
Mg (%)	5-8
S (%)	3-5
Pb (%)	0,20-0,40
Cu (%)	0,20-0,40
Ag (ppm)	6-8
Cd (ppm)	20-50

Therefore, aligned with its ESG practices, Nexa is seeking to develop new treatment routes for the three types of tailings: the first, rich in talc; the second, obtained during zinc flotation, rich in quartz; and the third, a mixture of all process wastes, rich in silicon dioxide.

Difficulties and risks involved:

- Logistics - plant located in Aripuanã - Mato Grosso (MT) in Brazil;
- Consideration of the material's physical and chemical restrictions;
- Consideration of the problem of acid drainage that may exist due to the material's characteristics.

Theme: Circular Economy

CHALLENGE 2 New Applications for Pyrite Tailings

The Cerro Lindo Mining Unit (hereinafter referred to as "Cerro Lindo M.U.") is an underground polymetallic mine owned by Nexa Resources Peru S.A.A. (hereinafter referred to as "NEXA"), located in the Chavin district, Chincha province, Ica department, Peru, approximately 268 km southeast of Lima. It is situated at an average altitude of 1,825 meters above sea level. **Figure 2** shows the location of the Cerro Lindo Mining Unit.

Figure 2: Location of Cerro Lindo M.U.

Cerro Lindo M.U. develops mining exploration and mineral beneficiation activities, generating as rejected waste, mainly characterized by its significant content of pyrite, silicate, and to a lesser extent, barite.

Figure 3 shows the ore processing flow from the bulk flotation phase to the production of Cu, Pb, Zn concentrates, and final tailings.

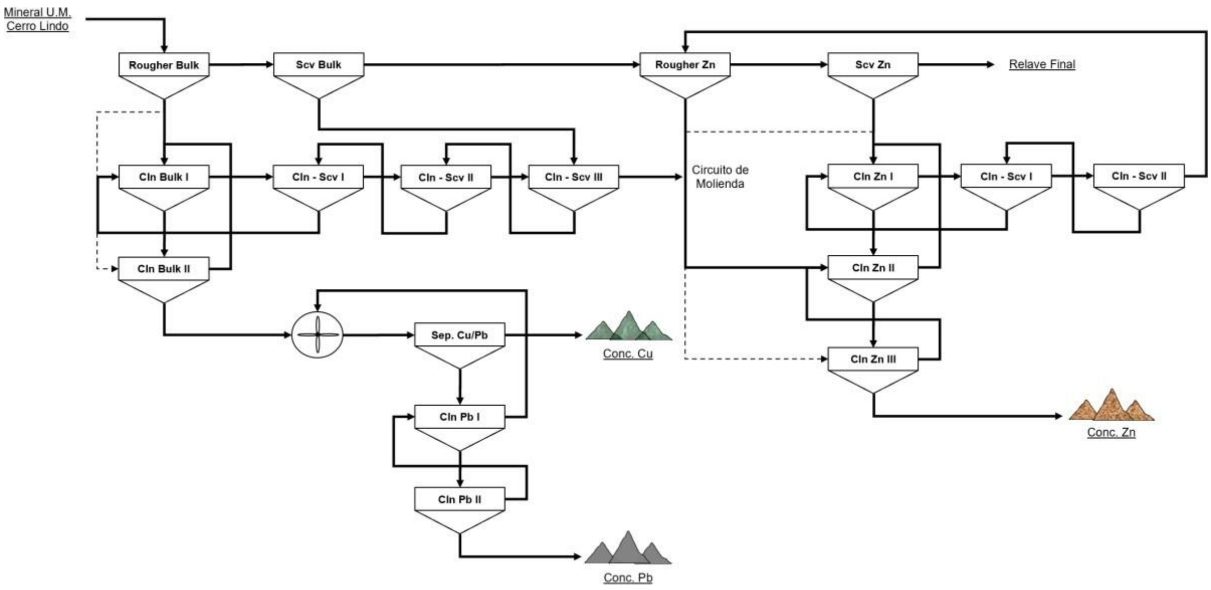

Figure 3: Process diagram of the Cerro Lindo M.U., flotation phase

The technology for disposing of the tailings is done dry, involving a thickening and filtration phase to achieve moisture levels ranging between 12% and 14%.

Approximately 50% of the filtered tailings are sent for application in mine backfill, with the remainder being deposited in piles[1]. These filtered tailings deposits (FTD) periodically require works to prolong their lifespan and ensure the continuity of the production process.

Figure 4: Pahuaypite II deposit, Cerro Lindo M.U.

Table 4 shows the chemical characterization of the main ore at the Cerro Lindo M.U, while Tables **5, 6**, and **7**[2] show the chemical characterizations of the tailings.

Table 4: Chemical analysis of the main ore at the Cerro Lindo M.U.

Flow	Oz/tn Ag	% Pb	% Cu	Zn	% Fe
Main ore	0.84	0.20	0.55	1.14	24.38

[1] Approximately 461 kt of tailings are generated monthly, of which 230 kt are deposited in the filtered tailings deposit (FTD).

[2] All chemical analyses presented refer to fresh tailings from the Cerro Lindo Mining Unit.

Table 5: Chemical analysis of the tailings at the Cerro Lindo M.U.

Flow	Oz/tn Ag	% Pb	% Cu	Zn	% Fe
Reject	0.21	0.05	0.06	0.1	24.90

Table 6: ICP-OES analysis for the tailings at Cerro Lindo.

Flow	Ag, ppm	Al, %	As, ppm	Ba, ppm	Be, ppm	Bi, ppm	Ca, %
Reject	4.0-8.0	3.0-5.0	50.0-80.0	350.0-380.0	0.5-0.8	<5	0.4-0.7
Flow	Cd, ppm	Co, ppm	Cr, ppm	Cu, ppm	Fe, %	Ga, ppm	K, %
Reject	2.0-6.0	0.4-0.6	110.0-140.0	650.0-690.0	>15.0	<10	0.5-2.0
Flow	La, ppm	Mg, %	Mn, ppm	Mo, ppm	Na, %	Nb, ppm	Ni, ppm
Reject	<0.5	0.4-0.7	350-380	2.0-5.0	0.3-0.7	<1	9.0-13.0
Flow	P, %	Pb, ppm	S, %	Sb, ppm	Sc, ppm	Sn, ppm	Sr, ppm
Reject	0.01-0.05	560.0-580.0	>10.0	18.0-24.0	2.0-5.0	<10.0	60.0-90.0
Flow	Ti, %	Tl, ppm	V, ppm	W, ppm	Y, ppm	Zn, ppm	Zr, ppm
Reject	0.02-0.06	5.0-8.0	40.0-50.0	<10.0	2.0-5.0	700.0-1000.0	20.0-30.0

Table 7: X-ray diffraction for the tailings at the Cerro Lindo M.U.

Mineral name	General formula	Results approximate (%)
Pirite	FeS2	46
Quartz	SiO2	
Mica (moscovite)	KAl2 (Si3 Al)O10 (OH,F)2	
Plagioclase (Oligoclase)	(Na,Ca)(Al,Si) O48	10
Clorito (Clinochore)	(Mg,Fe)5 Al(Si3 Al)O10 (OH)8	
Feldspar- K (Ortoclásio)	KAlSi O38	
Barite	BaSO4	
Mica (Biotite)	K(Mg,Fe)3 [AlSi O310 (OH,F)]2	
Gesso	CaSO4 .2(H2 O)	<L.D.
Calcite	CaCO3	<L.D.
Andaluzia	Al2 SiO5	<L.D.

Aligned with the company's environmental, social, and governance (ESG) objectives, where circular economy is considered one of the fundamental pillars, NEXA is seeking solutions for the use of the tailings from the Cerro Lindo basin, whose main component is pyrite.

I. Utilize the tailings or pyrite directly as raw materials for industrial applications;

II. Package the tailings or pyrite, through hydrometallurgical, pyrometallurgical, or other treatment, so that they can be used as raw materials in an industrial application.

Previous work:

Nexa has been seeking solutions for the reuse of pyrite within the circular economy framework. The solutions that have been worked on are:

- **Treatment of industrial effluents through the application of pyrite as an adsorbent for heavy metals from flotation tailings:**

With the aim of reusing pyrite, considering its adsorptive characteristics, tests were carried out to create a new product based on pyrite (a formulation of pyrite with activated carbon) for the adsorption market. The proof of concept was carried out for a synthetic effluent (containing a mixture of Cu^{2+}, Zn^{2+}, and Mn^{2+} ions) and for a Nexa effluent. From the results with the synthetic effluent, it was concluded that the formulation (pyrite/activated carbon (AC)) at pH 9 can remove up to 99% of copper and zinc when together and up to 42% of manganese, present in the synthetic effluent.

The results obtained so far are encouraging, demonstrating the feasibility of the formulation (pyrite/AC) for the treatment of industrial effluents and the identification of suitable conditions for its implementation. However, further tests are needed to demonstrate the stability of the formulation during the treatment of other effluents.

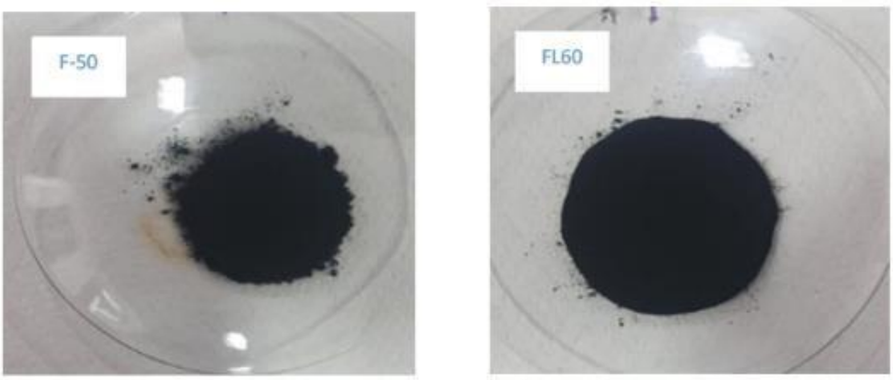

Figure 5: Formulation of pyrite with activated carbon, types F50 and F60

- **Iron Salts:**

The objective is to reuse the pyrite from the tailings to produce ferric sulfates. The project development began with the chemical evaluation of pyrite (FeS_2) for its conversion into pyrrhotite (FeS), followed by hydrothermal synthesis tests using the precursor pyrrhotite (FeS) to obtain iron salts such as heptahydrated iron (II) sulfate ($FeSO_4.7H_2SO_4$), iron (III) bromide ($FeBr_3$), iron (III) chloride ($FeCl_3$), and lithium iron phosphate ($LiFePO_4$).

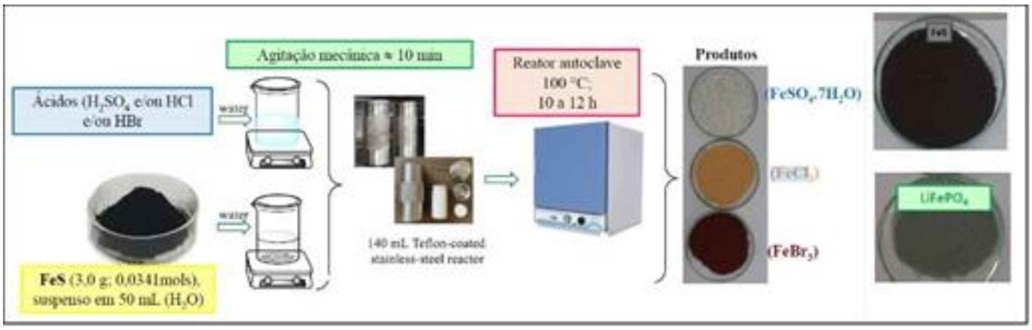

Figure 6: Process of obtaining iron salts from the pyrrhotite precursor (FeS) and different inorganic acids

This is the challenge of Mining Lab Beginnings 2024! We are looking for innovative solutions that allow the reuse of the rejects from U.M. Cerro Lindo, turning it into a viable input for creating a new marketable product, thus promoting its reuse within the circular economy. We are looking for proposals that add value, as well as other strategies that improve the previously studied work.

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Theme: Decarbonization

CHALLENGE 3

Production of bio-briquettes

The Nexa is a company that operates in the zinc production, from mineral exploration to the production of metallic zinc. Its units are in Brazil and Peru and are divided between mines and smelters (refineries). In the refineries, there is the receipt of ore and other raw materials used to produce metallic zinc and its derivatives. In addition, there is the need for consumption of gaseous, liquid, and solid fuels. Among the solid fuels is the bio-briquette of charcoal. Such material provides part of the energy and carbon necessary for the zinc recovery process. This is a pyrometallurgical step called the Waelz process. In this process, the zinc-containing raw material is fed with solid fuel, coarse coke, for heating and reduction reactions at temperatures close to 1100 °C.

The process is based on the reduction of the ore/waste and the volatilization of zinc and other substances. The final solid material that does not volatilize, the slag, is cooled at the furnace outlet and discarded. The gases containing Zn are directed by depression in the furnace to a treatment system, where they are cooled for solidification of the material and subsequent capture in bag filters. The recovered material is the Waelz oxide (rich in zinc and lead).

The furnace is divided into five distinct sections, where the charge (called mix or blend) passes through treatment zones to its reaction zone. They are: Wet Zone or Material Drying, Preheating and Combustion Zone, Pre-reaction Zone, Main Reaction Zone, and Slag Outlet Zone.

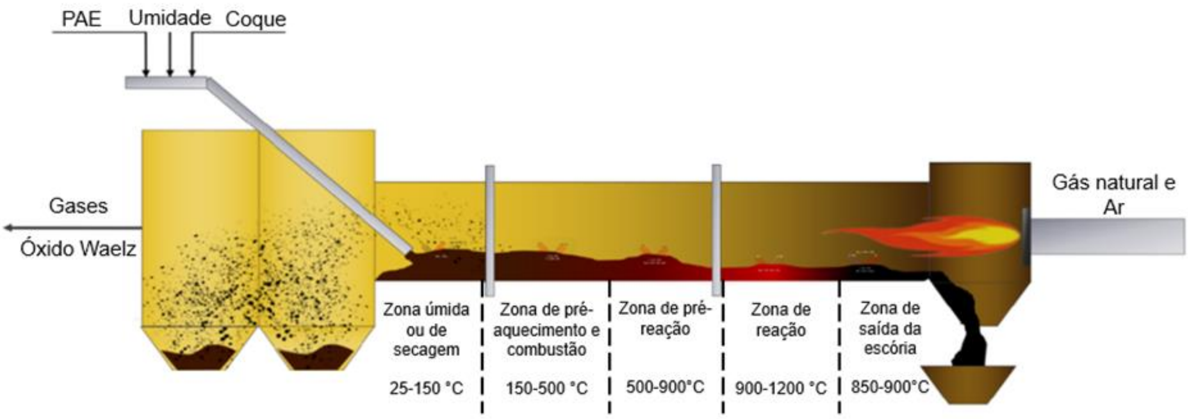

Figure 7: Waelz Furnace

The Wet or Material Drying Zone is the initial section of the Waelz furnace, where steel mill dust (SMD) and coke are introduced. This zone is characterized by its higher moisture content, as the materials may contain water or other volatile components. The drying zone serves to remove the moisture from the raw material and prepare it for further processing. The increase in temperature of the solid charge comes from contact with the heated gases coming from the hotter zones of the furnace. The temperature in this zone rises from 25 to 150 °C.

After passing through the Wet Zone, the raw material enters the Preheating and Combustion Zone. In this section, the raw material is gradually heated by hot gases generated by the combustion of fuel from the hotter zones. The preheating process raises the temperature of the materials, allowing them to reach the desired reaction temperature for subsequent steps. The temperature in this zone rises from 150 to 500 °C.

The Pre-reaction Zone follows the Preheating and Combustion Zone and is where the partially heated raw material undergoes thermal and chemical transformation. Halogens and some salts begin to volatilize due to the temperature being above 500 °C. In this zone, volatile components, such as organic compounds, are eliminated, while materials containing iron and zinc begin to react with the carbonaceous material present. This pre-reaction stage prepares the raw material for the main reaction in the subsequent zone. The temperature in this zone rises from 500 to 900 °C.

The Reaction Zone is the main region of the Waelz furnace, where the main chemical reactions occur. Here, the high temperatures facilitate the reduction of zinc oxide to metallic zinc. Iron oxides are largely reduced in this stage. The carbonaceous material and CO act as reducing agents, reacting with zinc oxide to produce zinc vapor. Other materials, such as lead and cadmium, may also volatilize or form stable compounds. The temperature in this zone rises from 900 to 1200 °C.

The final section of the Waelz furnace is the Slag Discharge Zone. After the main reactions in the Reaction Zone, the remaining materials, including non-volatile impurities and solidified slag, are discharged from the furnace. At this stage, all reduction reactions are completed and there is reoxidation of iron. The air entering the furnace receives a lot of energy from the reoxidation reactions and from the slag for temperature increase. The slag leaves the furnace at a temperature between 850 and 900 °C.

Aligned with ESG practices, Nexa has been seeking biogenic fuels to replace coarse coke in the Waelz process. A promising alternative is bio-briquettes, which can be produced from these biogenic residues. However, developing new biogenic fuels for the Waelz process is quite challenging, due to the inherent characteristics of the process and the fuel used, listed below, and maintaining process efficiency.

<u>Characteristics of the Waelz Furnace:</u>

- Furnace Length
- Rotation
- Inclination
- Reaction Zones
- Zn Feed
- Zn in the Slag
- Metal Yield

<u>Fuel Characteristics:</u>

- High fixed carbon content
- Calorific value
- Fuel reactivity
- Mechanical strength

Over the past few years, Nexa has developed the bio-briquette as a solution for processing the coal for its feeding. This briquette is composed of ground charcoal agglomerated with tar. The production involves the mixing, briquetting, and curing stages of the material to ensure fixed carbon and hardness.

This is the challenge of Mining Lab Beginnings 2024: new suggestions to produce alternative bio-briquettes. Such briquette needs to have thermal resistance (be less reactive to provide energy and carbon at 900-1000 ˚C). Additionally, it needs to have high compressive strength compared to coke to withstand rotation and the first zones of the Waelz furnace.

The bio-briquette was developed to have the characteristics presented in **Table 8.**

Table 8: Characteristics of coarse coke and bio-briquette

Insumes	Fixed Carbon (%)	Volatiles (%)	Ashes (%)	Humidity (%)	Sulfur (%)	LCV (Gcal/t)	Mechanical Strength (kgf)
Coke	90,7	9,3	1,4	12,8	6	8,2	20,4
Bio-briquette	70,0	28,3	1,7	1,6	0,034	7,12	19,3

New biomass sources and binders can be analyzed.

Suggested binders: Water, Dextrin, Starch.

Suggested biomass: Vegetable peels (coffee, rice), sugarcane bagasse.

Considerations:

In addition to technical aspects, other factors should be evaluated in the development of solutions, such as:

- Cost feasibility of the proposed bio-briquette production;
- Logistics, availability, and supply of raw materials for energy input production;
- Consider possible adjustments in the existing process that may be necessary;
- Regulations for the transport, storage, and handling of solid fuels.

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Theme: Decarbonization

CHALLENGE 4

Reducing the corrosive effect of bio-oil

ZnO, a white chemical compound widely used in the production of paints, pharmaceuticals, ceramics, among others, is produced by Nexa. The process is based on the volatilization of metallic Zn and oxidation of the formed vapors, as described in **Equation 1.**

$$Zn + \frac{1}{2}O_2 \rightarrow ZnO$$

Equation 1: Zinc oxide synthesis.

The zinc oxide production process consists of 47 crucible-type furnaces, as shown in **Figure 8**, arranged in four batteries as shown in **Figure 9**. In this type of furnace, the material to be heated does not come into contact with the combustion gases. The flame formed by the combustion surrounds the entire crucible, and the combustion gases generated are removed through the furnace chimney, while the material to be vaporized is isolated inside the crucible. The internal temperature in the combustion chamber can reach over 1,200°C. The oxide is formed by the reaction of zinc vapor with the oxygen present in the ambient air and is captured by two dust removal circuits (primary and secondary), and then retained in bag filters. The energy not directly used for the volatilization of metallic zinc is dissipated to the atmosphere, and the fuel oil currently used is mainly fossil fuel.

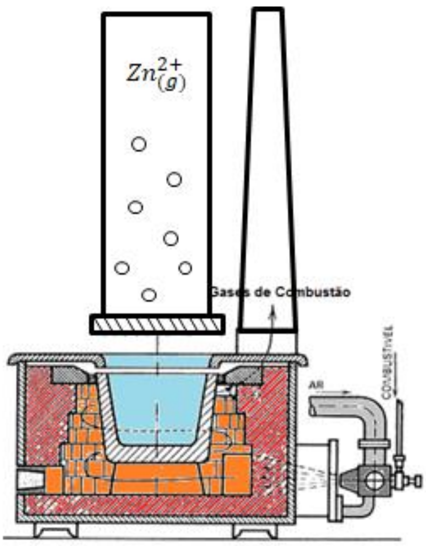

Figure 8: ZnO production furnace

Figure 9: Battery of zinc oxide production furnaces

Nexa, as part of its strategy, is always seeking new partners and opportunities to diversify its energy matrix, testing new alternative oils and aiming for a more efficient, sustainable, and safe operation. One of the fuels used as an alternative is bio-oil.

Bio-oil is the liquid fraction of fast pyrolysis (<2 seconds) of biomass in a reactor at an average temperature of 500°C (thermal degradation). The pyrolytic gases that exit along with the particulate matter (charcoal or bio-char) pass through a cyclone (solid recovery = bio-char). The clean gases without charcoal are passed through a condenser for the precipitation of the liquid fraction of the pyrolytic smoke, this liquid fraction divides into two, a light one (short chains) and a heavy one (heavy chains).

Crude bio-oil is composed of more than 200 chemical components, generally, oxygen-rich hydrocarbons with short chains - carboxylic acids, alkanes, alkenes, and heavy chains equivalent to mineral oils (olefins and paraffins). The high oxygen content in its chemical formulation implies two basic characteristics:

- **Acidity -** It has a low pH requiring storage, pumping, and distribution facilities using stainless steel;

- **Stability -** With increasing temperature, the lighter components tend to volatilize at temperatures below 100°C and allow reactions that generate other chemical compounds. Therefore, the oil should be stored and used at temperatures below 90°C.

For this challenge, proposals are expected to involve one of the two technological routes mentioned below and/or an additional measure to meet Nexa, namely:

- **Route 1: Pyrolysis plant** - install a fast biomass pyrolysis plant using eucalyptus chips to generate bio-char and bio-oil. The former can be used in the Waelz furnace at Nexa Juiz de Fora unit. The crude bio-oil, after distillation, is divided into heavy and light bio-oils. The one with heavy characteristics, after blending, is sent to the zinc oxide factory. And the light bio-oil, after distillation, is transformed into pyroligneous liquor and can be sold to the agricultural market as herbicide, fungicide, or can be processed to become liquid smoke for the food industry;

- **Route 2: Use of vegetable tar from the steel industry -** Minas Gerais is the world's largest producer of charcoal. The main use of this coal is for reducing iron oxide in blast furnaces, with the main hub being the city of Sete Lagoas. In the charcoal-making process, horizontal masonry retorts are traditionally used, which may or may not have multiple units connected by masonry galleries to a chimney where the pyroligneous gases are burned or discharged directly into the atmosphere. Part of these gases can be recovered by centrifuges at the base of the chimneys, liquefying into vegetable tar. In the underground galleries, there is also smoke settling, forming tar that can be pumped. The charcoal-making process is technically considered as slow pyrolysis at low temperature (350˚C);

- **Additional Measure -** presentation of new possibilities for separating fines present in the bio-oil currently used.

Henceforth, we will use the term bio-oil (See **Figure 10**) for both fast pyrolysis oil and charcoal from carbonization (slow pyrolysis) considering the addition of ethanol aiming at improving viscosity and pH.

Figure 10: Fast pyrolysis bio-oil from biomass

In both processes, a distillation and filtration step can be included to improve the quality of the input. The transformation of this substance into bio-oil, as seen, involves two stages: filtration and ethanol addition.

The main characteristics of bio-oil are seen in Table 9, where it is possible to compare its properties with respect to the two petroleum-derived fuels currently used in the production process. Results of laboratory analyses at the Energy and Fuels Laboratory (LEC) at UFMG.

Table 9: Characteristics of bio-oil and petroleum-derived oils

		Bio-oil	BTE	BPF
Elemental Composition		APERAM/WT	BRASKEM	PETROBRAS
C	%	56,5	81,6	77,1
H	%	6,6	12,3	18,2
O	%	35,8	0,0	2,8
N	%	0,4	1,5	1,9
Others	%	0,9	0,3	0,0
Sulfur	*mg / kg*	0,170	0,610	5,787
Humidity	*%*	11,8%	0,12%	
Density	*kg / m3*	1.150	1.064	1.014
Lower Heating Value	*kcal / kg*	5.409	9.200	9.650

Routes studied:

Since 2018, Nexa's Energy Innovation Management has been developing an R&D project called Industrial Tests at Battery IV using bio-oil with samples of various fuel characteristics such as water content, ash content, calorific value, additive content, and viscosity.

For this purpose, a combustion skid was used that has monitoring and control of temperature (oil, air, and chimney), pressure (oil and air), flow measurement (oil and air), heating resistors in oil tanks and lines, and cold and hot oil storage tanks.

Type of bio-oil: Bio-oils made from eucalyptus biomass were tested, such as:

- **Crude bio-oil** - Oil with light and heavy fractions from fast biomass pyrolysis, without additives;
- **Distilled bio-oil** - Oil distilled at 200°C, removing water and concentrating heavy components (more carbon and hydrogen) and higher calorific value, but with more viscosity. It can be additivated;
- **Additivated heavy bio-oil** - Heavy fraction of bio-oil without distillation additivated.

The option chosen in the tests is to use the additivated heavy bio-oil. This fuel is currently in operation in a productive battery identified as number IV of the factory. Its operation involves heating the bio-oil, transporting it in pressurized pipelines, and mixing it with atmospheric air at a minimum air pressure of 800mmca.

The Mining Lab Beginnings challenge involves developing solutions that reduce the corrosive effect of the biofuel and allow the use of equipment made of or coated with carbon steel. Additionally, new possibilities for separating fines present in the bio-oil may be evaluated as an additional measure.