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ANALYSIS OF THE THERMAL PROPERTIES OF THE SODIUM AND POTASSIUM NITRATE AS HEAT EXCHANGER IN A HELIOTHERMIC POWER PLANT

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Abstract. *The search for renewable energy sources is increasing in the world today. With the aim of reducing the emission of polluting gases, government legislation and research institutes have begun to invest in the development of technologies for such alternative energy sources. Among alternatives, heliothermic or Concentrated Solar Power (CSP) technology shows great potential for clean energy generation. The present study will analyze a mixture of Sodium Nitrate (NaNO_3) and Potassium Nitrate (KNO_3) used by the solar power plant, called Gemasolar for energy generation and storage. Several analyses of the salts were accomplished melted at the laboratory, at different temperatures, in order to know how long it takes for the composition to pass for the heat receiver and to be totally in a liquid state. Besides, we analyzed the temperature ranges to which the solution presents better thermal and electrical conduction, as well as the values at which these properties are lost. With the obtained results it was possible to know that the temperature range at which the salts remain in the liquid state is 260 to 800 °C, and the range which presents the best thermal conductivity is around 500 to 600 °C this is the ideal temperature range to be applied in the heliothermic plant.*

Keywords: *solar, thermal fluid, Concentrated Solar Power, heat capacity of the salt, thermal conduction.*

1. INTRODUCTION

Solar energy is a very important thing these days, especially with global warming from fossil fuels, which in turn is a non-renewable fuel. With that, create a solar power plant that is capable of generating energy 24 hours a day and 7 days a week, even in times of darkness.

A solar power plant called GemaSolar, located in Andalusia, Spain is the first to reach the goal, producing energy even in the absence of sunlight. The project is pioneering and uses molten salt to keep the turbines running after dark.

There are 2,650 large mirrors, a receiver of heat in the top of a central tower of 450 meters to a temperature of 600 degrees Celsius [°C] that can supply energy for 27.500 families in the south of Spain and to generate economy of more than 30 thousand tons of carbon dioxide emissions (MATTOS, 2011).

Gemasolar can operate for 15 hours, without receiving any solar energy, thanks to its storage system. In the summer, there are many days with enough radiation to operate during the day and fill the storage system to the upper limit. Under these conditions, it operates 24 hours, day and night, at full power. Already in winter, the days are shorter, so most of the time the storage system is not complete by the end of the day. For this, we have the option of reducing the capacity of the turbine at night to adjust the amount of electricity supplied depending on the demand. This storage system allows the plant to increase their hours of electric production for besides the sunset, independently of the covering of clouds (FONSECA, 2014).

Due to the storage system, the turbine operation is not affected immediately by any cloud or wind. The secret behind that plant that does with that the energy continues being generated by 24 hours comes from the storage of the melted salts, initially the cold fluid is sent to the receiver where it will warm up to temperatures reaching 900 °C, then it is taken to the tanks (responsible for storing and maintaining the heat capacity of the salt) which fills to the maximum and as there is need for electricity generation the fluid is pumped to the heat exchangers. The already superheated salt tank is fired and sent to a heat exchanger, as shown in figure 1, which is filled with water generating a non-toxic vapor which activates the generator of a turbine, meanwhile the rest of the unused heated salts is stored in the tanks so that it can activate the turbines when needed. The molten salt consists of 60 % of potassium nitrate (KNO_3) and 40 % of sodium nitrate ($NaNO_3$), which makes the plant generate energy for 15 hours without any sunlight.

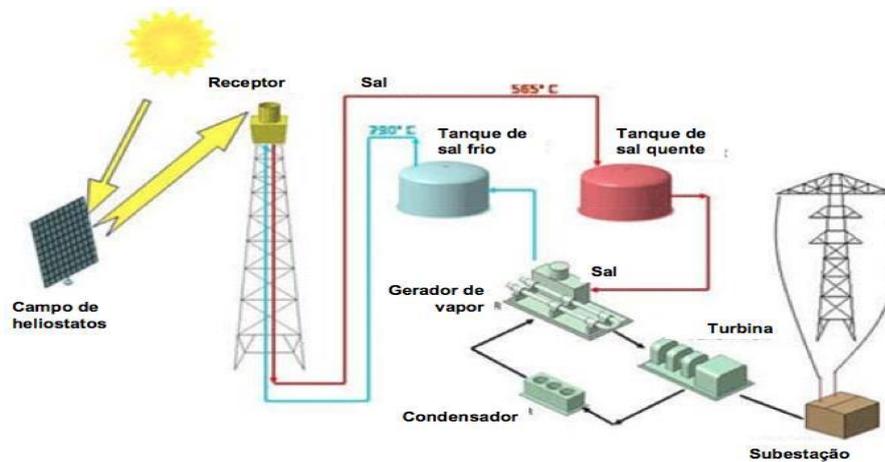


Figure 1- Illustration of a CSP plant with two tank arrangement
Source: Lodi, 2011

The fluids of transfer of Heat for the technology CSP (*Solar Concentrating Power*) of solar tower need to have high chemical stability in the work temperatures (which due to technical limitations of the receiver assembly and the commercially developed HTF or *Heat Transfer Fluid* should be between 500 and 600 °C), and physical characteristics that favor heat transfer, such as high thermal capacity and low melting point, maintaining the heat exchange of the sensitive type, that is, solidification in the plumbing can result in a complete interruption of heliothermic plant activity (PERUCCHI, 2013) .

The fluid can be directly sent to steam turbines connected to electrical generators, or indirectly passing through heat storage tanks and when needed are pumped to the heat exchangers with the water vapor that will feed the steam *Rankine* cycle (LODI, 2011 e CHEN, 2011). In a plant that just possesses a storage tank of heat, it uses the technology *Thermocline*, acted in the illustration represents 2, in reference to the layer thermocline discovered originally by studies oceanographic. This thermocline layer has displayed a range of 28 at sea level where there is greater thermal stability, this is, the heat gradient is large between the length of the strip, separating a hotter fluid above, and a colder fluid below. This strip can be optimized using a tank of porous fixed bed filled out of specific granulated materials, as quartzite and sand (RADDE, 2011).

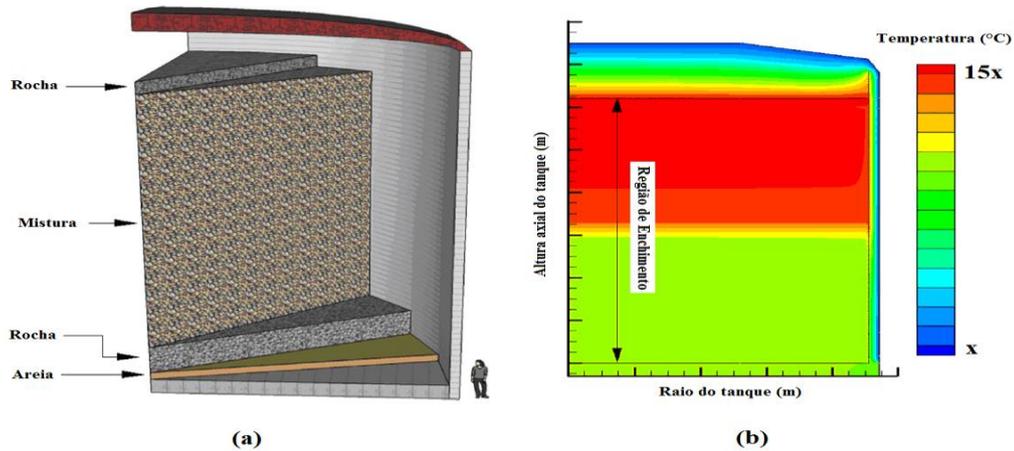


Figure 2- Thermocline Technology. (a) Longitudinal section of the fixed bed tank; (b) Thermal distribution in scale after 30 h.

Source: Garimella, 2012.

The storage systems of a CSP plant can be classified in several ways, such as passive or active. The active system is characterized when the heat transfer to the heat accumulation medium occurs through convection, that is, both fluids are in motion. While, in the system of passive storage, the working fluid goes through the middle of thermal accumulation just for load and discharge; the system of passive storage usually uses the middle of storage in the solid state (GIL, et al., 2010).

The storage system is the sensible heat where it is associated with temperature variation, usually liquid or solid. The SM (Molten salts), in turn, is stored in tanks, which is a disadvantage of storage via sensible heat (GIL, et al., 2010). Thermal accumulation materials exist through sensitive heat, the table below detaches the main characteristics of the same ones.

Table 1 - Solid materials that use sensible heat and its characteristics

Source: GIL, et al., 2010

Storage Material	Temperature (°C)		Average Density (Kg/m ³)	Average thermal conductivity (W/m ² .K)	Average heat capacity (kJ/kgK)	Thermal capacity by volume (kWh/m ³)
	200	300				
Mineral oil, sand, and stone	200	300	1700	1,0	1,3	60
Reinforced Concrete	200	400	2200	1,5	0,85	100
NaCl(solid)	200	500	2160	7,0	0,85	150
Cast iron	200	400	7200	37,0	0,56	160
Steel	200	700	7800	40,0	0,60	450
Silica Brick	200	700	1820	1,5	1,00	150
Magnesium Brick	200	1200	3000	5,0	1,15	600

According to Raade (2011), the choice of transfer fluid influences the overall efficiency of the thermodynamic cycle for electricity generation, and the main desired characteristics are: high thermal stability; low vapor pressure in the temperature range used; high thermal capacity (for heat storage to be viable) ; lowest possible melting point (to reduce costs in preventing solidification in pipes); high density; low viscosity; chemical compatibility with steels and costs compatible with the project. In the table below we observe some substances that can be used in the CSP system.

Table 2: Transfer Fluids Available for CST Applications
 Source: Raade (2011). Adapted by Perucchi (2013)

Name	Components	Fusion point (°C)	Thermal stability (°C)
VP-1 / Dowtherm A	Diphenyl Oxide and Biphenyl	12	400
Hitec XL	Sodium, calcium and potassium nitrates	120	500
Hitec	Sodium and potassium nitrate, sodium nitrite	142	538
Hitec Solar Salt	Sodium and potassium nitrates	240	593

Mixtures of salts are particularly advantageous for solar tower type plants since the thermal stability required by the operating conditions is above 500 °C and such mixtures have the same behavior as pure substances when subjected to melting, although they are formed by two elements they have a lower melting point and higher thermal stability. The mixture that is most applied in solar towers consists of 60% sodium nitrate and 40% potassium nitrate, having its ideal point of operation near 593 °C, with begins of decomposition to nitrites which accelerate corrosion of the pipes when they reach above 600 °C.

The Heliostats field is the only one that uses a set of hundreds of mirrors, each with four flat or slightly concave reflecting mirrors of 50 to 150 m² each, spaced apart in a large field surrounding the receiving tower. These mirrors have a two-axis tracking system that through independent movement, controlled by a computational program, they constantly search for the highest solar irradiation and the focus of reflected rays precisely directed at the receiver (PERUCCHI, 2013).

Currently, with the high investments in research in the CSP technology, there was an increase in the construction of heliothermic plants that makes the use of molten salts for the generation of energy. The Spanish solar tower PS10 was a first commercial plant in the world with a capacity of 10 MWe, another famous is a CrescentDunes located in the desert of the state of Nevada in the United States with a generating capacity of 1,100 MG / h (MALAGUETA, 2012).

2. OBJECTIVE

Discover the properties of the molten salt in order to know the reason for choosing this method and why these inorganic salts were chosen for the generation and storage of electric energy.

3. MATERIALS AND METHODS

In the laboratory provided by Tiradentes University (UNIT), several experiments were carried out using the substances that make up the molten salt. The substances indicated in figure 3 were divided according to the specifications provided by the Gemasolar plant, through the analysis of these data it was possible to reach 60% of sodium nitrate (NaNO₃) and 40% of potassium nitrate (KNO₃).



Figure 3: Sodium nitrate (NaNO₃) and Potassium nitrate (KNO₃)

The prior was carried out the separation of the substances in crucibles (a glass of porcelain resistant to high temperatures). The weighing of these compounds was carried out on an analytical balance. After being weighed the blends that were placed in the high temperature furnace (mufla), shown in Figure 4, at temperatures ranging from 245 °C to 900 °C, remaining for 10 minutes each test, as they were withdrawn from the greenhouse the conductivity test was done on a test device created by technicians of the chemistry laboratories to test the thermal and electrical

conductivity. After conducting the test to measure the conductivities (at an ambient temperature of 25 °C) the cooling time was observed and timed until the molten salt crystallized.



Figure 4: Mufla (oven used to heat the salts)

4. MATHEMATICAL EQUATIONS

When a temperature body T is exposed to a room temperature T_m so that $T \neq T_m$. It is noticed that after some time the object reaches the thermal balance with the atmosphere. Comparing the results of different situations involving cooling of a body we can verify that the cooling rate depends on factors, such as: the temperature difference between the body and the external middle, the surface of the body exposed, the specific heat of the substance that constitutes it, the conditions of the environment in which this body was put; the time in that the object stays in contact with the atmosphere. (BROCKMAN, 2013)

This can be represented by an equation:

$$\frac{dT}{dt} = k(T - T_m) \quad (1)$$

On what:

$\frac{dT}{dt}$: It is the variation of the temperature in relation to the time;

k : It is a proportionality coefficient that depends on the exposed surface of the heat specify of the body and also of the environmental and climatic characteristics;

T : It is the initial temperature of the body;

T_m : It's the room temperature.

It was taken: $T(0) = 250^\circ\text{C}$ (Temperature of the solution when leaving the mufla)

T (external temperature of the object) = 25°C (Room temperature)

$T(3) = 224^\circ\text{C}$ (Temperature of the solution after 3 minutes submitted to room temperature after the exit of the mufla).

With this, we have equation (2), where $(T - 25)$ is the Temperature found after t minutes and 25 is the ambient temperature. Applying the ambient temperature variable in the equation.

$$\frac{dT}{dt} = K(T - 25) \quad (2)$$

Performing the operation of means by extremes and substituting the value of the ambient temperature in equation (2), we have that.

$$\frac{dT}{T - 25} = kdt \quad (3)$$

Integrating equation (3) and using the Euler's method, we calculate the natural logarithm (ln).

$$\int \frac{dT}{T - 25} = \int kdt$$

$$\ln(T - 25) + C_1 = k * t + C_2$$

$$e^{kt+C} = T - 25$$

Finding the equation: $T(t) = 25 + e^{kt} * c$ (4)

Being considered $t = 0$ and substituting in the equation (4) we have to, $T(0) = 250$, that is the value of the temperature of the fluid when he left the mufla:

$$T(0) = 25 + e^{k*0} * c$$

$$250 = 25 + c$$

As soon, obtaining the constant C_1 : $c_1 = 225$

With the value of the constant C_1 found, it will be applied in equation (4) formulating the general equation, found below:

$$T(t) = 25 + 225 * e^{kt}$$
 (5)

Considering the temperature of the solution after 3 minutes ($t = 3$), and knowing that $T(3) = 224$, these variables are applied to equation (5).

$$T(3) = 25 + 225 * e^{k*3}$$

$$224 = 25 + 225 * e^{k*3}$$

$$e^{3k} = \frac{199}{225}$$

$$3k = \ln(0.884)$$

Finding the value of the negative proportionality constant we find that there is a reduction of fluid temperature. Determining the constant of proportionality, have to $k = -0.041$, with this will be replaced in equation (5).

$$T(t) = 25 + 225 e^{-0.041t}$$
 (6)

Knowing $T(t) = 220$, it will replace in equation (6) in order to find the cooling time when exposed to ambient temperature:

$$220 = 25 + 225 e^{-0.041t}$$

$$155 = 225 e^{-0.041t}$$

$$-0.041t = \ln\left(\frac{155}{225}\right)$$

$$t = 3 \text{ minutes e } 29 \text{ seconds}$$

It was taken: $T(0) = 300^\circ\text{C}$ (Temperature of the solution when leaving the mufla)

T (external temperature of the object) = 25°C (Room temperature)

$T(3) = 229^\circ\text{C}$ (Temperature of the solution after 3 minutes submitted to room temperature after the exit of the mufla).

In this way, we have equation (2), where $(T-25)$ is the Temperature found after t minutes and 25 is the ambient temperature. In this second case will also use equation (2).

$$\frac{dT}{dt} = K(T - 25)$$
 (2)

Accomplishing the operation of means by extremes and substituting the value of the ambient temperature in equation (3) previously seen, we have:

$$\frac{dT}{T - 25} = k dt \quad (3)$$

Integrating equation (3) and using the Euler's method, we calculate the natural logarithm (ln).

$$\int \frac{dT}{T - 25} = \int k dt$$

$$\ln(T - 25) + C1 = k * t + C2$$

$$e^{kt+c} = T - 25$$

$$\text{Finding the equation: } T(t) = 25 + e^{kt} * c \quad (4)$$

Being considered $t = 0$ and substituting in the equation (4) we have to, $T(0) = 300$, that is the value of the temperature of the fluid when he left the mufla:

$$T(0) = 25 + e^{k0} * c$$

$$300 = 25 + c$$

As soon, obtaining the constant C_2 : $c_2 = 275$

With the value of the constant C_2 found, will be applied in equation (4) formulating the general equation, found below:

$$T(t) = 25 + 275 * e^{kt} \quad (7)$$

Considering the temperature of the solution after 3 minutes ($t = 3$), and knowing that $T(3) = 229$, these variables are applied to equation (7).

$$T(3) = 25 + 275 * e^{k*3}$$

$$229 = 25 + 275 * e^{k*3}$$

$$e^{3k} = \frac{204}{275}$$

$$3k = \ln(0.7418)$$

Finding the value of the negative proportionality constant we find that there is a reduction of fluid temperature. Determining the constant of proportionality $k = -0.041$. In this way, it will be replaced in equation (7).

$$T(t) = 25 + 275 e^{-0.0995t} \quad (8)$$

Knowing $T(t) = 220$, it will replace in equation (8) in order to find the cooling time when exposed to ambient temperature:

$$220 = 25 + 275 e^{-0.0995t}$$

$$195 = 275 e^{-0.0995t}$$

$$-0.0995t = \ln\left(\frac{195}{275}\right)$$

$t = 3 \text{ minutes e } 27 \text{ seconds}$

5. RESULTED E DISCUSSIONS

Tests were initially run to establish the melting point of temperatures ranging from 245 °C to 900 °C. In this way, obtaining different results, for example, when subjected to a temperature of 900 °C for 10 minutes, the solution has completely carbonized or when subjected to 245 °C, enters the liquid state. The results are quite accurate because they have a small uncertainty, therefore showing the effectiveness of the experiments. However, it was not possible to compare with results of existent nuclei in the literature and to talk about the accuracy of the experiment, for not treating of real nuclei.

The first rehearsal was heated up her/it a temperature of 245 °C, the substances melted presented a colorless coloration, this proves that there was not smash of particles, altering the initial properties of the salts. After solidification, shown in Figure 5, which was heated to 245 °C tends to a white coloration. Note some cracks originated during the solidification process.



Figure 5: Substance submitted to 245 °C, 1°- In liquid state and 2°- In solid state

When heating to 600 °C, we can see a change in the color of the solution represented in figure 6, this phenomenon occurs from the fact that the electrons of the last layer of sodium are excited to a higher energy orbit and when it returns, it brings the absorbed energy to its original orbit as an electromagnetic energy, releasing light and that light is reflected in the solution. When the solution solidifies, it presents white coloration and few cracks originated in that process.



Figure 6: Substance submitted to 600 °C, 1°- In liquid state and 2°- In solid state

Heating up to 700 °C, the yellowish coloration appears darker in the illustration 7, because there is carbonization of some particles. The solution that was heated up begins to present a perfect crystal after the solidification, of coloration totally white.



Figure 7: Substance submitted to 700 °C, 1°- In liquid state and 2°- In solid state

As well as when heated to 700 °C, the solution presented in the illustration 8 when heated to 800 °C presents coloration yellowish, however darker, because a number of charred particles are larger. After the solidification of the mixture of salts is perceived that there was a break of particles in the formation of the crystal, presenting charred borders and central cracks.



Figure 8: Substance submitted to 800 °C, 1°- In liquid state and 2°- In solid state

When subjected to 900 °C, the solution of figure 9 carbonizes completely, showing a reddish coloration, similar to volcanic lava. After solidifying, the substance has a slightly reddish yellowish color, due to the complete breakdown and carbonization of the sodium particles.



Figure 9: Substance submitted to 900 °C, 1°- In liquid state and 2°- In solid state

6. CONCLUSION

With the results obtained it was possible to verify that the solution of molten salt supports a temperature of up to 800 °C, as specified in the literature, which makes it possible to exchange heat for a long time with the water in order to evaporate it. It is known that the water must be at 100 °C to evaporate, with the solution at 800 °C (eight times the temperature that the water needs to change from the liquid to the gaseous state) a good evaporation can be obtained which is essential for the operation of the propeller of a turbine of the motor generating electric power.

In order to have a low material waste, this type of plant, seen in figure 1, uses a heat exchanger that when generating the steam (caused by the encounter of the water with the superheated salts) leads to the turbines, then it is sent to the condenser which makes it possible for the evaporated water to return to the heat exchanger in state liquid, so that it can be heated again without a great loss of mass. The superheated salts that with the heat exchange ended lowering their temperature are sent to a second tank, returning to the same heating process.

By virtue of the obtained data, starting from the accomplished experiments it was possible to verify the good thermal conductivity that the salts have, can be to think of other options for the generation of electric energy, for example, the use of other salts or substances that have a good conductivity and does not cause any impact to the environment.

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8. RESPONSIBILITY NOTICE

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