



POWER GENERATION POTENTIAL FROM CYANIDIZED WATER USING OSMOTIC PROCESSES.

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Abstract: Substances such as sodium cyanide are highly toxic and are indiscriminately dumped into rivers and watersheds by mining industries, exposing communities to a high level of environmental risk. Looking for alternatives to mitigate the impact, the objective of this research was to estimate the electrical power potential in a lab scale osmotic power generator through the use of sea water and cyanided water gradient concentration (25 and 700 mg/L NaCN) using flat polymeric membrane. 60 tests were performed in two osmotic generators, using a dead-end filter operation scheme, one with vertical and another with horizontal membrane orientation. By using a solution of 700 mg/L, water concentrations similar to those found at the tailing of South Bolivar were achieved. This allowed the GE Osmonics SE membrane to develop a maximum achieved power density of $2.45E-04$ W/m² at a value of 1.9 cm of water for the reactor with the vertical configuration. Seawater tests were performed with concentrations hundred times that of cyanide, at 71 g/L, a power density of $2.27E-04$ W/m² and a head pressure of 3.3 cm were found for the reactor with the vertical configuration. The results show higher yields under the same operating conditions when replacing NaCl found in seawater by cyanide salts, thereby decreasing the concentration by 70.3 g. Through this research, an efficient alternative for the reuse of cyanide salt contaminated water is shown.

1 Introduction

The Renewable Energy (RE) sources is in continuous search for cost-effective relation and has taken many dimensions and directions. Trying to mitigate the current urgency of dwindling world supplies of conventional fossil fuels, increasing oil prices and the most important, climate change (Sharif, Merdaw, Aryafar & Nicoll. 2014). Nowadays, a carbon plant emits more than one billion metric tons of greenhouse gases every year (Elimelech, Yin Yip, Hoover, Phillip, & Tiraferri, 2011). The salinity gradient is one of the resources that use osmosis and electro dialysis. The power production by pressure retarded osmosis (PRO) and waste water treatment or desalination by forward osmosis (FO) may be economically feasible option to overcome this inadequacy problem of energy and water supply as compared to other available techniques. In an ideal PRO process, pure water permeates through a semipermeable membrane from dilute feed solution into a pressurized and concentrated draw solution; the resultant highly pressurized solution is further split into two streams. Fresh water enters the membrane modules; part of fresh water is transferred by osmosis across membrane into sea water. Then, the pressurized sea water comes out as brackish water. Generating power through osmosis between river and sea water has been known since 1970s (Attarde, Jain, Chaudhary, Gupta. 2015).

Water is a resource that has been approved for the generation of electric energy as the example of hydroelectric plants, which have become a sustainable source of energy throughout the world. Although in some cases it is questioned by the environmental impact it entails. In Colombia, the large number of rivers make the utilization of this type of energy an enticing prospect. The rivers make up 65% of the energy supply of Colombia, more than half of the national supply. However, there are zones that do not have electricity service. Zones affected by illegal armed groups, insular or ones that are hard to access are in need of a source of energy and presently are considered non-interconnected zones (ZNI). The unsatisfied

energy demands in the ZNI in 2011 increase to 65.0 GW/h with a growth rate of 35.6% compared to 2010. This meant that by 2014, the unmet demand reached 80 GW/h (Ministry of Mines and Energy, 2011-2012).

Colombia is an example of the necessity for the creation of this type of plant since, there are areas where water is sometimes not properly supplied or arrives contaminated due to the human activities at the source of supply. The most common case being mining, which corresponds to 25% of the general mining activities throughout the country (De La Hoz, 2009). South of Bolivar is a prime example of the effects of mining on the quality of water. The continuous mining activities in the region have led to an increase in the concentrations of cyanide salts in the region of 700 to 800 mg/L. These high values of cyanide salts allow the production of osmotic energy due to its high degree of salinity. The potential of power generation however, comes with a drawback in the form of the toxicity of the water and poses a threat to the general health of the population (Ramos Avilez, 2012). Cyanide in some forms, is highly potent and a fast-acting toxicant. Its toxicity is related to its physicochemical specification (Hilson & Monhemiusb, 2006) and depends on its particular form. Thus, while free cyanide is a very dangerous metabolic poison metal complexes of cyanide vary in toxicity and the function of the ease with which cyanide releases them.

A large number of theoretical research has opened up a positive outlook for potencies between 2.7 and 5.1 W/m² for waters with salt concentrations between 35 and 60 g/l using flat-sheet cellulose membranes (Achilles, Cath, & Childress, 2009). The general consensus is that in order to produce energy at a competitive price, a minimum power of 5 W/m² should be reached. The world's first 4 kW osmotic plant was inaugurated by Statkraft on 24 November 2009 in Tofte, Norway. It is estimated that each year 1,600 TW/h could be generated worldwide, and with only 12 TW/h in Norway, would be enough to meet 10% of total electricity demand (Statkraft Company, 2009). Likewise, the possibility of rejection of sodium cyanide by polymer membranes is shown, by increasing the pressure up to a range of 15-20 atm; the maximum separation obtained was about 95% (removal of cyanide). These results show a pattern in the possibility of obtaining energy through sodium cyanide (Murthy & Gupta, 1999).

The implementation of the pilot plant using cyanide water allowed for the evaluation of the potential that this type of water can provide. The experiment took place in the civil engineering sanitation laboratory of the University of Cartagena and modeling laboratory of chemical engineering of the University of Ryerson. The reactor was developed using two stainless steel reactors, the first one with a horizontal configuration and capacity of 16 L and the second with a vertical configuration with a capacity of 10 L. A set of GE Osmonics SE polymer membranes generated the required pressure and a metering tube was used to indicate the potential generated by the water in each test. The results showed the existence of the potential that can be obtained when reusing the cyanide waters and also consolidated the important source for the advancement in this type of energy.

2 Osmotic power generation via the PRO process

The principle of this type of energy is based on the use of the pressure generated in the natural phenomenon of osmosis. To have an idea this phenomenon can be considered as an inverse process of the separation energy that the desalination plants use. Instead of using energy to separate a mixture in its constituent elements, the energy in this case is released when the elements are combined. When two solutions with different degree of salinity (salinity gradient) are mixed, a free energy of mixture is released (Elimelech, Yin Yip, Hoover, Phillip, & Tiraferri, 2011).

The performance of the PRO membranes is usually evaluated in terms of the energy density W , which is defined as the output force per unit area of membrane (W/m^2). A PRO membrane with a high W is essential because this determines the requirements between the membrane area and the size of the PRO plant to guarantee an energy production capacity. Mathematically, W is determined by:

$$[1] W = J_w \Delta P$$

Where ΔP is the applied effective hydraulic pressure and J_w the water permeate flow through the membrane. Without considering the effect of polarization, the ideal J_w through a perfect semipermeable membrane can be calculated by the ideal condition equation:

$$[2] J_w = A * (\Delta\pi - \Delta P)$$

Equation [1] shows that J_w is determined as the product of the system permeability to water, A , and the net trans-membrane driving pressure, which is the net difference between the osmotic pressure, $\Delta\pi$, and the net hydraulic pressure, ΔP . The density of the power obtained from the PRO process, W , can be estimated as the product from multiplying the water flux by the hydraulic pressure:

$$[3] W = J_w * \Delta P$$

$$[4] \Delta P = \frac{P_{DS_{in}} + P_{DS_{out}}}{2} - \frac{P_{FW_{in}} + P_{FW_{out}}}{2}$$

And similarly for $\Delta\pi$:

$$[5] \Delta\pi = \frac{\pi_{DS_{in}} + \pi_{DS_{out}}}{2} - \frac{\pi_{FW_{in}} + \pi_{FW_{out}}}{2}$$

Where, the subscripts DS and FW refer to the Draw Solution (the high concentration side) and the Feed Water (the low concentration side), respectively, To determine $\Delta\pi$, the osmotic pressures of the diluted and concentrated solutions must be determined, giving approximate values using the Van't Hoff equation:

$$[6] \pi = V_i C_i R T$$

Where V_i is the number of ions formed with the solution of solute (i is 2 for NaCl and NaCN), C_i the molar concentration of solute, R is the ideal gas constant equal to 0.082 liters atm/mol, T the absolute temperature in (K), C_i is the total concentration of ions in kmol/m³. On the other hand, using differential equations of equation [3] respect to ΔP , the maximum power density (W_{max}) occurs when ΔP is equal to half of the osmotic pressure difference ($\Delta\pi/2$) across the membrane.

$$[7] W_{max} = A * \Delta\pi / 4$$

3 Experimental Setup

The GE Osmotic membrane (YMAGSP3001) was selected to achieve the stated objectives for the present research. The membrane is a 305-305 mm flat sheet - thin film commonly used for acid concentration, starch/sugar concentration and laundry and dye house wastewater reclamation. These membrane characteristics allows the operation of the osmotic generator at pressures higher than 60 MPa, cyanide concentrations up to 1000 mg/L at different pH ranges. The thin film membranes were further characterized using a JSM-6380LV Electron Microscope Scanner at magnifications of 100x, 1000x, 10000x, and 100000x to analyze the cyanide effects on membrane surface structure. Five membranes samples of 30 x 10 mm size were first immersed for 24 hours in cyanide solutions of 0.0, 25, 50, 100 and 200 NaCN mg/L, respectively. Then, all membrane samples were dried in a vacuum desiccator for 24 hours. Before SEM analysis, Samples were subjected to bombardment of gold ions in a Denton Vacuum Desck IV for two minutes. In addition to the surface study the chemical composition of the membranes was determined using the microscopic scanner and X-ray spectroscopy.

Two osmotic generators were designed and constructed at lab scale, one with a horizontal membrane and another with a vertical membrane orientation as shown in Figure 1. Similar operation schemes have been used in previous studies (Hernández Sanchez, Ríos Ponce Vicencio & Medina, 2010). The two reactor were made of stainless steel with a total volume capacity of 12 L for the vertical and 25 L for the horizontal. The surface area of the membranes were 0.05 m² for the horizontal and 0.03 m² for the vertical generator.

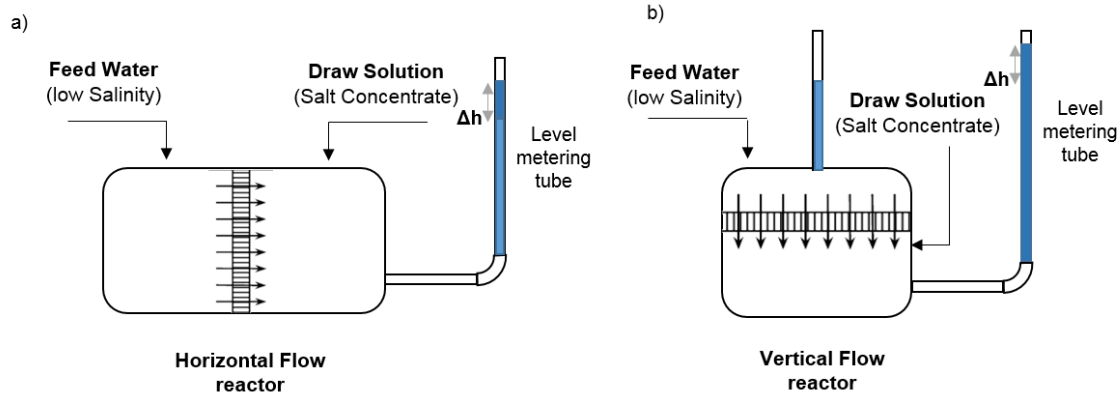


Figure 1: Schematic diagram of the Reactor a) Horizontal Flow configuration b) Vertical Flow Orientation.

For all tests in the vertical reactor five liters were used for feed water and seven liters for draw solution, the feed water tank was one meter high with reference to the base of the reactor. In the case of the horizontal configuration, a constant volume of 25 L was used on the draw solution side and for the feed water side a 500 L supply tank was used, using valves to control the flow to the reactor. In addition, it is important to note that the height difference between the outlet of the fresh water tank and the reactor was approximately 40 cm.

The first process that was performed after verification of the correct operation of the osmotic power generator was the calibration of the conductivity meters YSI and Consort C5010, which allowed reliability in the values thrown during the tests. The calibration consisted of using 15 concentrations of salt and 7 of cyanide, from which a graph was constructed that relates the conductivity and the concentration, allowing to establish equivalences of salinity and relation between NaCl and cyanide.

In the two reactors were initially carried out with clean water tests to determine the behavior of the membranes against it and thus have a point of comparison and calibration. On the other hand, it was also decided to perform tests with synthetic salt water (NaCl), which allowed to simulate the type of water normally used in PRO (seawater) systems with concentrations of 35, 17.5 and 70 g/L. Finally, cyanide was used for the tests, as planned, taking 5 different concentrations of 700, 200, 100, 50 and 25 mg/L.

4 RESULTS AND DISCUSSION

4.1 Water and membrane characterization

Measurements of the water were made to determine the approximate values of conductivity and therefore of salinity of the samples studied. Fifteen salt concentrations and six for cyanide by the risk with their manipulation. When comparing the conductivities, the NaCN samples are slightly higher than those of NaCl. Taking a sample of 500 mg/L, for cyanuric waters the conductivity was 1283 $\mu\text{S}/\text{cm}$ and for salt water 1023 $\mu\text{S}/\text{cm}$; about 20% higher for the vertical configuration. Taking the same concentration for the horizontal configuration, samples had a conductivity of 1291 $\mu\text{S}/\text{cm}$ for cyanided waters and 1060 $\mu\text{S}/\text{cm}$ for the salted, approximately 18% higher. These two situations provide a positive outlook for obtaining good results in testing PRO waters with cyanide as the process of osmosis depends on the concentration differences.

With the help of the Microscopic Electron Scanner and specifically with the X-ray spectroscopy test, a series of images can be obtained that allowed the physical chemical analysis of the membranes according to the different concentrations at which the samples were exposed.

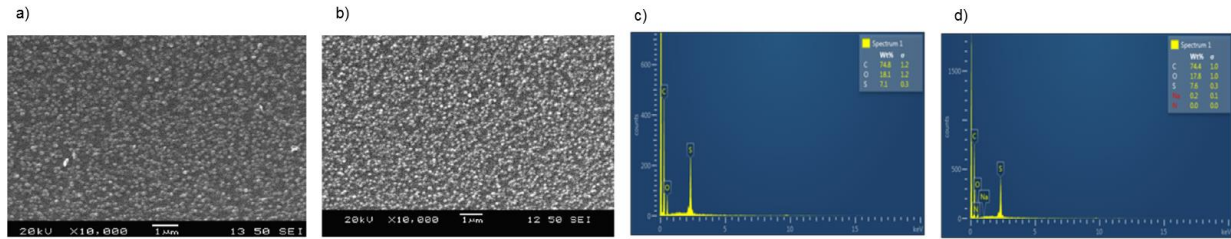


Figure 2: Microscopic Scanner a) white b) 200mg/L NaCN and Dispersive Energy X-ray Spectroscopy c) white d) 200mg/L NaCN for reference samples, active membrane layer.

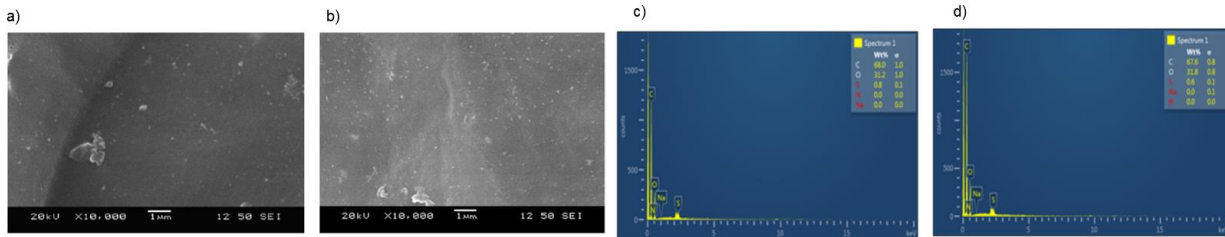


Figure 3: Microscopic Scanner a) blank b) 200mg/L NaCN and Dispersive Energy X-ray Spectroscopy c) blank d) 200mg/L NaCN for reference samples, Support membrane layer.

Figures 2 and 3 show that there were no significant changes in the membrane composition between the blank and the membrane exposed to the different concentrations of salts that were plated in the tests, showing it is not hydrophilic as assumed. Moreover, it should be noted that these samples were only submerged in the cyanide salts and were not subjected to pressure; an additional phenomenon that was not taken into account at this stage of the investigation but to which the membranes have to be exposed to. Low percentages of sulfur were also found. This is because, in order to improve the properties of the polymers, amounts of sulfur between 5 and 10% were added, allowing the polyamides to develop thermostability properties. Besides helping with the elastic and permeability properties, it has been established that with this addition, the aromatic structure of the polymer can withstand 70°C, a 42-68% increase from temperatures they are normally exposed to. This makes it more resistant to high temperatures (Shockravi, Abouzari, and Javadi, 2009).

4.2 Osmotic scale reactor operation

4.2.1 Fresh Water

Table 1: Fresh water test in an osmotic scale reactor

Solution	Flow Configuration	Concentration (g/L)	Average Initial h (cm)	Average Final h (cm)	Δh prom (cm)	Time (s)
Distilled Water	Vertical	0	39.1	32.33	-6.8	189.5
Tap Water	Horizontal	0	6.4	22.55	16.2	583

As show in Table1, in both configurations an immediate increase in the water reference level was observed. In the case of the vertical configuration, around three minutes the system reached a maximum average equilibrium value of 32.33 cm, while for the horizontal configuration, around nine minutes the average height in the measuring tube was 22.55 cm. Therefore in the following tests it was considered that the water alone experiences a pressure head. In addition it was obtained that the flow through the membrane was 3.58E-

04 m/s and 2.77E-04 m/s for the vertical and horizontal configuration respectively. This value was relevant for tests with concentrations of salt and cyanide.

4.2.2 NaCL Solution

Table 2: NaCL Solution test in an osmotic scale reactor

Solution	Flow Configuration	Concentration (g/l)	Average Initial h (cm)	Average Final h (cm)	Δh Average (cm)	Time (s)
NaCL Solution	Vertical	17.5	39.5	38.1	-1.4	187
		35.5	40.0	40.74	0.7	189
		71	39.8	43.1	3.3	189.6
NaCL Solution	Horizontal	17.5	6.5	31.5	25.1	574.0
		35.5	6.4	34.3	27.9	576.0
		71	6.5	37.2		584.0

The variation of the concentrations by 17.5, 35.5 and 71 g/L show that by increasing salt concentrations the measurement of the meter tubes also increases. By raising the minimum concentration by four times in the case of the reactor with vertical configuration, the head is increased by about 5 cm, while in the horizontal the increase was just under 6 cm. In the same way in the observed water differences, that is to say the variation between the final and initial level with respect to the concentrations handled, a notable increase was observed for both configurations.

Comparing the results obtained from water head, it is identified that for the horizontal configuration these are drastically superior for each one of the concentrations compared with the values obtained in the vertical. In spite of the great difference existing on the basis of this variable it is not possible to define which of the two has a greater potential, since this strictly only depends on the power of density.

Table 3: Membrane permeability and Power density calculation for NaCl solution test

Flow	Con (g/l)	Ci (MCon)	$\Delta\pi$ (bar)	Δp (bar)	Jw (m/s)	$\Delta\pi-\Delta p$ (bar)	A (L/m ² ·h·bar)	W (W/m ²)	W max.
Vertical	17.5	0.043	12.6	0.1	2.04E-03	12.54	1.63E-04	2.04E-04	4.90E-02
	35.5	0.087	26.3	0.1	2.16E-03	26.17	8.25E-05	2.16E-04	5.18E-02
	71	0.174	56.1	0.1	2.27E-03	56.01	4.05E-05	2.27E-04	5.45E-02
Horizontal	17.5	0.043	12.6	0.04	5.49E-04	12.6	4.36E-05	2.20E-05	1.32E-02
	35.5	0.087	26.3	0.04	5.96E-04	26.23	2.27E-05	2.38E-05	1.43E-02
	71	0.174	56.1	0.04	6.37E-04	56.07	1.14E-05	2.55E-05	1.53E-02

Table 3 shows variable values for the permeability coefficient, varying according to the concentrations. However, a representative value must be found for this membrane and specifically for the solute studied. For this reason, the slopes of the curve are calculated by means of linear regressions, which are described by the function that forms the points.

In the same sense when analyzing the power density produced by the different configurations, it is observed that the vertical is the most effective and that as shown in Graph 1.a. There is a linear proportionality between the osmotic pressure and the generated power, although this power in turn depends directly on the permeability coefficient, a fundamental parameter for the reached results. The maximum values obtained are 2.27E-04 W/m² for a concentration of 71 g/L in vertical flow, while for the horizontal configuration the maximum value under the same concentration was 2.55E-05 W/m².

NaCN Solution

Table 4: NaCN Solution test in an osmotic scale reactor

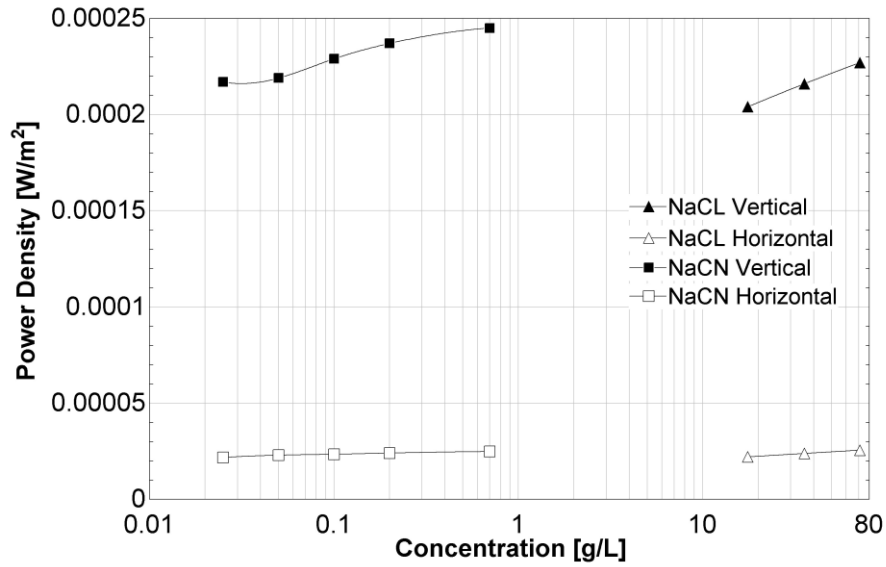
Solution	Flow Configuration	Concentration (mg/l)	Average Initial h (cm)	Average final h (cm)	Δh prom (cm)	Time (s)
NaCN Solution	Vertical	25	43.0	40.3	-2.7	186
		50	43.9	41.57	-2.3	190
		100	41.2	42.13	0.9	184
		200	43.5	44.47	1.0	188
		700	43.7	45.53	1.9	186
NaCN Solution	Horizontal	25	6.37	30.87	24.5	570
		50	6.43	32.53	26.1	568
		100	6.43	33.73	27.3	578
		200	6.43	34.83	28.4	580
		700	6.57	35.77	29.2	578

Table 5: Membrane permeability and Power density calculation for NaCN solution test

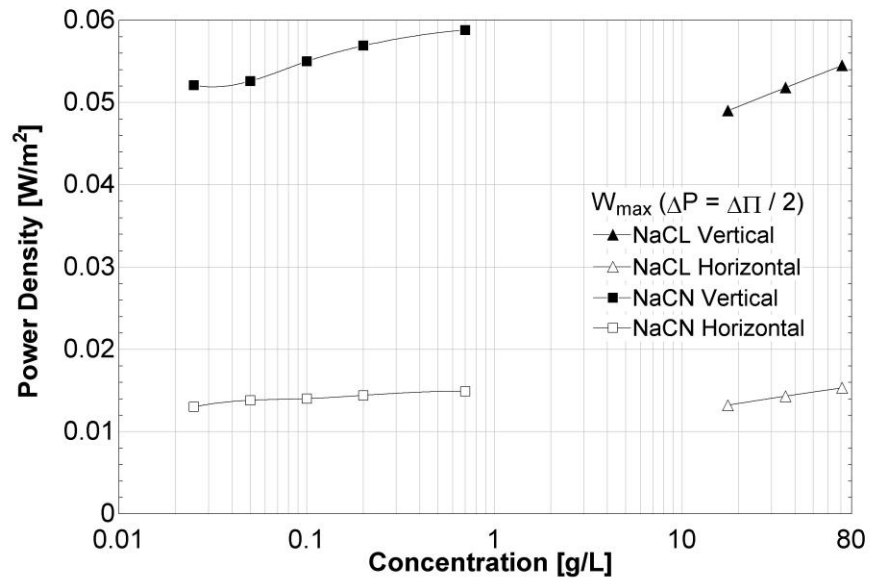
Flow	Con (mg/l)	Ci (MCon)	$\Delta\pi$ (bar)	Δp (bar)	Jw (m/s)	$\Delta\pi-\Delta p$ (bar)	A (L/m ² ·h·bar)	W (W/m ²)	W máx.
Vertical	25	7.29E-05	0.0195	0.1	2.17E-03	-0.081	-2.70E-02	2.17E-04	5.21E-02
	50	1.46E-04	0.0388	0.1	2.19E-03	-0.061	-3.58E-02	2.19E-04	5.26E-02
	100	2.92E-04	0.0772	0.1	2.29E-03	-0.023	-1.01E-01	2.29E-04	5.50E-02
	200	5.83E-04	0.1534	0.1	2.37E-03	0.053	4.44E-02	2.37E-04	5.69E-02
	700	2.04E-03	0.5263	0.1	2.45E-03	0.426	5.75E-03	2.45E-04	5.88E-02
Horizontal	25	7.29E-05	0.0195	0.04	5.42E-04	-0.021	-2.64E-02	2.17E-05	1.30E-02
	50	1.46E-04	0.0388	0.04	5.73E-04	-0.001	-4.86E-01	2.29E-05	1.38E-02
	100	2.92E-04	0.0772	0.04	5.84E-04	0.037	1.57E-02	2.34E-05	1.40E-02
	200	5.83E-04	0.1534	0.04	6.01E-04	0.113	5.30E-03	2.40E-05	1.44E-02
	700	2.04E-03	0.5263	0.04	6.19E-04	0.486	1.27E-03	2.48E-05	1.49E-02

Comparing the values of average hydraulic height reached by the salt and cyanuric waters in the vertical configuration has shown that salt water with one hundred times greater concentration produced a little less than half compared to the cyanide solution. With a concentration of 71g/L for salt water and 700 mg/L for cyanide solution, a height of 3.3 cm and 1.9 cm was produced respectively, showing the potential that exists in the cyanide water. Likewise for the horizontal configuration, values obtained were even more encouraging with the maximum concentration of cyanide of only 700 mg/L and a head of 29.2. In contrast to 30.7 cm for the experiments with common salt at 71 g/L, the most outstanding results in these tests are the proximity of the heads of water and the remoteness of the concentrations used. However, it should be noted that the membrane was selected for use in more aggressive conditions, yet it is a reliable and very telling point of comparison.

A)



B)



Graphic 1: Variation of the concentration influence on the Power density produced. A) Experimental condition

The average values of energy production according to the maximum concentration used, which corresponds to the concentrations found in the aquifer tailings in the south of Bolivar were $2.45E-04$ W/m² for the vertical configuration. The maximum power density calculated for the system was $5.88 E-02$ W/m². It was possible to determine the partial concordance in the values as the coefficient of permeability in the studied references. These were around $1.87E-09$ ms⁻¹Kpa⁻¹ and $2.02E-09$ ms⁻¹Kpa⁻¹ using operating pressures between 7 and 15 bar in different combinations of sea water, fresh water and brine (Achilli, Cath, & Childress, 2009) (Gang, Sui, Xue, & Tai-Shung, 2015). Also, these studies used modified thin film

membranes to improve performance in PRO and FO tubular hollow configuration membranes (Helfer, Lemckert & Anissimov, 2014), reaching densities of up to 3.8 W/m². Figure 1 shows the results calculated for the tests with both solutions in the two different studied configurations; vertical and horizontal flow. Clearly it is seen in both solutions that the vertical configuration demonstrates a better performance than the horizontal system.

Comparing results, the most significant power density was 5.88 E-02 W/m² achieved in the vertical configuration, with a thin film membrane designed to operate in RO conditions, under very low pressure and flow times of less than 10 minutes. The calculated density is still far from meeting the needs of the system, as its viability is estimated at 5 W / m² [Helfer, Lemckert and Anissimov, 2014]. The results expressed in the research shows how small amounts of cyanide salts have a higher performance than that generated using NaCl solutions. The NaCl solution consists of approximate concentrations of brine, which is the source with the highest concentration currently evaluated for this technology. This provides a new possibility to take advantage of contaminated water with cyanide.

Conclusion

Estimating the variation of the electric potential as a function of the osmotic pressure, it was found that there was a linear proportionality between them, for both salty and cyanuric waters. In addition, a maximum power density of 5.88E-02 W/m² was tested, using the GE Osmonic SE polymer membrane with solutions of cyanide concentrations of 25, 50, 100, 200, 500 and 700 mg/l for osmotic membrane reactors of different configurations (vertical and horizontal). This project can act as a preamble for the generation of eco-friendly energy and sustainable development, reusing contaminated water from mining activities in the south of Bolivar in Colombia.

Determining the physicochemical characteristics of the GE Osmonics SE membrane implemented in the research was found to be non-hydrophilic. This means that it does not allow the adhesion of cyanide particles and thus, being suitable to withstand the abrasion to the different concentrations of cyanuric waters to which it was exposed. In addition to the expected carbon and oxygen chains, sulfur content in small proportions of 5 -10% was also found. This guarantees the elasticity of the membrane, avoiding ruptures and allows the obtaining of a high energy potential while maintaining good efficiency in the system.

The reactors built in the University of Cartagena and the University of Ryerson allowed to generate a potential of energy represented in head of pressure by means of the use of a polymeric membrane and based on different configurations, through the tests carried out it was possible to identify that the reactor of vertical configuration is more effective for the use of the osmotic pressures. This is due to the force offered by gravity during the filling process in addition to the immediate contact with the membranes of the water sheets with different concentrations, allowing a more effective osmosis process.

The pilot plants demonstrated good performance under different conditions. A range of power densities was obtained at varying concentrations with the highest value of 2.45E-04 W/m² being generated at a concentration of 700 mg/L of NaCN. This represents the energetic potential of the developed system. In addition, through good monitoring and management the permeability coefficient of the membrane used was 3.26x10⁻⁵ms⁻¹ kpa⁻¹. This is close in order of magnitude to that obtained in previous investigations between 1.89x10⁻⁹ms⁻¹ kpa⁻¹ and 1.02x10⁻⁹ms⁻¹ kpa⁻¹.

These differences distance these results from those that the scientific community commonly obtains. However, the relationship between the potential obtained between salt water and cyanide water evaluated in the same system opens the possibility of finding great potential using cyanide water in more optimal systems like those found in previous studies.

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