Comparative study of the energy potential of cyanide waters using two osmotic membrane modules under dead-end flow

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Abstract. The energy potential of the osmotic pressure gradient of cyanide waters is evaluated using two membrane modules, horizontal and vertical, operated under dead-end flow. The membrane was characterized using Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray Spectroscopy (EDS). The membrane is mainly composed of carbon, oxygen, and sulphur. The properties of the membrane were unchanged and had no pore clogging after exposure to the cyanide waters. Potentials of $1.78 \times 10^{-4}$ and $6.36 \times 10^{-5}$ Wm$^{-2}$ were found for the horizontal and vertical modules, respectively, using the Van’t Hoff equation. Likewise, the permeability coefficient of the membrane was higher in the vertical module. Although the energy potential is low under the studied conditions the vertical configuration has a greater potential due to the action of gravity and the homogenous contact of the fluid with the membrane.

1. Introduction
Power generation by osmotic pressure due to the salinity gradient consists in the use of a semipermeable membrane, which divides two solutions with different salinity and chemical potential [1]. The transport of water from the solution with a low concentration towards the concentrated solution generates a pressure on the water of low concentration. The pressure generated could be exploited with the use of a hydraulic turbine and an electric generator [2].

The current installed capacity of this type of energy is merely 0.05MW worldwide [3], and the characteristics of the membranes and configuration must be improved to make the system competitive [4]. On the other hand, this technology has outstanding benefits, such as having the lowest emission of greenhouse gases (GHGs) [5], it does not consume either water or salt in the process, and requires low flow to generate enough energy to supply remote populations [6]. It can also be used in hybrid applications, including its combination with other renewable energies, wastewater treatment plants [7,8], and drinking water systems [9].

Cyanide waters from tailings in the mining industry present an enormous potential because of the high concentrations of NaCN salts in the range of 700–800mg L$^{-1}$. These NaCN concentrations have a negative impact on the environment, reducing growth and swimming performance in fishes [10]. NaCN is also a potent inhibitor of respiration, acting on mitochondrial cytochrome oxidase, blocking electron transport, which results in decreased oxidative metabolism and oxygen utilization causing lactic acidosis, which can be fatal [11].

It has been appraised that the global energy potential by salinity gradient is between 1600 and 2000TW per year [12] and can generate 1MW·m$^{-3}$·s$^{-1}$ of water passing through the membrane [13]. In
the case of Colombia research has been carried out on the potential of the salinity gradient [14] but it should be noted that its scope has been only theoretical.

The objective of this study is to determine the energy potential of cyanide waters using the osmotic pressure and salinity gradient. Membrane systems fed with cyanide waters were used with two types of osmotic modules with a vertical and horizontal configuration as a precedent for process optimization and scale-up.

2. Theoretical calculations
The energy density in an osmotic pressure system is defined as the power (W) per unit area of membrane (A). A high W value determines the requirements between the area of the membrane and the size of the plant. The ideal output force is obtained by equation (1):

\[ W = A(\Delta \pi - P)\Delta P \]  

where \( P \) is the initial pressure, \( \Delta \pi \) (bar) is the pressure difference, and \( \Delta P \) is the effective hydraulic pressure. For diluted solutions, the osmotic pressure (\( \Delta \pi \)) is found by approximation using the Van’t Hoff equation:

\[ \pi = V_i C_i RT \]  

where \( V_i \) is the number of ions of solute formed in the solution (\( V_i = 2 \) for NaCN), \( C_i \) is the molar concentration of solute, \( R \) is the gas constant, and \( T \) the absolute temperature (K), \( V_i C_i \) is the total concentration of ions (kmol·m\(^{-3}\)).

3. Experimental procedure
Thirty tests were performed in each module configuration (vertical and horizontal) to determine the energy potential. A General Electric (GE) Osmonics membrane was used for each module under six concentrations of NaCN (25, 50, 100, 200, 500, and 700mg·L\(^{-1}\)). The experimental procedure was developed in three phases described below.

3.1. Polymeric membrane characterization
The membranes were subjected to a preparation and drying test in which four 3cm×1cm membrane samples were immersed in cyanide water with four concentrations of NaCN (25, 50, 100 and 200mg·L\(^{-1}\)) for 24 hours. After the immersion period, the samples were taken to a vacuum desiccator with a volume of 1.5L for 24 hours. Then, dried membrane samples were passed to a Scanning Electron Microscope (JEOL JSM-6380LV, Tokyo, Japan) where images were taken on both sides of the membrane samples. The approximations were 100×, 1000×, 10000× and 100000×. Finally, the elemental composition of the membranes was determined by Energy Dispersive X-ray Spectroscopy (EDS) for each membrane sample.

3.2. Experimental runs
As seen in Figure 1, each membrane module (vertical and horizontal) had a stainless-steel and a perforated Teflon sheet as support media. Neoprene gaskets were used to seal the points of attachment of the two containers. The volume of each module was 8L. Cyanide water and fresh water were fed into each container side by hydrostatic pressure. The only difference between the modules was the orientation of the membrane, performing on an active layer facing draw solution (AL-DS) orientation.

3.3. Energy potential calculation
The permeability coefficient of the membrane and a correlation between the hydraulic and osmotic pressure differences (\( \Delta \pi - \Delta P \)) were established to determine the energy potential. The time at which the
pressure change has started was also measured. Then, having the permeability coefficient and pressure differences for each concentration, the potential of energy potential could be calculated using equations (1) and (2).

**Figure 1.** Schematic diagram of the osmotic modules (a) horizontal (b) vertical.

4. Results

4.1. Polymeric membrane characterization

The spectrum analysis by EDS (Figure 2) revealed contents of carbon (C) and oxygen (O) due to the presence of polyamide (polymer). Low percentages of sulphur (S) were also found, which is added to improve the thermal stability and other characteristics of the polymers in percentages between 5 and 10% [15].

**Figure 2.** SEM and XRD images of (a) dry membrane sample and (b) membrane samples after being submerged into 200mg NaCN L\(^{-1}\).

The surface of the membrane did not suffer any changes, such as variation or adhesion of material on the surface, and had no pore obstruction after being exposed to cyanide waters. However, it is
observed trace values of Na and N in the EDS as expected due to the exposure of the membrane to the cyanide water.

### 4.2. Energy Density

The slope values correspond to the permeability coefficient which was $3.26 \times 10^{-3} \text{m} \cdot \text{s}^{-1} \cdot \text{bar}^{-1}$ for the vertical module and $7.51 \times 10^{-4} \text{m} \cdot \text{s}^{-1} \cdot \text{bar}^{-1}$ for the horizontal module (Figure 3). Results demonstrate the flow rate that passes through the vertical module is about 23% higher than that of the horizontal configuration.

![Figure 3. Pressure difference with respect to permeate flow for permeability coefficient determination.](image)

Table 1 revealed the maximum pressure reached in the horizontal module was about 25% lower than that of the vertical configuration. The exposure time suggests the vertical module doubled the response time of the horizontal one. Finally, the energy density per membrane area was determined using equation (1).

| Table 1. Pressure variation, osmotic starting time and power in experimental set-up. | Concentration (mg·L$^{-1}$ of NaCN) | Pressure (cm) | Time (s) | Power density (Wm$^{-2}$) |
|---|---|---|---|---|
| Horizontal module | 25.0 | 30.87 | 570 | $5.51 \times 10^{-6}$ |
| | 50.0 | 32.53 | 568 | $5.97 \times 10^{-6}$ |
| | 100 | 33.73 | 578 | $6.88 \times 10^{-6}$ |
| | 200 | 34.83 | 580 | $8.71 \times 10^{-6}$ |
| | 700 | 35.77 | 578 | $1.78 \times 10^{-5}$ |
| Vertical module | 25.0 | 40.30 | 186 | $3.27 \times 10^{-5}$ |
| | 50.0 | 41.57 | 190 | $3.39 \times 10^{-5}$ |
| | 100 | 42.13 | 184 | $3.62 \times 10^{-5}$ |
| | 200 | 44.47 | 188 | $4.07 \times 10^{-5}$ |
| | 700 | 45.53 | 186 | $6.36 \times 10^{-5}$ |

On the other hand, an exponential relationship between the electric power and the cyanide concentration is shown in Figure 4, where the vertical module exhibits a more favourable performance with a maximum value of $6.36 \times 10^{-5}$ Wm$^{-2}$ for the concentration of $700 \text{mg} \cdot \text{L}^{-1}$ of NaCN.

![Figure 4. Potential relationship between power and NaCN concentration.](image)
5. Conclusions
The energy density of vertical and horizontal configurations of an osmotic module with dead-end flow using cyanide waters as the draw solution was evaluated. The results show that the horizontal module has an energy potential of $1.78 \times 10^3$ Wm$^{-2}$; whereas, the vertical module achieved $6.36 \times 10^4$ Wm$^{-2}$ for a maximum NaCN concentration of 700 mg L$^{-1}$. The membrane permeability coefficient was $7.51 \times 10^{-4}$ m$^{-1}$s$^{-1}$bar$^{-1}$ and $3.26 \times 10^{-4}$ m$^{-1}$s$^{-1}$bar$^{-1}$ for the horizontal and vertical modules, respectively, which means an increase in permeability of 23% in the vertical module. On the other hand, the start time of the osmotic pressure in the vertical module was over 50% faster than that the horizontal configuration. The characterization of the membrane confirmed its properties did not change or presented pore obstruction due to contact with cyanide waters. Thus, it is recommended to optimize the process by testing diverse types of membrane and different configurations for future scale-up.

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