A Study of Thermodynamic (Cylinder-Piston) Model Energy Production By Pressure Retarded Osmosis (PRO) (Case Study of Lake Orumiyeh)

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ABSTRACT   *The renewable energies are infinite sources of energy that, unlike fossil fuels, have no environmental problems; therefore, interest in such sources is increasingly growing in recent years. In this study, we have studied the thermodynamic model for production of osmotic energy through the Pressure Retarded Osmosis (PRO) and its dominant equations. The thermodynamic cylinder-piston model was utilized for calculation of the produced work. Through this model we have investigated the possibility of producing osmotic energy from waters of Lake Orumiyeh and the rivers entering it, in order to decide about establishment of an osmotic power plant in Iran. The results indicated that the amount of osmotic energy attained from mixture of Lake Orumiyeh water with that of its rivers, respectively with different concentrations of 320 gram/lit (5641.042 mol/m3) and 1 gram/lit (17.1 mol/m3), is -15.5487 mega-Joules per one cubic meter of mixed water. Therefore, the Pressure Retarded Osmosis confirmed that economically it is a method comparable with other methods of energy production.*

1. Introduction

As renewable energies are sustainable unending sources of energy without the environmental problems of fossil fuels, interest in these sources of energy has increased (Brogioli 2009). One type of renewable energy is salinity gradient energy or osmotic power which, based on thermodynamic principles, can be extracted from mixture of freshwater and saltwater entropy (Skilhagen.et al. 2008; Seppak and Lampinen 1999) . When we mix seawater and river water, salt concentration difference between the two solutions with different concentrations produces entropy (Loeb 1988). The achieved work results from cooling of the mixture for less than 0.08°c for an optimized process. This kind of energy has many advantages; here we mention some of these advantages: Salinity gradient is a special renewable, frequent and environment-friendly source of energy. It is a source of energy with permanent yield, that is, its energy production does not depend on climate conditions, and it can produce power constantly for 24 hours. Osmosis is a natural process that releases no carbon dioxide. This type of energy is harvested with no interference in environmental parameters. In places like estuaries where the saltwater mixes with freshwater a large amount of potential energy

released, which can be used for power production. This kind of energy can be obtained through methods like PRO, reverse electrodialysis and condenser(Post et al. 2007; Post et al. 2010). In PRO the flow of water results from distribution of over a permeable membrane with selective permeation which allows small molecules to cross but stops large ones(McCutcheon and Elimelech 2008; Thorsen and Torleif 2009). Nowadays many studies are conducted on the issue of PRO method for energy production, and in future it will be more developed and enhanced. In the present study the thermodynamic cylinder-piston model for production of osmotic energy via PRO method and its dominant equations have been investigated.

2. Methodology

2.1 Osmotic Pressure

To obtain osmotic energy from the process of mixing cylinder-piston, we consider Fig (1), the piston is a permeable membrane which only allows for water molecules to cross and holds salt molecules (the cylinder is isolate and has no heat dissipation). It is assumed that river water and seawater just contain NaCl, so we filled two sides of the cylinder with seawater and river water with specific initial concentrations and specific primary volumes (these solutions are not refreshable).

Water molecules cross the membrane from river water side and entering the seawater make the solution dilute; consequently volume of water in seawater side gradually increases. This action continues until that salt concentration in both sides of the cylinder equals. Fig (2a) and (2b) show the primary and final condition of the process. Regarding mass balance the final volumes of the sides for seawater and river water can reach to the following measures:
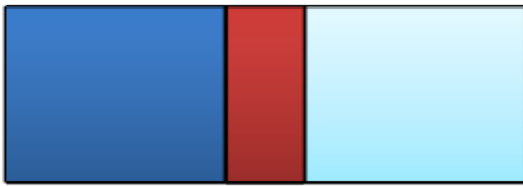

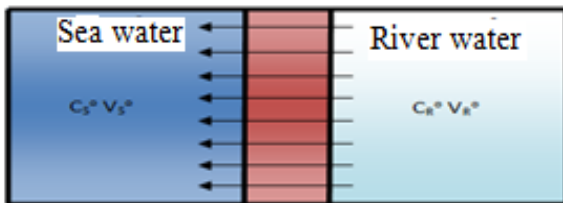**Fig**.1. Primary condition of cylinder-piston condition in the permeable membrane

Fig .2a. The primary condition for permeation of river water through the membrane into seawater.
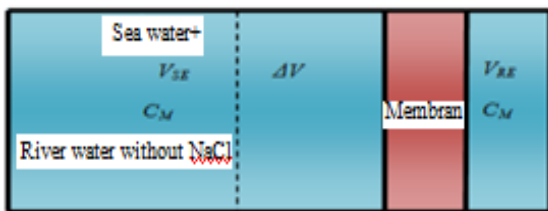

Fig.2b. The final condition of permeation (as the amount of work done) in cylinder-piston model.

2.2 Cylinder-piston formulation for production of energy through Pressure Retarded Osmosis (PRO)

As Fig 2a shows a permeable membrane (only for water molecules) separates the diluted solution with initial concentration of C_R^0 and initial volume of V_R^0, from another solution with initial concentration of C_S^0 and initial volume of V_S^0. With the assumption of an ideal membrane, which completely rejects NaCl and only water can cross it, and based on Vant Hoff relations (ideal solution) osmotic pressure the of solution is as follows:

$$\pi = \Phi.i.C.R.T$$

(1)

Difference in osmotic pressure forces water from the feeding solution side to the other side; as water crosses the membrane it dilutes the other side solution (seawater) this dilution process continues until concentration of seawater reaches to the following amount: (Elimelech and Bhattacharjee 1998) :

$$C_S = \frac{C_S^o . V_S^o}{[V_S^o + \Delta V]}$$

(2)

As a result of complete rejection of salt, concentration in river water increases and hydraulic pressure persists until concentrations of the two solutions become equal. So while the concentrations are balanced the osmotic power reaches to zero ($\Delta \pi = 0$). Concentration of the solution in this point is calculated through equation (3):

$$C_R^f = C_S^f = (1 - \Psi).C_S^o + \Psi.C_R^o = C_M$$

(3)

$$\Psi = \frac{V_R^o}{[V_R^o + V_S^o]}$$

(4)

As in comparison with water, salt amount is insignificant, Ψ almost equals mole fraction. According to Vant Hoff rule difference of osmotic pressure can be expressed by the following equation :

$$\Delta\pi = \Phi.i.R.T.\Delta C = \Phi.i.R.T.\left[\frac{C_S^o.V_S^o}{[V_S^o+\Delta V]} - \frac{C_R^o.V_R^o}{[V_R^o+\Delta V]}\right]$$

(5)

In which, ΔV is volume of the water that crossed the membrane, and according to equation (6) it has a linear proportion with concentration difference. The process is generally toward decreasing hydraulic pressure, this processing continues with short paces towards reduction of ΔP to reach to ΔP=Δπ on a point throughout the process.

$$\Delta C = (CS - CR)$$

(6)

2.2.1. *Calculation of Ideal Work*

It is expected that in the thermodynamic reversible process of PRO the achieved work be ideal. While the volume of seawater is increasing, through integrating ΔP, we can write:

$$W_{ideal} = \int_0^{\Delta Vf} \Delta P.d(\Delta V)$$

(7)

By placing equation (5) in equation (7) considering (ΔP=Δπ) and integrating it the ideal work per volume unit is obtained as the following equation in which negative sign is indicative of work production by the system (Achilli., et al. 2009).

$$-\left[\frac{W_{Ideal,V_R^0}}{\Phi.i.R.T}\right] = \left(\frac{C^f}{\psi}\right).Ln(C^f) - (C_R^o).Ln(C_R^o) - \left[\frac{(1-\Psi)}{\psi}\right].(C_S^o)Ln(C_S^o)$$

(8)

2.2.2 *Calculation of Real Work*

In the real process of PRO the saltwater side experiences a hydraulic pressure, and then permeation of water through the membrane starts; it continues till pressure reaches to Δπ, therefore, we can write:

$$\Delta V^f = \Delta V$$

(9)

that ΔV^f is the volume of the final permeation.

$$\Delta\pi = \Delta P$$

(10)

$$\Delta P = \Delta\pi = \Phi.i.R.T.\left[\frac{C_S^o.V_S^o}{[V_S^o+\Delta V]} - \frac{C_R^o.V_R^o}{[V_R^o+\Delta V]}\right]$$

(11)

$$W_P = \Delta P.\Delta V = \Phi.i.R.T.\left[\frac{C_S^o.V_S^o}{[V_S^o+\Delta V]} - \frac{C_R^o.V_R^o}{[V_R^o+\Delta V]}\right].\Delta V$$

(12)

The permeation volume is function of ΔV and W_P, therefore maximum ΔV and maximum ΔP obtains of equation flow:

$$\frac{dW_P}{d\Delta P} = 0$$

(13)

$$\frac{dW_P}{d\Delta V} = 0$$

(14)

$$\Delta V^* = \left[\frac{\sqrt{C_S^o} - \sqrt{C_R^o}}{\sqrt{C_S^o} + \frac{\psi}{1-\Psi}\sqrt{C_R^o}}\right].V_R^o$$

(15)

$$\Delta P^* = \Phi.i.R.T.\left[(1-\Psi).C_S^o - \Psi.C_R^o + (2\Psi - 1).\sqrt{C_S^o}.\sqrt{C_R^o}\right]$$

(16)

So, maximum work that obtain of the PRO proceeding as flow (Lee et al., 1981) :

$$W_{P,MAX} = \Delta P^*.\Delta V^* = \Phi.i.R.T.(1 - \Psi).\left[\sqrt{C_S^o} - \sqrt{C_R^o}\right]^2.V_R^0$$
(17)

2.2.3 Frictional Dissipation

As the process of constant pressure PRO is not a totally reversible, the real work is less than the attainable ideal work. While water crosses the membrane, friction force among molecules of water and membrane resist to reach to hydraulic pressure (overcoming the resistance formed by hydraulic pressure). In order to get to a nonzero amount the water flow crossing the membrane spends a part of osmotic force to overcome resistances. Equation (18) shows friction losses.

$$Fractional\ losses = \int_0^{\Delta V^*} \Delta P.d(\Delta V) - \Delta P^*.\Delta V^*$$
(18)

2.2.4   Unusable Energy

In a constant pressure PRO the real volume of permeation is a bit less than the volume of the water needed for pressurizing saltwater, which, is due to permeation limits. When difference of osmotic pressur equals the hydraulic pressure (ΔV^f-ΔV^*) volume is not applied for production of useful work, called unusable energy. The following equation indicates this fact (Loeb 1976; Loeb et al.1990).

$$Unutilized\ Energy = \int_{\Delta V^*}^{\Delta V^f} \Delta P.d(\Delta V)$$
(19)

$$\Delta G_{mix} = W_{P,max} + Fractional\ Losses + Unutilized\ Energy$$
(20)

2.2.5 Energy of Mixture

When two solutions with different components are mix, the mixture's Gibbs Free energy releases. Consider a two solution system with a strong electrolyte, for example solutions A and B are different solution contents of M. Difference between Gibbs Free energy of the mixture (G_{Mix}) and that of the primary solutions (G_A & G_B) shows energy changes of the mixture. For the system Gibbs free energy per mole equals ΔG_{Mix} which can be expressed by the following equation.

$$-\Delta G_{Mix} = R.T.\left[\left[\Sigma X_i.Ln(Y_i.X_i)\right]_M - \Psi_A.\left[\Sigma X_i.Ln(Y_i.X_i)\right]_A - \Psi_B.\left[\Sigma X_i.Ln(Y_i.X_i)\right]_B\right]\Psi_B$$
(21)

Ψ_A and Ψ_B are total mole fraction ratios in solutions A and B, which are related to each other as follows:

$$\Psi_A + \Psi_B = 1$$
(22)

ΔG_{Mix} depends on the primary conditions of Ψ_A and Ψ_B solutions (and X_i and Y_i for mixing processes) in constant pressure and temperature; and the sign of it indicates the least energy needed for decomposition of the solution M into solutions A and B. for a binary system with strong electrolyte with particles of water and salt completely separate from each other (w for water and s for salt). Mole fraction and activation of solutions with low concentration almost equals one. Therefore, $l_n(y_w.X_w)$ for the primary solutions is zero. Then equation (21) after simplification becomes equation (23) (Post et al; 2009)

$$-\left[\frac{\Delta G_{MIX}}{\Phi.i.R.T}\right] = \left[\left[\Sigma X_i.Ln(y_i.X_i)\right]_M - \Psi_A.\left[\Sigma X_i.Ln(y_i.X_i)\right]_A - \Psi_B.\left[\Sigma X_i.Ln(y_i.X_i)\right]_B\right]$$
(23)

As the system volume remains constant during mixing process ($V_A+V_B=V_M$) and the salt volume fraction is ignorable compared with water volume. Therefore, the mole fraction is almost equals volume fraction, and Gibbs free energy of the mixture per volume unit of mixture $\Delta G_{Mix,VM}$ is defined as follows:

$$-[\frac{\Delta G_{MIX,V_M}}{\Phi.i.R.T}] =$$
$$C_M.Ln(\gamma_{s,M}.C_M) - \Psi_A.C_A.Ln(\gamma_{s,A}.C_A) - (1 - \Psi).C_B.Ln(\gamma_{s,B}.C_B) \quad (24)$$

For production of power from salinity gradient, seawater is often unlimited and river waters that enter it are limited. In the diluted solution energy of mixing is accessible and measureable per volume unit. Since:

$$\frac{V_M}{V_A} \approx \frac{1}{\Psi}$$
(25)

Gibbs free energy of mixing process (in the diluted solution) is given by equation (26). For mixing G_{Mix} is a function of seawater, river water and mole fracture of river water.

$$-[\frac{\Delta G_{MIX,V_M}}{\Phi.i.R.T}] \approx [\frac{C_M}{\Psi.ln(\gamma_{S,M}.C_M)}] - C_A.Ln(\gamma_{s,A}.C_A) -$$
$$[\frac{(1-\Psi)}{\psi}].C_B.Ln(\gamma_{s,B}.C_B)$$
(26)

2.2.6 Thermodynamic Cylinder-Piston Model for Theoretical Energy Production in PRO

The processes of solving and permeation can be similar through a cylinder-piston in which the piston is a permeable membrane. Water permeates from river water-side to the sea water-side and seawater-side increase and produces energy (Images 2a and 2b). Due to the insignificant temperature drop during the process, we can assume it an isothermal processing. The work done in this process can be calculated by the classic equation of osmotic pressure and Vant Hoff equation:

$$(\pi.V) = n.R.T$$

(27)

$$C = \frac{n}{V} \quad and \quad \pi = i.C.R.T)$$

Entering the osmotic reflection coefficient and concentration amount in the equation (27) equation (1) forms, which can be rewritten as the following.

$$\pi = i.\Phi.\frac{n}{V}.R.T = \frac{i.\Phi.n.R.T}{V}$$
(28)

Using the relation $C = \frac{n}{V}$ we can write:

$$n_S = C_S.V_S = C_S^o.V_S^o = C_M.V_{SE}$$
(29)

So the thermodynamic work of the expansion process is defined as:

$$W_{PROexp} = -\int \pi.dV$$
(30)

When concentrations of water in both sides of the permeable piston equals to C_M (the final concentration of seawater at the end of permeation process) the process stops, from mass balance the final volumes of seawater side V_{SE} and river water side V_{RE} reach to the following values:

$$C_M = \frac{C_S.V_S+C_R.V_R}{V_S+V_R}, \quad V_{SE} = \frac{C_S.V_S}{C_M}, \quad V_{RE} = \frac{C_R.V_R}{C_M}$$

The amount of the work produced (expansion process) by the volume increase that resulting permeation river water into the seawater side in PRO model, is obtained as follows:

$$W_{PROexp} = -[i.\Phi.R.T].[C_S.V_S.Ln\left(\frac{V_{SE}}{V_S^o}\right)]$$

(31)

Therefore, The work produced by condensation process (the energy consume for contraction of river water) can be computed as well. Considering $n_R=C_R^0$. $V_R^0=C_M.V_{RE}=C_R.V_R$, like expansion work, condensation work can be expressed as follows:

$$W_{PROcon} = -\int \pi.dV$$

entering similar relations and integration leads to the following relation:

$$W_{PROcon} = -[i.\Phi.R.T].C_R.V_R.Ln\left(\frac{V_{RE}}{V_R^o}\right)]$$

(32)

Net work is obtained by summing up the works produced from both expansion and condensation processes (equations (31) & (32)) which equals the energy attained from entropy of mixing seawater with river water (McCutcheon and Elimelech 2012)

$$W_{PRO} = WPROexp + WPROcon =$$

$$-[i.\Phi.R.T].[\ C_S.V_S.Ln\left(\frac{V_{SE}}{V_S^o}\right) + C_R.V_R.Ln\left(\frac{V_{RE}}{V_R^o}\right)]$$

(33)

3   Result and Discussion

3.2   The potential of Lake Orumiyeh for production of energy through PRO model

Lake Orumiyeh is located 17 kilometers east of Orumiyeh, north-west of Iran. It is the second one of its type for salinity, size and Artemia habitat, after the Great Salt Lake in United State of American . It is also the twentieth lake in the world, and one of the highest and largest lakes in Iran. Lake's surface area is about 51450 square kilometers, of which about 5750 $_{klm}{}^2$ is the area of the lake itself and 35120 $_{klm}{}^2$ is for the 21 rivers entering it. The average height of the lake form sea level is about 1278 $_m$; its average depth is about 6$_m$,

and the utmost depth has been reported to be about 22$_m$. Due to the high amount of salts the lake's water is very heavy; most frequent cations are sodium and magnesium, and most frequent anions are magnesium and sulfurs respectively. Its water's difficulty degree and conductivity is high. Water temperature varies in different seasons and months (from zero to -21 in winter to 35 to 40 degrees in summer). Special weight of the lake water is 1.113 to 1.28, or in other words its average salinity has been reported to be 320 $_{gr/Lit}$. Total amount of water flow of its rivers is 127.75$_{m3/s}$. the following table indicate the annual water flow of the Lake.

Table. 1. The annual water flow of the rivers entering Lake Orumiyeh

River Name	River lenth (Km)	Area (km^2)	Volume annual (10^6 m^3)
Zareine Rod	340	11897	1642
Simine Rod	145	3656	503
Mehabad chay	80	2151	351
Godar chay	100	2137	425
Barandoz chay	70	1318	268
Shahr chay	70	720	260
Nazlo chay	85	2267	399
Roze chay	51	453	41
Zola chay	84	2090	140

2.3 Osmotic energy obtained from mixing Lake Orumiyeh water and interring rivers water with use thermodynamic model processing (cylinder-piston)

Table (2) shows the experimental concentration and volume of Lake Orumyeh water and its rivers'. As the data of the table indicate Lake Orumiyeh has a high potential for a good electrolyte with high

entropy degree. Lake's salt is mostly NaCl, for which in an ideal diluted solution Vant Hoff's Coefficient (i) is 2 (i=2) and its osmotic coefficient is (Φ= 0.9). The value of the released energy via the above thermodynamic model is computed as follows:

Table .2. Average specifications of sample volume (water of Lake Orumiyeh and its rivers)

Type	Volume sample (m^3)	Concentration (g/lit)	Molarity (mol/m^3)	V_{SE}, V_{RE}, V_M
Orumyeh Lake	1	330	5641.042	1.9939
Rivers interring	1	1	17.1	0.0061
Mixing (Lake and River)	2	165.5	2829.062	2

3.2.1 Calculation of the work produced in expansion stage (W_{PROexp})

According to the data obtained from various samples and simulation of osmosis with cylinder-piston model we can attain the specifications of the mixture of sea water (saltwater) and river water, and then calculate the amount of the work produced (in expansion stge) from volume increase of osmosis process on the seawater side in PRO model as follows:

$$C_M = \frac{(5641.042*1+17.1*1)}{2} = 2829.062 \ mol/m^3$$

$$V_{SE} = \frac{(5641.042*1)}{2829.062} = 1.9939 \ m^3$$

$$V_{RE} = \frac{(17.1*1)}{(2829.062)} = .0061 m^3$$

$$R = 8.314 \ \frac{KJ}{Kmol} \quad , \quad T = 298.15K \quad , \Phi = 0.93$$

$$R*T = 8.314*298.15 = 2478.8191 \frac{Kj}{Kmol}$$

$$W_{PROexp} = -\int \pi.dV = -[i.\Phi.R.T].[C_S.V_S.Ln\left(\frac{V_{SE}}{V_S^o}\right)]$$

$$W_{PRO \ exp} = -(2*0.93)$$
$$* \ 2478.8191 \Big\{(5641.042*1)$$
$$* \ln(\frac{1.9939}{1})\Big\} = -18.14 \ MJ$$

3.2.2 Calculation of the work produced in condensation stage (W_{PROcon})

In PRO model the work produced in contraction phase is done by flow of water from seawater side toward river water (a part of energy spent for contraction of river water); as $n_R = C_R^0$. $V_R^0 = C_M.V_{RE} = C_R.V_R$ then it is calculated like that of expansion process.

$$W_{PROcon} = -\int \pi.dV = -[i.\Phi.R.T].C_R.V_R.Ln\left(\frac{V_{RE}}{V_R^o}\right)]$$

$$W_{PRO \ con} = -(2*0.93)*2478.8191$$
$$* \Big\{(17.1*1*\ln(\frac{0.0061}{1})\Big\}$$
$$= +0.402048Mj$$

As the pure work is the total amount of expansion work and contraction work, we'll have:

$$W_{PRO} = W_{PROexp} + W_{PRO\ con} = -17.74\ kj$$

The expansion work and the condensation work have been shown in fig (3) and (4). As temperature drop in this process is insignificant we assume it an isothermal process. The area under the diagram (P-V) indicates the work done by the expansion and contraction systems.
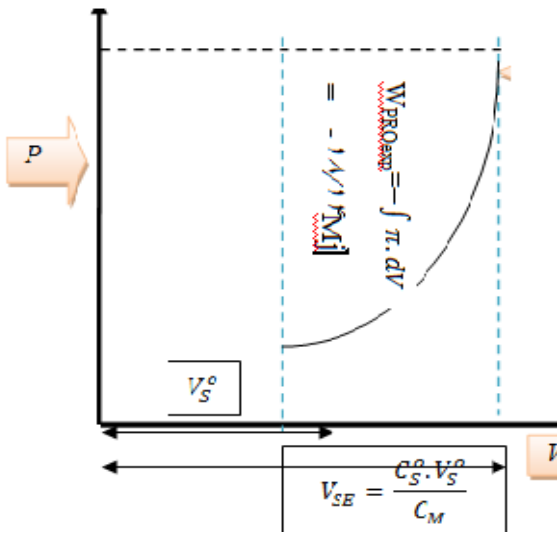

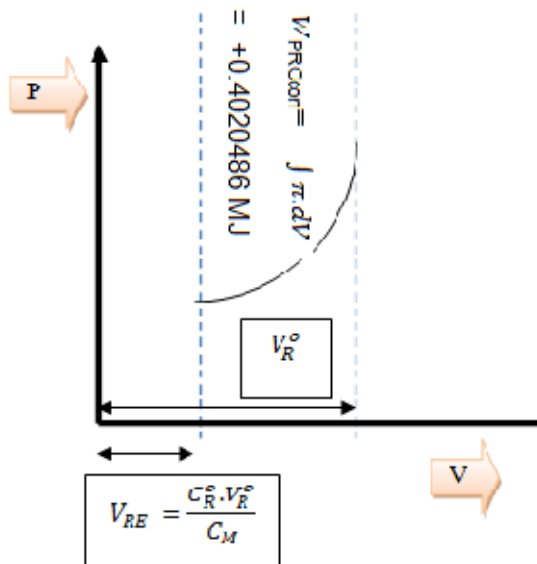**Fig. 3.** Expansion work of the isothermal process

Fig. 4. Contraction work in cylinder- piston model

Table (3) shows world's electricity consumption during the years 2003 to 2012. The average consumption in this time period has been $16300\ Twh$, while the potential osmotic energy of the rivers all over the world is about $14400\ Twh$, of which due to ecologic and economic conditions only $1600\ Twh$ is usable. Osmotic energy will not solve the world's energy crisis but it is a cheap and sustainable source of energy which supplies about 10 percent of the world's energy. This amount can be increased considerably if we use natural and artificial lakes too, therefore, salty lakes will have a remarkable growth, and in local size osmotic energy will be an important source for supplying energy.

Table.3 Consumption electrical energy in the world (TWH)

year	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012
Consume (TWh)	13810	13940	14280	15450	16330	16880	17480	17930	17780	19090

Conclusion

In this study we investigated the thermodynamic model for production of osmotic energy by PRO method and its dominant equations. We also studied production of osmotic energy from Lake Orumiyeh and its rivers by thermodynamic (cylinder- piston) model, and establishment of an osmotic power plant in Iran. In thermodynamic model the amount of pure work is produced by

osmosis process, directed from freshwater (river water) side to the saltwater (lake water) side. This force increases the height of piston in cylinder-piston model which is equivalent for osmotic pressure. Difference in osmotic pressure makes water to flow from feeding solution side to the other side of the system, consequently water crosses the membrane and makes the other side solution (seawater) diluted; this dilution process continues till concentration of seawater reaches to $C_S = \frac{C_S^o . V_S^o}{[V_S^o + \Delta V]}$ .This concentration decrease and pressure increase in dense water side leads to production of osmotic pressure in saltwater. Because of high amount of salts in salty lakes their water density is much higher than normal water.

anions are chlorors and sulfates respectively. The results obtained from this study indicate that the amount of osmotic energy attained from mixture of Lake Orumiyeh water with that of its rivers, respectively with different concentrations of 320 gram/lit (5641.042 mol/m^3) and 1 gram/lit (17.1 mol/m^3), is -15.5487 mega-Joules per one cubic meter of mixed water. Therefore, the Pressure Retarded Osmosis showed that economically it is a method comparable with other methods of energy production.

Name	Abbreviation	Unit	Name	Abbreviation	Unit
Work of contraction phase	W_{PROcon}	Mj ; j	Absolute Temperature	T	K
Work of contraction phase	W_{PROexp}	"	Primary Volume of Seawater	V_S^o	Lit, m^3
Maximum Extractable Work	$W_{P,MAX}$	"	Primary Volume of River water	V_R^o	"
Gibbs Free Energy of Mixing, for volume unit of mixture	$\Delta G_{mix,VM}$	"	Volume of the Water Crossed the through Membrane to Seawater	ΔV	"
Osmotic Pressure	π	Atm, Pa	Volume of Mixture	V_M	"
Solution Concentration	C	g/lit	Mole Fraction of particle i	X_i	--
Seawater Concentration	C_s	"	Osmotic Reflection Coefficient	Φ	-
Primary Seawater Concentration	C_S^o	"	Number of Ions	i	-
Final Seawater Concentration	C_S^f	"	Total Molar Ratios in Solutions A&B	Ψ_A , Ψ_B	-
Final River water Concentration	C_R^f	"	General Gas Constants	R	$\frac{KJ}{Kmol.k}$
Saltwater (produced mixture) Concentration	C_M	"			
An actiivity coefficient for the behavior of the solution which is a function of temperature, pressure and mixture composition.				Φ	--

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