The DesEl System – Capacitive Deionization for the Removal of Ionic Contaminants from Water

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Abstract

ENPAR's DesEl System represents a new approach to the treatment of a variety of water/wastewater streams including sea water desalination applications. The DesEl system combines high water recoveries with high ion removal efficiencies. The system operates on the principle of capacitive deionization to remove ionic compounds referred to as total dissolved solids (TDS).

A significant advantage of the DesEl System over conventional water treatment systems for the removal of total dissolved solids is the fact that a sustained concentrate is not formed thereby eliminating the need for pretreatment at high recoveries when treating hard waters.

Using bench scale units consisting of a single cell with a total electrode surface area of 0.7 m^2 and an operating flow rate range of 300 to 500 mL/min, water recovery rates of greater than 98% and ion removal rates of greater than 99% have been achieved.

This paper presents results from five test cases typical of a number of studies that have been conducted over the past twelve months.

Capacitive Deionization

The main component of the DesEl System is a novel, electrostatic charging system which behaves as a capacitor and is comprised of inexpensive carbon electrodes. The capacitor is energized using direct current, creating positive and negatively charged surfaces. Ionic compounds such as iron, chloride, arsenic and nitrate are attracted to and electrostatically adsorbed onto the surface of the electrodes (Figure 1).

To regenerate the system, the polarity of the cell is reversed causing the capacitor to release the contaminants into the cell channels. The contaminants are removed from the cell by flushing with a small quantity of liquid forming a concentrated solution.

The operating potential is relatively low (approximately 1.2V) such that no electrolysis reactions occur precluding breakdown of the capacitor material and the formation of secondary solid phases.

Previous designs of capacitive deionization systems were limited to the treatment of relatively low ionic strength solutions (<3000 mg TDS/L). The reason for its limited application has been identified as the high pore volume to surface area characteristic of the carbon electrode material. The high pore volume of the material traps salts like a sponge resulting in Coulombic inefficiencies.

In order to overcome this limitation, the DesEl unit employs the "Charge Barrier" innovation consisting of ion selective layers. This innovation enables >90% water recoveries for brine with similar potential for seawater.

Lifetime testing has been demonstrated treating hard water at 80% water recovery for extended periods with insignificant reductions in efficiency and minimal pretreatment consisting of a 15 micron cloth prefilter only (Bino et. al., 2003).

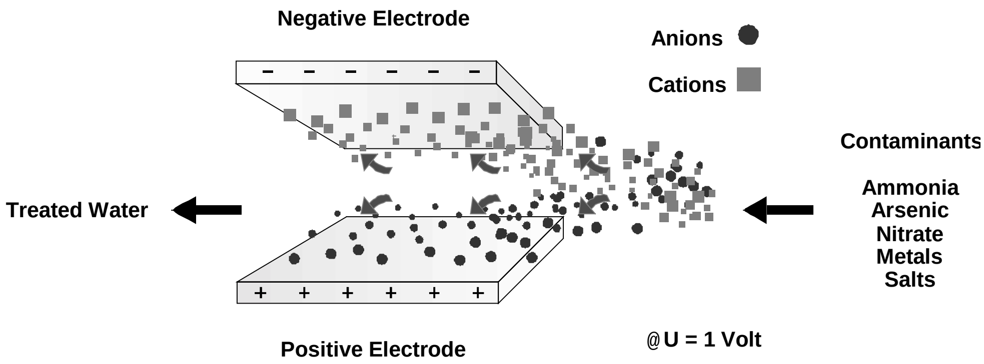

Figure 1. Capacitive Deionization

The main advantages of the DesEI System over conventional water treatment technologies are:

1. No sub 15 micron-filtration required.
2. No sustained concentrate leading to the formation of precipitates and fouling.
3. Extremely high water recoveries coupled with high ion removal efficiencies.
4. Long life cycle of capacitor materials.
5. Low maintenance.
6. No continued addition of salts to treated water as with ion exchange.
7. Chemically stable components preclude the introduction of foreign materials into the treatment stream.
8. Readily removes problem contaminants such as nitrate, perchlorate and arsenic.
9. Can be designed to preferentially remove contaminants without complete deionization of the water stream.
10. Can be operated at various levels of ion removal and water recovery efficiencies.

DesEI System

Testing has been conducted using bench scale units (Figure 2) consisting of a single capacitor cell with a total electrode surface area of 0.7 m^2 (Figure 3). With an operating flow rate range of 300 to 500 mL/min, water recovery rates of greater than 98% and ion removal rates of greater than 99% have been achieved.

Figure 2. DesEI Bench Scale Test Unit

In a comparative examination of water treatment technologies, life cycle testing conducted over a period of 90 days showed no reduction in the average ion removal efficiency for the capacitive cell at a constant water recovery of 80%. In contrast, a 15 % decline in water recovery (reduced from 35% to 30%) was noted for reverse osmosis within a 60 day period and a substantial decrease in ion removal efficiency at 30% water recovery was noted for electrodialysis with TDS increasing from 120 mg/L to 550

Figure 3. The capacitor cell

mg/L in the treated water within a 140 minute run time (Bino et. al., 2003)

TDS Removal from Intake Process Water

Tests using the DesEl System were conducted using water from Hamilton Harbour located at the extreme east end of Lake Ontario in the Province of Ontario, Canada. This water is typically used as process water by local industries.

In collaboration with a steel company, a study was initiated to reduce the concentration of calcium and chloride to 40 mg/L and to 60 mg/L respectively in the treated water stream. The unit was operated at a water recovery of 90%. The concentration of TDS in the treated water was decreased by >80% compared to the input water (Table 1). The objective of the test was greatly exceeded. The concentration of calcium was reduced by 90% from 55 mg/L to 5.4 mg/L. The concentration of chloride was reduced by more than 80% from 121 mg/L to 21 mg/L.

Selective Removal of Nitrate from Drinking Water

Collaboration with a party located in the middle east focussed on the application of the DesEl System to selectively remove nitrate from a potential source of drinking water. The water sample collected from the site contained an average nitrate-N concentration of 31 mg/L, which is three times the maximum concentration of nitrate-N of 10 mg/L allowed in drinking water based on US Environmental Protection Agency (EPA) guidelines. The primary objective of the work was to adapt the DesEl technology for the selective removal of nitrate from the drinking water source while preserving the original taste of the water. Concentrations of nitrate were to be reduced to **just less than 10 mg/L** in order to minimize the removal of counter-ions and consequently minimize changes in taste.

The DesEl reactor was modified to target the selective removal of nitrate. The tests were conducted to optimise the operating parameters of the reactor to suit the particular chemistry of the sample. Chemical analyses for the input water (mean of 3 samples) and an example of the clean and waste streams produced by the DesEl unit are provided in Table 2.

The DesEl unit preferentially removed mono-valent ions resulting in the reduction in the concentration of nitrate-N from 31 mg/L to 9.6 mg/L and the recovery of 92% of the input water. The concentrations of sodium, potassium and chloride in the clean water were reduced by about 50% compared to the input water, while conductivity values were reduced from 1.3 to 0.87 mS/cm only.

The TDS of the treated water was reduced from 787 mg/L to 512 mg/L, which approaches the US-EPA secondary standard (aesthetic standard) of 500 mg/L (US EPA Publication 816-F-03-016, June 2003). The EPA secondary standard (non-enforceable guidelines regulating aesthetic effects influencing taste, odour or colour) is one of the few indices available to gauge taste.

Treatment of Ammonia/Nitrate Contaminated Groundwater

Two hundred liters of ground water containing elevated levels of nitrate and ammonia were submitted to our laboratory for testing (Table 3). The DesEl system was used to remove nitrate and ammonia from the hard groundwater, measuring a relatively high conductivity of 8.1 mS/cm, to a combined ammonia/nitrate-N concentration of less than 10 mg/L. The hard water was characterized with 240 mg calcium/L and 98 mg magnesium/L. In this application, testing, including treatment of the high

Table 1. Hamilton Water Test Results

Parameter (unit)	Input Sample	Treated Water	Waste Stream
pH	7.6	6.7	8.3
Conductivity (μS/cm)	757	117	13,450
TDS (mg/L)	462	77	Approx. 8200
Na (mg/L)	66	11	2000
Ca (mg/L)	55	5.4	208
Mg (mg/L)	15	1.6	71
Fe (mg/L)	0.37	0.12	ND
Cl^- (mg/L)	121	21	>3900
SO_4^{2-} (mg/L)	57	6.3	628

Table 2. Nitrate Water Test Results

Parameter (unit)	Symbol	Input Water (mg/L)	Cleaned Water (mg/L)	Waste Water (mg/L)
Calcium (mg/L)	Ca	69	68	170
Magnesium (mg/L)	Mg	17	17	31
Sodium (mg/L)	Na	127	59	770
Potassium (mg/L)	K	56	23	510
Nitrate Nitrogen (mg/L)	NO_3-N	31	9.6	270
Chloride (mg/L)	Cl^-	130	72	940
Sulfate (mg/L)	SO_4^{2-}	130	120	270
pH		8.0	8.0	8.0
Alkalinity (as $CaCO_3$)	$CaCO_3$	200	180	370
Total Dissolved Solids	TDS	787	512	4110
Conductivity (mS/cm)	E.C.	1.3	0.87	6.8
Percent of Input (Recovery)		100%	92%	8%

Table 3. Test results using two-stage purification

Parameter (unit)	Groundwater	Treated Water - Run Number				
		C1-14	C2-10	C2-12	C2-20H	C2-30
pH	7.7	5.99	5.92	5.96	6.02	6.36
Conductivity (uS/cm)	8,100	109	588	775	442	168
Ammonia-N (mg/L)	**493**	**3.2**	**5.6**	**6.4**	**6.3**	**5.3**
Nitrate-N (mg/L)	**270**	**3.8**	**2.9**	**2.7**	**5**	**2.3**
Water recovery (%)	n.a.	87	79	82	90	87
Water recovery following waste concentrating step (%)	n.a	95	91	92	96	95

ammonia/nitrate concentrate using our patented electrochemical process, was used to convert the nitrogen compounds to environmentally-friendly nitrogen gas.

The DesEl system was found to be effective at removing the ammonia-N and nitrate-N compounds to below the target level of 10 mg/L total nitrogen from initial concentrations of 500 and 270 mg/L respectively (Table 3). Water recoveries up to 95% were achieved using a multi-stage system.

Finally, no evidence of fouling resulting from the formation of secondary solid phases was noted.

Treatment of Brackish Mine Waste Water

Mine wastewater with high TDS from the northern region of the Province of Quebec, Canada, was submitted for testing using the DesEl System. The main objective was to develop a multi-stage process to reduce the conductivity of the wastewater from 30 mS/cm (TDS = 25,000 mg/L) to less than 3.2 mS/cm (TDS <2,500 mg/L), a 90% reduction in conductivity. The second objective was to optimize the operation of the system to achieve a water recovery of 90% (Table 4).

Test results showed that a three-stage treatment system was readily capable of removing 90% of the conductivity (Table 4). The operation of the multi-staged system was designed such that the first two stages removed approximately 33% of the total mass while Stage III removed the remaining 24% of the total mass required to meet the 3 mS/cm objective. However, the water recovery after the three-stage treatment process failed to exceed 65%.

The solution was to include a fourth stage to recover water from the system concentrate stream. Optimization of Stage IV showed a marked increase in water recovery from 78% to the 90% level (Table 4).

Recovery of drinking water from neutralised mine water

Industrial effluents rich in sulphate, acid and metals are produced when sulphuric acid is used as a raw material, and when pyrite is oxidised due to exposure to the atmosphere, e.g. in the mining industry. Acid mine waters contains high concentrations of dissolved metals and sulphate, and can have pH values as low as 2.5. Acidic industrial effluents require treatment prior to discharge into sewage networks or into public watercourses. In water-rich countries the main causes of concern are the low pH and metal content of acidic effluents. Salinity is not a problem due to dilution with surplus capacity of surface water. In water-poor countries, such as South Africa, the high salinity associated with acidic industrial effluents is an additional concern.

The DesEl technology was evaluated for the desalination of neutralized acid mine water to produce water to meet the following requirements:

- Suitable for re-use in the coal washing plant. The main requirements in this case are that the water needs to be non-corrosive and non-scaling. The sulphate concentration needs to be reduced from 2000 to 500 mg/L.
- Suitable for drinking water. The main requirement is that sulphate needs to be removed to less than 200 mg/L.

Table 5 shows the quality of the feed and treated water when neutralized mine water was treated with the DesEl unit in two stages (primary for treatment of water suitable for discharge into public streams and secondary for treatment of drinking water). The treated water of Stage 1 was used as feed water for Stage 2. The unit was operated to achieve approximately 84% salt removal with Stage 1 and 81% with Stage 2. It is noted that:

- 77% water recovery was achieved in Stage 1 and 80% in stage 2.
- Sulphate was removed from 2400 mg/L to 499 mg/L in Stage 1 and to 118 mg/L in Stage 2. The results indicate that mine water can be treated to drinking water quality by passing it through two stages in series.

The water recovery could be increased significantly for waters with low sodium and chloride concentrations, such as shown in Table 5, through implementation of the following steps:

- Recycle the brine of Stage 2 to the feed of Stage 1.
- Allow the over-saturated gypsum in the Brine of Stage 1 to crystallize to its solubility level. The only waste is the thickened gypsum/$Mg(OH)_2$-rich sludge.

Figure 4 shows the integrated process flow diagram while Table 6 shows the predicted chemical composition of the treated water with the integrated process. It is noted that:

- Sulphate and calcium are removed to the level of the Stage 2 DesEl unit.
- Sodium and chloride are similar to the feed concentration.

This approach offers the following benefits:

- No brine treatment is required.
- A high water recovery of 98.6 % is achieved.

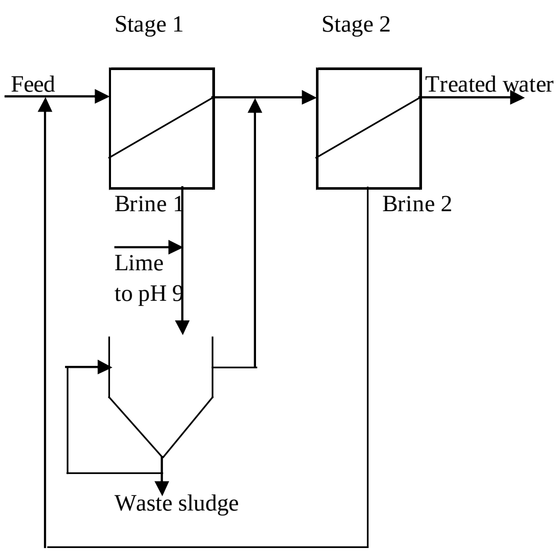

Figure 4. Integrated Process Flow Diagram

Conclusion

There is a current need for reliable high efficiency, low maintenance, minimal pretreatment technologies for the treatment of drinking water, waste water and industrial process waters. Furthermore, these technologies should be efficient at addressing problem contaminants such as nitrate and arsenic.

Finally, these treatment technologies must be capable of a high level of water recovery resulting in a low level of concentrate requiring disposal or further treatment.

The results of the studies conducted to date show the DesEl System to represent a potential solution to a several water related issues ranging from the production of deionized water and treatment of problem contaminants through to desalination applications.

Table 6. Chemical composition of

Parameter	Feed water	Final water
pH	7.5	6.5
TDS (mg/L)	3425.9	228.0
Na(mg/L)	32.0	32.0
Ca (mg/L)	914.9	45.1
Mg (mg/L)	44.0	2.2
Mn (mg/L)	5.0	0.2
SO_4 (mg/L)	2400.0	118.4
Cl (mg/L)	30.0	30.0
Water recovery (%)		98.6

References

1. Bino, M.; Kuran, S.; Andelman, M.; and Craft B. Flow Through Capacitor Technology, 2003. The International Workshop on Marine Pollution and the Impact of Seawater Desalination Plants on the Coastal Environment, at The International Center for Biosaline Agriculture Headquarters, Dubai, UAE, December 1-3, 2003

2. US EPA Publication 816-F-03-016, June 2003

Table 4. High TDS Mine Water Test Results

	Trial 1	Trial 2
Stage 1		
Input H_2O (mS/cm)	28.0	28.0
Treated H_2O (mS/cm)	18.7	19.6
Concentrate (mS/cm)	64.2	62.0
Stage 2		
Input H_2O (mS/cm)	18.7	19.6
Treated H_2O (mS/cm)	9.83	10.0
Concentrate (mS/cm)	65.8	72.0
Stage 3		
Input H_2O (mS/cm)	9.83	10.0
Treated H_2O (mS/cm)	3.00	3.10
Concentrate (mS/cm)	49.5	65.0
TDS Removal (%)	89.2	88.8
Water Recovery (%)	51	65
Stage 4		
Water recovered after Concentrate Reduction (%)	78	90

Table 5. Chemical composition of feed and treated water when neutralized mine water is passed through a two-stage DesEl unit.

Parameter	Stage 1			Stage 2		
	Feed	Treated	Waste	Feed	Treated	Waste
pH	7.7	6.3	6.4	7.5	6.3	6.5
TDS (mg/L)	3425.9	711.9	12511.8	711.9	169.1	2883.1
Na(mg/L)	32.0	6.6	116.9	6.6	1.6	26.9
Ca (mg/L)	914.9	190.1	3341.2	190.1	45.1	769.9
Mg (mg/L)	44.0	9.1	160.7	9.1	2.2	37.0
Mn (mg/L)	5.0	1.0	18.3	1.0	0.2	4.2
SO4 (mg/L)	2400.0	498.7	8765.2	498.7	118.4	2019.7
Cl (mg/L)	30.0	6.2	109.6	6.2	1.5	25.2
Water recovery (%)	0.0	77.0	0.0	0.0	80.0	0.0
Salt load (%)	0.0	16.0	84.0	0.0	19.0	81.0
Volume (ml)	4270.0	3287.9	982.1	3000.0	2400.0	600.0