Collaborative Project
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capmix:

Capacitive mixing as a novel principle for generation of clean renewable energy from salinity differences

Publishable Summary

wetsus
centre of excellence for sustainable water technology

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REDSTACK

MAST

Executive Summary

Capmix is a collaborative project gathering 6 different partners from 5 different countries. The aim of Capmix is to develop an innovative concept for energy extraction from Salinity Gradient Energy.

To this day, no Salinity Gradient Energy reached the market yet. Some technical difficulties such as fouling of the system due to real environment elements (humic acids, biofouling, multi-valent ions, scaling…) or due to technical limitation (high pumping energy costs). This is the reason why the Capmix consortium believes that there is space for a new technology that could overcome these issues.

The Capmix project relies on the properties of activated carbon based electrode to change electrical potential when the salinity of the solution it is in contact with changes. Ion exchange membranes can be added to the process to increase the potential change when solutions are switched.

During the project, the work focused on several aspects:

- modelling, to understand the fundamental properties of the system and to identify its limiting parameters and set priorities for further development
- materials, to develop new materials that are adapted to the process in place
- cell design and operation, to develop the system and its implementation, how the electrodes are set together and how the solutions are in contact with the electrodes
- early technology validation, to test the system in real conditions to identify the possible troubles that cannot be foreseen in a laboratory environment
- dissemination, to communicate and spread the knowledge about this new concept.

The Capmix project successfully met all the milestones set before the start and considerably improved the performances of the system. To this date, the Capmix technology remain behind the competitive technologies but big steps have been made and further research is needed to improve further. New applications of this technology have been made, such as the recovery of energy from other gradient sources such as carbon dioxide mixing between air and exhaust gases. These major breackthrough are opening a brand new stream of technology for the energy sector.

Summary description of project context and objectives

What is Capmix? Context of Salinity Gradient Energy and basic principles of Capmix

Salinity difference energy is the energy that can be gained by mixing two kinds of water with different salinity. The idea was formulated first in 1954 by R. Pattle in Nature [1]. Mixing 1 m^3 of fresh river water with a large amount of sea water gives a mixing energy of 2 MJ. If one would like to extract the same amount of energy from fresh water via conventional hydropower, one would need a dam with a height difference of 200 m. The power available globally in the form of salinity difference has been estimated in the 1970s (based on average ocean salinity and annual global river discharges) to be around 2 TW [2, 3]. Thus, in terms of available power, the flow of all fresh water streams combined has the potential to satisfy the current global electricity demand (≈2 TW).

In addition, the extraction of energy from salinity differences is not limited to the use of fresh water from rivers. In desert-like regions, it is possible to use the salinity difference between sea water and a more concentrated salt solution, obtained from sea water through evaporation ponds.

In principle, this type of energy generation is inherently clean as this process is based on mixing, and happens wherever the rivers flow out into the seas and oceans. There is no exhaust of CO_2 or other polluting combustion emission, and no thermal pollution will occur. This energy source is renewable as it is based on the hydrological cycle powered by the sun. However the technology to economically harvest this energy has not been developed yet.

The term has been thus coined of Salinity Gradient Energy. In it, two main technologies emerged so far: Reverse ElectroDialysis (RED) and Pressure Retarded Osmosis (PRO). These two technologies are now at the demonstration phase and are getting close to the market (especially RED). In this context, one can wonder where the need of a third technology is coming from. Capmix aims at developing a new app roach for energy extraction from salinity differences. For this, the Capmix technology uses capacitive electrodes that can adsorb ions present in the sea water and desorb these ions in river water. In the process, energy is generated. This energy generation is linked with an increase of the electrical potential of the capacitive electrodes when the solutions are changed from high salinity solutions to low salinity solutions and it is this potential increase that allows energy to be recovered. This technique is called Capacitive energy extraction based on Double Layer Expansion (CDLE).

Alternatively, the changes in potential of the electrodes proceed without the use of an external power source for the initial charging: this can be achieved by coupling the electrodes with ion exchange membranes (The technique is then called Capacitive energy extraction based on Donnan Potential: CDP). These membranes have the ability to selectively allow only one type of ions to go through them, either positive ions (cations) or negative ions (anions). With membranes, the electrical potential obtained when switching the solutions is considerably higher than without them, and thus leads to more energy being extracted.

The two approaches, i.e., with or without membranes, present fundamental differences in the physico-chemical processes involved, as well as the way they are operated. As mentioned, if no membranes are used it is initially necessary to use an external power supply in order to bring the electrodes to the condition of maximum voltage rise upon salinity exchangeIn contrast, if membranes are used, the simple exchange of solutions suffices to generate a maximum potential. They both have in common to be cyclic processes, in which sea and river water are alternatively fed to the system.

The reasons why the Capmix consortium believes that this technology is worth being developed is because it has the potential to overcome issues that are common to both RED and PRO. First of all, the very nature of the system allows more design flexibility than the other technologies. Where RED and PRO are mostly configured as stacks of membrane layers between which water has to be pumped, Capmix offers the possibility to have other configurations in which intensive pumping energy costs can be saved. RED, for example, is based on stacks of ion exchange membranes between which the water is pumped through a 100-200 µm spacers. Pumping a liquid through such a small space is very energy intensive, and this directly affects the net power production of the system. With Capmix, the possibility to have different configurations indicates that these costs can be saved if the proper design is developed.

Another major issue of these technologies is their susceptibility to fouling. In real sea and river waters, different chemical deposits are likely to be formed on the membranes and progressively inhibit their performances; in addition, micro-organisms or algae can also grow on the membrane and generate the same type of malfunction. Because Capmix is a cyclic process, the Capmix consortium believes that these fouling issues can be limited. For instance, regularly changing the salinity of the solutions going through the system is used in RED to regulate fouling; moreover, constantly changing these conditions makes it more difficult for organisms to adapt and grow on the membrane. As Capmix is by essence a cyclic process, we believe that fouling can be limited in comparison with the state of the art technologies.

Main objectives of the project

The processes have been described above in an idealistic way, to make it clear how a clean renewable power plant based on mixing fresh and sea water clear can be constructed and operated. Important is to note that for both technological concepts proof-of-principle experiments have been performed that show the possibility of this technology.

To transform this proof-of-principle into a viable technology, further insight is needed both in the scientific area, i.e. what is happening, as well as in the technological area, i.e. how can we use these principles. The research needed to achieve this objective is at the heart of this proposal. Two key measures will be used to monitor the progress in the technology development program, namely, energy recovery and power density.

The determination of energy recovery tells us how much of the energy available in the water due to the salinity difference is actually transformed into electricity. To give a considerable contribution to the electricity production, the energy recovery aimed at is high, namely, an ambitious 70%. The key measure of power density describes how much power is generated per unit volume of the plant. A high power density implies that the power plant can be smaller and less materials are needed. We aim at a power density of 100 W/m^3.

These key targets have been selected to show that the capacitive mixing process can achieve a performance level far above that of a laboratory curiosity. In this way we can show that the mixing process warrants future development to explore the huge energy resource contained in the salinity difference between sea and river water.

Based on our conviction that the capacitive principle can be the basis for a completely new green electricity generating device we set the following overall project objective: *To obtain further scientific insight in the capacitive mixing for energy generation and to create innovative designs and technology such that the capacitive mixing can be developed with a power density of 100 W/m^3 and an energy recovery of 70%.*

Sub-objectives of the project

Next to the main performance objective of the project, the Capmix work plan aimed at developing several aspects necessary to further improve on the technology:

- Fundamental understanding of the Capmix processes: through mathematical modeling the aim is to identify the main parameters limiting the Capmix technologies in order to know where to focus the efforts
- Development of new materials: to improve the performances of the Capmix technologies, new materials were developed for instance to increase the capacitance or the wettability of the capacitive electrodes or to improve the properties of the polymer based materials (less resistance, more selectivity…)
- Developing new cell designs and operational modes: creating new design that allow less electrical resistance but also less hydraulic resistance. Moreover, the Capmix systems can be operated in various ways, for instance by controlling either the potential or the current flowing between the two electrodes.
- Real life testing: Even though this project takes place in a very early stage of development, we aimed at having a first upscaled prototype operated in real conditions in order to test the effects of real sea and river water on the system.

Main Science & Technology results

The main objective of Capmix to reach a system able to operate at 100 W/m^3 at 70% efficiency was reached through various laboratory experiments. A power density of 300 W/m^3 was reached in lab conditions with an efficiency of 76%. This efficiency is defined by the portion of the energy theoretically available that can be extracted in one cycle.

We report here results that are not sensitive to be disseminated at this point.

Milestones reached:

Capmix was a 4 year project, gathering 6 European partners from 5 different countries. In order to monitor the progresses during the project, a number of milestones were set. All of them were successfully met. The milestones that are worth noting are the following:

- We successfully developed mathematical models describing the processes taking place in the electrodes for both the membrane based process and the process without membranes.
- In the same way, a mathematical model was developed to describe the effect of multivalent ions, present in both real sea and river waters. The experimental determinations confirmed the validity of the models elaborated.
- Overall, optimum locations for a future possible plant were suggested from the above results.
- We successfully developed different cell designs for both approaches (with or without membranes).
- We listed and investigated the feasibility of upscaling different types of reactor and we selected one to be practically implemented in a real environment (on the Afsluijtdikj, a dike in the north of the Netherlands that separates the sea on one side and a fresh water lake on the other side)

Capmix Spin-offs concepts:

In addition to the planned achievements, the research done in Capmix led to unexpected results which might have a great potential for further development.

- *Wire shaped electrodes:* Within Capmix, we exploited the flexibility of the system to create new, very promising electrodes which are not anymore in the form of flat stacked sheets but instead have a cylindrical shape, and which we call "*wire electrodes*". These wires consist of an electronically conductive core (graphite or platinum), covered with activated carbon (capacitive layer) and by ion exchange membranes. With such design, we can now have the electrodes virtually touching each other, considerably decreasing the electrical internal resistance of the system (which is of course a function of the distance between the electrodes), something confirmed both theoretically and in the laboratory. Moreover, it appeared that such electrodes present a much faster building up of the potential when switching the solutions. With the more traditional flat electrodes, the membrane system takes several tens of seconds to build up a steady potential, while with the wire electrodes only 1 or 2 seconds were necessary. This faster response is of great importance as when the switching takes place no power can be harvested. The relatively low duration of the switching steps compared to the duration of the whole cycle becomes very favorable for higher power production.

- *Spontaneous potential:* During the research on materials, the Capmix consortium noticed that different activated carbon materials presented different potential rise when switching solutions. This led our researchers to investigate how the system would work when the two electrodes are made of different materials. By carefully selecting the materials, it became possible to operate the membrane-less approach without the need of an external power supply. The surface properties of the materials were enough to generate the potential rise.

Based on these observations, the material development took the direction of modifying activated carbon in order to give its surface the desired properties. This led to a new generation of materials that allowed the membrane-less approach to compete in terms of performance with the approach using membranes.

- *Extracting energy from Carbon Dioxide emissions:* Salinity Gradient Energy technologies were so far focused solely on solutions with different concentrations of salt (sodium chloride). Within Capmix, we had the idea to extend the concept to other sources of gradients, other situations where a concentrated fluid is mixing with a dilute one. The first idea that emerged was to use a process that exists since the dawn of humanity: combustion. Whenever something is combusted, a gas containing a high concentration (10-15%) of CO_2 is emitted and subsequently mixed with the surrounding air containing low amounts of CO_2 (0.04%).

We proved experimentally that we could extract energy from this mixing process by applying the Capmix technology to this new gradient source. This discovery is opening a new era in the field of salinity gradient energy. We estimated through theoretical calculations that such technology applied to combustion gases from power plants could potentially increase the efficiency of these plants by up to 5%. This represents a very important market and we are very enthusiastic about further investigating this new stream of technologies.

Specific Science and Technology Results

Basic Processes & Process Modeling

- The basic principles of the membrane-less approach have been elaborated. We began with a macroscopic circuit analysis of the porous electrode response, which demonstrated experimentally that thin electrodes are optimum for minimizing current leakage. The electrode cannot be modeled as a single capacitor.
- The analysis of the electrochemical double layer in steady state conditions shows that the consideration of true ion sizes is essential for the prediction of energy output. An optimum charging voltage is predicted for given ion sizes.
- A simple model of the voltage evolution upon solution exchange permits to simulate the evolution of the electrode signal, using only one adjustable parameter, namely, the capacitance of the Stern layer. The predicted times for voltage evolution coincide with the experimentally measured ones.
- Predictions were made available concerning: electrode and cell dimensions, kinetics of charging and discharging, external load selection, maximum energy expectable.
- We may recall that one of our objectives related to "*factors that determine this performance relate to the composition of the water, structure and (surface) chemistry of the material. The models will show where advances can be made related to design, operation and material choice*". Regarding this task, we found that the composition of the exchanging solutions is of fundamental importance. Studies on material properties have shown that if, adequately selected, the membrane-less approach method can be largely improved as to power production and rate of self-discharge. Other properties such as pore size distribution or

hydrophobicity of the carbon, and surface modification by adsorbed polyelectrolytes are of major importance and are presented under the *materials* section of these results.

- As in the case of the membrane-less approach, the basic principles of the membrane-based Capmix cell (CDP) have been elaborated. Again, the macroscopic modeling allowed to describe with great accuracy the experimental results obtained.
- It was also found that during the charging step, an external power supply can be used to force the charging cycle, supplying additional charge. This so-called 'forced cycle' leads to increased useful energy extraction.
- The detailed analysis of the evolution of the double layer parameters and hence of the extracted energy can be calculated by means of a numerical solution of the differential equations of the problem. Predictions were obtained concerning the effect of the pore size and the porosity on the voltage evolution and the extracted energy per cycle.
- The developed model takes into account the different kind of pores, including macroporous ones, with pores so big that they can be modeled as having flat walls.
- The above mentioned findings concerning the improvement represented by the cylindrical wire shape, was well founded by proper modeling of the effect of alternative geometries. This contributed a solid theoretical basis to future designs of the technology.
- Our results here confirmed that the original objective of considering the effect of solution composition on Capmix technologies was an essential issue. Our calculations indicated a clear effect of multi-valent ions, always acting towards energy reduction, as compared to simple 1-1 salts. This appeared true for the two techniques, i.e., with and without membranes.
- This theoretical observation has been confirmed through experiments both at the laboratory scale and in real conditions. Divalent ions such as calcium or magnesium have a very strong effect on the potential rise of the Capmix systems. One way that can be foreseen to prevent this effect is to develop monovalent selective membranes.
- All the Capmix-based techniques involve prolonged contact of the carbon electrodes, or of the membranes covering them, with natural waters (at most, filtered in practical, large-scale applications) with moderate to high ionic strength, containing ions of various properties, salts with different solubilities and, eventually, varied compositions depending on location. This

makes the techniques quite prone to environmental alterations which might certainly compromise their performance: covering extensive parts of the active surfaces with chemicals not participating in the charge transport processes will reduce the energy production per unit apparent area of the electrodes.

- Although calcium carbonate is a principal source of scaling, it is a fortunate fact that sea water can retain substantial supersaturation in calcium carbonate, as magnesium has a high tendency to adsorb on the small crystals initially formed, and stops the growth. In the case of CAPMIX techniques, there is another point in our favor, namely, the residence time of the water is low, because cycles last typically between 0.5 and 2 minutes. Keeping in mind that seawater is acidified when electrodes are biased and that the time of water exchange is relatively short in our techniques, it is unlikely that a strong scaling effect can be produced.
- Additionally, modified electrode surfaces as well as ion-exchange membranes are well-wettable by water. Hence, the probability of surface generation of precipitated salt nuclei is rather poor. In such conditions, it is expected that electrodes should not be scaled and system should remain clean for its time of service.
- A simple model was elaborated, based on the hypothesis that comparatively large crystals deposited on the surface clog the larger pores, and small deposits can proceed to the low-radius pores instead. It is assumed that the pores affected by the crystallization do not participate in the process any more. The results of this simple model showed that even in the worst conditions, (small average pore radius, rapid heteronucleation of nuclei, 10 % of pores of the size below the scale particles occluded) after 1 hour, that is, after many CAPMIX cycles, about a 10 % decrease in energy production is predicted. Since in addition the solution going through is alternatively fresh and sea water, some washing is expected and the effect will not be as accumulative as predicted.
- Laboratory experiments based on membrane-less method indicated that there was not an important decay on the voltage rise in the first hours and therefore, neither in the extracted energy. In contrast, the CDP results show a significant decay of the voltage rise during the first hour after experimentation, although the voltage rise is maintained almost constant afterwards. We undertook a systematic investigation on the use of natural sea waters in our

experiments. In spite of the demonstrated contents of shells and sand particles, SEM observations of the electrodes after CAPMIX experiments carried out without prior water filtration showed no indication of significant contamination.

- Again, the method seems to contain in itself the healing of the contamination: this is related to the comparatively large amount of fresh water that is used during the exchange process, and the fact that the flow is tangential to the electrode and not through it.

Electrode & Material development

- Different samples of activated carbon, AC, were prepared and their pore structure was evaluated. They were compared with commercially available materials. In preparation synthetic resins and tar-pitch were used as AC precursors. These materials were carbonized and activated with KOH or CO2. Obtained activated carbons allowed to select several samples as potential candidate for energy extractions by CDP method.
- At this stage of evaluation of electrode materials the best AC seemed to be meso- and macro-porous carbon with wettable surface. To get reasonable extraction of energy from salinity gradient the best electrodes should be as thin as possible. It implies to prepare very fine AC powder with particles as small as 20 or less micrometers.
- The capacitance of commercial electrodes is higher than the homemade Capmix electrodes (28.13 F/g vs. 20.91 F/g) and their performances in the CDP system are comparable to Capmix electrodes.
- Commercial electrodes represent a viable, practical and cost-effective material for upscaling of the system.
- Various methods for surface modifications has been tested. They included chemical modifications by oxidation or amination, ammonization with NH3 followed by activation with CO2 or polymerization of polyelectrolytes within activated carbon particles. All these methods affect surface chemistry but do not alter pore structure significantly.
- Modified particles have different electrochemical character, zeta potential and electrophoretic mobility. Some materials show good enough properties as electrodes with

low current leakage and acceptable capacitance. It was possible to extract energy from salinity gradient up to power densities of several hundreds of mW/m2.

- Evaluation of extraction efficiency when electrode is prepared from the same activated carbon with different degree of surface modification is the goal of planed studies. The effect of asymmetric electrodes (one bearing negative one positive charge) will be checked regarding energy extraction.
- One of the partners studied a new procedure for oxidizing the electrodes and for modifying the electrode surface and the effects of these procedures were evaluated
- Addition of ionophores improves the electrode wettability. The electrode pores are open and not plugged with bubbles of air. It is suggested to blend binding agents with ionophores and use them in preparation of electrodes.
- In construction of a cell for energy harvesting it is suggested to use asymmetric system with two different electrodes. They should be selected to have similar spontaneous potential but different potential raise.
- The effect of ionomer use has been evaluated in two dimensions: when ionomer appear on the electrode surface and when it was used within the electrode body and mixed with a polymer binder. Both reconnaissance approaches showed interesting feature and promising performances of modified electrodes.
- The effect of the ionomer use has been evaluated in two fields: as ion-exchange membrane on the electrode surface and as the additional binder. Both approaches showed that the use of polymeric ionophores can modify the electrode properties.
- Surface charge can be regulated by pre-adsorption of ionic compounds with hydrophobic structural fragments also.
- The effect of the binder replacement to more cheaper and environmental friendly polymers showed that it is possible to obtain electrodes with new polymers. Some of their properties were better than for PVDF electrodes.
- Continuation of a search for new conductive materials like: carbon nanotubes, carbon nanofibers or inorganic materials should be carried out. The studies will be supplemented with the search for polymer binders that can be used for manufacturing electrodes.

- Different Carbon materials have been tested for the capacitive layer. Different carbon can be used depending on the process (CDP or CDLE) and the way they are operated (cycle duration…)
- Various green binders made from natural products were considered together with pre-treatment modifying their properties
- Surface hydrophilization was tested using different approaches (deposition of titanium hydr(oxide) ; mixing of AC with titania, zirconia or alumina ; deposition of chitosan on the surface ; deposition of nanoparticles of silver)
- Different polymers were tested regarding the ion sorption properties
- PVC showed better performances for ion sorption than PVDF
- The best sorption was obtained for electrodes coated with titanium hydr(oxide)
- The use of Chitosan reduces sorption of NaCl, possibly because of plugged pores
- The most hydrophilic surface was obtained when the surface was covered with titanium hydro(oxide)
- Silver nano particles were reducing the sorption of NaCl but showed good properties against bacterial growth which indicates that it could reduce biofouling issues.

<u>Cell design and operation</u>

- The research conducted in Wetsus focused on the development of the CDP process and particularly on how to operate an energy extraction cycle. Operation at constant set potential or constant current were investigated and a simple model was developed. The main results are first of all an improved power output reaching 200 mW/m2
- The University of Milano-Biccoca research unit explored the various possibilities of CDLE cell configurations. In particular it was evaluated the effect on the cell performances of the different draining, flowing time, stirring, and water exchange systems.
- The Wrocalw University of Technology research unit has performed experiments in order to evaluate the effect of the carbon electrode thickness on capacitance and leakage current. The leakage current was found proportional to electrode thickness, while the capacitance is not strongly dependent on it, confirming the conclusions of UNIMIB unit. New cation and

anion exchange membranes with better properties having polyelectrolyte within the pores has been developed.

- The Granada research unit has designed three experimental apparatuses and methods for the CDLE approach. The best results were obtained with a cylindrical glass cell with perforated platinum electrodes. The carbon samples (TE7 and TE11 obtained from MAST Carbon) were kept in contact with the electrodes by means of a fitted cellulose membrane. Solution exchange was automatic and it was found that TE11 was a better sample than TE7, and that charging voltages in excess of 400 mV produce a decrease in signal.
- The consortium, each partner from its side, developed a flow through cell contributing to select the key parameters for the further development of the prototype.
- All cells reached the minimum performance milestone of 1 W/m^3 at 25% efficiency.
- Both Wetsus and MIB developed an alternative cell configuration, respectively a new cell with water entering the side without going through the electrodes and a robotic arm. REDstack introduced two novel concepts: “Capacitive deionization and capacitive mixing using slurry electrodes” and “Capacitive deionization and capacitive mixing using suspension electrodes”. For each patent idea a document was prepared. MAST Carbon and Wetsus developped rope shaped electrodes. MAST carbon prepared them from different material: phenolic derived fibers and viscose
- An innovative wire design was proposed and tested. At present the technology for making this type of electrodes is not yet completely ready. The technology for reproducing this type of electrodes need to be further developed, particularly for the up-scaling of the design.
- Indications have been obtained on how to improve the performances of the wire system by suitably choosing the flow direction of the solutions, the flow rates and the chamber volume.
- Oxygen reduction was observed as a possible source of leakage in the Capmix system
- Different design for stacking the electrodes were proposed. After the evaluation it was decided to go further with the flat plate reactor and to leave the hollow shell and spiral wound reactors. Regarding the wire reactor: after having gained more knowledge on the

production and performances of the wires a promising up-scaled prototype should follow up the work done during the project.

- Stacks of CDLE (Capacitive Double Layer Expansion) CAPMIX cells have been realized, with good results in the case of parallel connections.
- When the cells are connected in series, the effect of parasitic currents has to be taken in consideration. However, numerical calculations performed for the design of the prototype stack of CDP cells indicate that the effect of short-cut current losses can be kept under control.
- By suitable functionalization processes, activated carbon electrodes have been produced which present potential rises largely different from one another also at their spontaneous potentials, i.e. without the need of any preliminary charging.
- By using couples of functionalized electrodes the problem of leakage can be strongly reduced, and power densities of about 80 mW/m^2 have been achieved with the CDLE technique.
- The use of new electrodes, made of activated carbon particles covered by a shell of charged polymers, allowed us to produce a cell with a behavior similar to CDP cells, but without making use of ion-selective membranes.
- It has been shown that good performances in the extraction of salinity gradient energy can be reached by using battery-like electrodes such as NMO and Ag/AgCl electrodes.
- Ways to minimize the time needed for the establishment of the Donnan potential in a CDP system were investigated. Future research will investigate cell designs in which the mixing can be improved without augmenting the energy spent on the pumping.
- The study of CDLE (Capacitive Double Layer Expansion) cycles has shown that there is an optimal length for the switching phase from salt to fresh water, and that a nonstop flow of fresh water is recommended.
- For CDLE cycles optimum values of the external load and of the electric current can also be determined.

- Useful formulas have been obtained for predicting the CAPMIX power production from the results of EIS measurements in the two solutions.
- For CDP (Capacitive Donnan Potential) cycles in two steps higher power outputs can by obtained by limiting the durations of the two phases.
- For CDP cycles in four steps with constant current, the presence of leakage can determine an optimal duration of the charge and discharge phases. When the leakage is negligible, longer durations lead to better performances.
- The consortium, each partner from its side, developed a flow through cell contributing to select the key parameters for the further development of the prototype.
- The different cells are reaching the minimum performance milestones of 1 W/m^3 at 25% efficiency.
- Investigation has been performed to improve the design and operation of a wire electrode based flow through cell, as a promising alternative cell configuration for CAPMIX.
- Indications have been obtained on how to improve the performances of the cell by suitably choosing the flow direction of the solutions, the flow rates and the chamber volume.
- When the cells are connected in series, the effect of parasitic currents has to be taken in consideration. However, numerical calculations performed for the design of the prototype stack of CDP cells indicate that the effect of short-cut current losses can be kept under control.
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- For CDP cycles in four steps with constant current, the presence of leakage can determine an optimal duration of the charge and discharge phases. When the leakage is negligible, longer durations lead to better performances.
- The Capmix concept has been extended to gaseous CO_2 gradients which is a major step in the field of Salinity Gradient Energy. A proof of principle has been published and more work is on the way to be published, for instance the fact that it can be operated directly with the gaseous fluids without energy expensive pumping requirements.

<u>Early Technology Validation</u>

Most development in this section have not been published yet and are still confidential.

The work here consisted in investigating several aspects:

- Energy balance & CO2 impact
- Site specific implementation
- Production manufacturing costs and market prospects
- Fouling & Pre-treatment requirements
- Real world testing

Energy balance & CO_2 impact and Production manufacturing costs and market prospects cannot at this point be made public.

The main output of the Site Specific Implementation work is the list of the 8 most promising sites in Europe:

Location: Europe Authors : Stenzel [3]				
Nr.	GIWA region	Theoretical potential [GW]	Technical potential [GW]	Ecological potential [GW]
21	Mediterranean Sea	40	8	0.8
17	Baltic Sea	39	8	0.8
22	Black Sea	38	8	0.8
11	Barents Sea	34	7	0.7
18	North Sea	34	7	0.7
12	Norwegian Sea	10	2	0.2
14	Iceland Shelf	7	1	0.1
17	Scotland Shelf	7	1	0.1

In order to test the up-scaling process and the testing of the Capmix system in real conditions, a first 10 cells pre-prototype was built and gave an open circuit voltage of 1.2 V and a 120 mW/m^2 average power density.

In the experiments with the pre-prototype we learned that the flow distribution and switching is far from perfect. Therefore, for the real prototype, new endplates and spacers were developed to allow for efficient switching of sea and river water enhancing the overall performance. In this new design, the effective surface area of the electrodes is increased by ~50%, reducing short-cut currents and increasing the power.

The biggest Capmix system built consisted in a 100 cells reactor that was operated on the Afsluitdijk, the Netherlands, where REDstack has a pilot plant in an ideal location where a dike separates sea water and fresh water.

The main outcome of the prototype testing in real life conditions are as follow:

• For both CDP and CDLE, the multivalent ion effect seems to seriously deteriorate the performance. Also $CaCO_3$ scaling was observed (Afsluitdijk exp.). The development of monovalent ion selective membranes might reduce these effects in CDP. Monovalent selectivity in CDLE (without membranes) is not straightforward and more research is needed to identify possible solutions to this problem.

- The CDP cell still shows water leakage between membrane and electrode. Sealing the electrode i.e. by gluing might solve many of the issues encountered in the large stack.
- Fouling is an issue, especially at higher flow-rates. Anti-fouling measures should be included to reduce the decrease in performance, i.e. chemical treatment, air-sparging, etc. However, there was no growth of life biological material, but only attachment of particulates to the membrane surface. Anti-fouling coatings might help in this particular case.
- Due to parasitic ionic short-cut currents, series connections lead to decreased potential. This can be prevented by parallel connection or significantly reduced by optimised design.
- The experiments were not performed with perfect electrical load conditions. To achieve better performance a maximum power-point-tracker with impedance matching (power conversion) should be implemented. It is suggested to research higher efficient power converters which can handle this relatively low AC voltage input.
- The net energy harvested at the start of the 100 cell experiment was 56%.

<u>Potential impact</u>

The Capmix technology is very young (technology readiness level of 4 or 5). As such, it is difficult to evaluate the impact of the technology as it not yet on the market.

The main impact of the project to this date is linked with how the Capmix technology was disseminated and spread to the public at large, to the scientific community and to policy makers.

A total of 21 scientific articles have been published so far and more will come in the coming months. Most of these articles are openly available free of charge.

A good indication of the impact of the project is the fact that external research groups picked up the Capmix technology. For instance, the group of the professor Logan, from Pennstate University (USA) is combining the Capmix system with bioelectrochemical systems to enable new concepts of energy extraction for various gradients (thermolytic salts, temperature gradients…).

More groups, particularly in China are developing Capmix related technologies. This is a major step as the Capmix community before the project was restricted to the partners in the project.

The project has been widely disseminated, among others through two dedicated conferences organized within the Frame of the project. The first conference took place in Milan (Italy) in September 2012 and the second in Leeuwarden (The Netherlands) in September 2014. Both events gathered 50 specialists in the field of Salinity Gradient Energy. After the second event it was decided to keep the community organizing such regular events where the community can grow and more collaboration can be generated.

During the last conference, a group of documentary film-makers, including an Emmy award winner, from France came to start a documentary project on the topic of salt and energy. This project is now on its way and by the end of the second quarter of 2015 a documentary on Salinity Gradient Energy should be available and broadcasted, not only for the French market but internationally.

Policy makers are also being addressed. Wetsus joined the Ocean Energy group based in Brussels that stirs development in the field of marine energy. The aim there is to add Salinity Gradient Energy on the agenda of policy makers so that more initiatives to develop the field can be taken. In the same order of idea, Wetsus joined the Institute for Infrastructure, Environment and Technology through its INES initiative, that aims at developing the network in the field of Salinity Gradient Energy.

These last initiatives are focusing on Salinity Gradient Technologies in general but a technology like Capmix can greatly benefit from the improved visibility.

In a more a more long-term vision, the foreseen impact of the technology are as follow:

- <u>Energy potential</u>

The European potential for Salinity Gradient is of 94 GW. To put this in perspective a modern coal fired plant has a capacity of 1GW, meaning that the European potential is equivalent to 94 coal plant. In 2006 the EU-27 produced 3354 TWh of electricity. Assuming 70% efficiency, salinity gradient energy extracted by Capmix technologies could power up to 17% of the European electricity needs.

Furthermore, developing this technology would yield an interesting economic activity as the potential outside Europe is even greater (1.6-2.4 TW worldwide potential).

- CO_2 savings

The CO_2 footprint of this technology will be evaluated in order to make sure that the CO_2 saved through the extraction of energy from a renewable source is not compensated by the CO_2 produced through the production of the necessary materials to build the Capmix power plants.

- Ecological constraints

Where fresh water flows into the sea, interesting delta ecology arises. This ecological niche is more and more under threat as a result of the climate change and sea level rising. Storm floods are increasing as a result of the climate change and sea level rising, caused by the greenhouse effect. Dikes and similar constructions change the mixing of fresh and sea water and disturb the ecology. Application of salinity difference energy such as Capmix is expected to restore this ecology. However, the effect of pumping large amount of water on living organisms should be investigated in order to assess the ecological benefits of this technology.

Project web address

More information on the Capmix project is available on the project website:

www.capmix.eu