FESC Research, Education and Outreach Project Progress Reports

(Attachement to Main Report)

November 1, 2012

USF Project Reports

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University of South Florida

Summary of USF Accomplishments

The funding provided to the University of South Florida by the State of Florida, through the Florida Energy Systems Consortium (FESC), has been used to support a number of excellent projects addressing present and future needs related to energy and the environment. Energy efficiency, production of electric power and biofuels by the use of renewable energy, water production through solar desalination, environmental cleaning by the use of photocatalytic technologies, advancements in manufacturing for photovoltaic module production and CO_2 sequestration and trade are some of the projects pursued. As a result of this funding a number of significant advancements in technology have being made resulting into useful **patents (9), journal publications (43) and presentations (76)** at national and international conferences. With this support, a number of **BS (7), MS (23), PhD (37) students and Post-Doctoral Fellows (3**) in the colleges of engineering and science have either received their degrees or are in the process of doing so. Extremely significant is also the leveraging of these funds in support of the development of a large number of proposals submitted to federal agencies and private industry **(Proposals applied for total: ($26,912,411); and funded grants total ($9,933.208); together these efforts total $36,845,619).** Many of these proposals have either already been funded or are presently pending.

Also included are the project reports on USF FESC funded "seed grants" on a variety of renewable energy projects, including:

- *Alternative Energy Potential For Florida From Mechanical And Solar Sources* (Weisberg, Pi)
- *Development Of A Highly Efficient Photocatalyst For Co2 Reduction With H2o By Hybrid Construction Of Transparent, Conductive Composite (Tcc) And Nano-Sized Mox/Invo4/Al2o3 Particles* (Alcantar, Pi)
- *Development Of A Smart Window For Green Buildings In Florida* (Witanachchi, Pi)
- *Feasibility, Sustainability And Economic Analysis Of Solar Assisted Biomass Conversion* (Joseph, Pi)
- *Hybrid Interfaces For Energy Conversion Devices* (Hoff, Pi)
- *Low-Cost Solar Power Through Assembly Of High Efficiency Microscale Photovoltaic Cells* (Crane, Pi)
- *Sustainable Algal Biofuel Production* (Ergas, Pi)

A more detailed description and associated results, for each of these funded projects, is given below.

University of South Florida

Beyond Photovoltaics - Nanoscale Rectenna for Conversion of Solar and Thermal Energy to Electricity

PI: E.K. Stefanakos **Co-PIs:** Yogi Goswami **Students:** Rudran Ratnadurai, Electrical Engineering/ Ph.D., Michael Celestin, Chemical Engineering/ Ph.D; Saumya Sharma, Electrical Engineering/PhD;

Description: The main objective of the proposal is to commercialize and scale up a new technology, the rectenna, to convert waste heat energy to electricity. Although the prediction of highly efficient (~85%) solar rectennas was published almost 30 years ago, serious technological challenges have prevented such devices from becoming a reality. Since the ultimate goal of a direct optical frequency rectenna photovoltaic power converter is still likely a decade away, our plan is to convert optical solar radiation to thermal radiation (~30 THz regime) using an innovative blackbody source. Leveraging the research efforts of the world-class team members, we plan to further develop the rectenna technology that is within reach of efficient radiation conversion at 30 THz. A fully integrated, blackbody converter and a ~30 THz rectenna system will be capable of converting at least 50% of the solar and thermal energy into usable electrical power, clearly demonstrating a truly transformational new technology in the renewable energy technology sector. For the reporting period, emphasis has been placed on the development of the plasmonic emitter that converts solar radiation to infrared radiation, and the diode that acts as the rectifier in the rectenna concept.

Budget: $598,500
Universities: USF
External Collaborators: Bhabha Atomic Research Center, India, Florida International University

Progress Summary

TASK 1. Development of a diode for the rectification of the antenna output.

Task 1A: Fabrication, characterization and testing of Metal-Insulator-Metal tunnel junctions
The main research objective of this sub-task is to develop a high efficiency MIM tunnel diode using inorganic materials. Towards this, the follow sub-tasks were pursued,

- Determine the AC and DC behavior of a Nickel Oxide-Zinc Oxide MIM tunnel diode.
- Investigate the effect of metal oxides as insulator layers in MIM junctions.

To simulate an asymmetric (P-N junction type) of diode Nickel Oxide-Zinc Oxide combinations wereused. Nickel Oxide (NiO) is known to behave as a p-type semiconductor and Zinc Oxide (ZnO) as an n-type. By combining the two, an effective P-N junction can be created. This P-N junction is in effect a Schottky Barrier Diode (SBD) and behaves similar to it. The carrier concentration is much lower in the NiO and tunneling of electrons from the ZnO layer to the NiO layer takes place across the very thin interface.

A top view of the MIM tunnel diode is shown in Fig. 1.

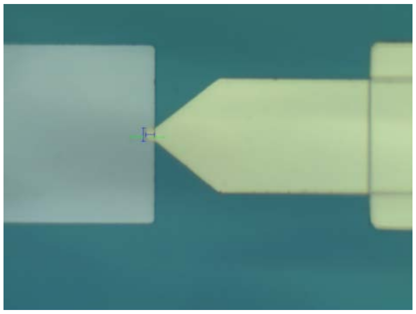


Figure 1 Top View of MIM tunnel junction

Figure 2

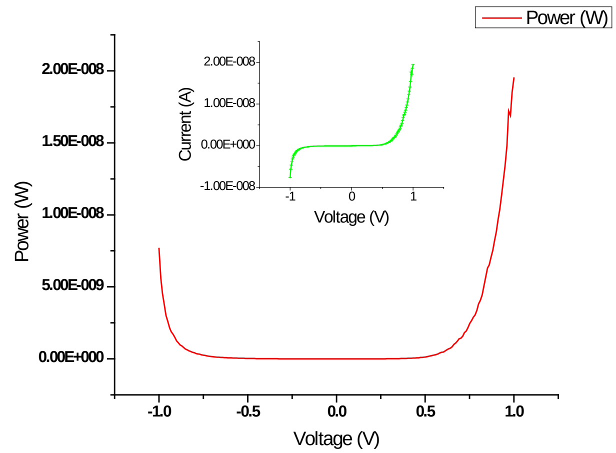


Figure 2 Power Vs Voltage Plot, Inset shows Current Vs Applied Voltage

Figure 2 shows the DC voltage current and power vs voltage characteristics of this diode.

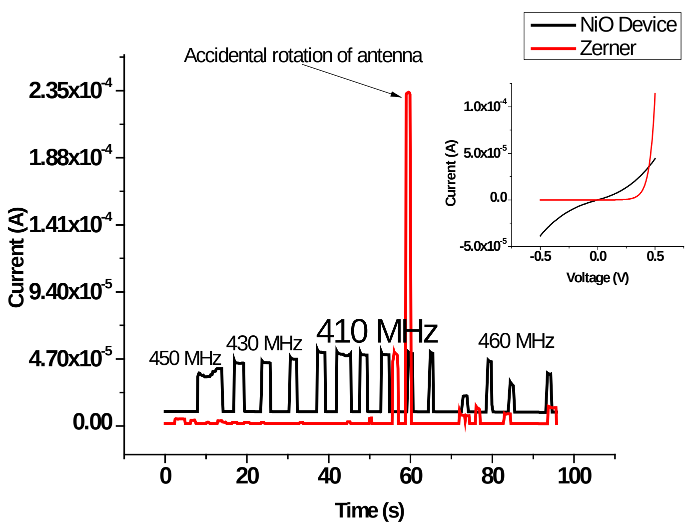


Figure 3 Comparison of Sensing Capabilities between NiO/ZnO junctions and commercial Zerner diodes.

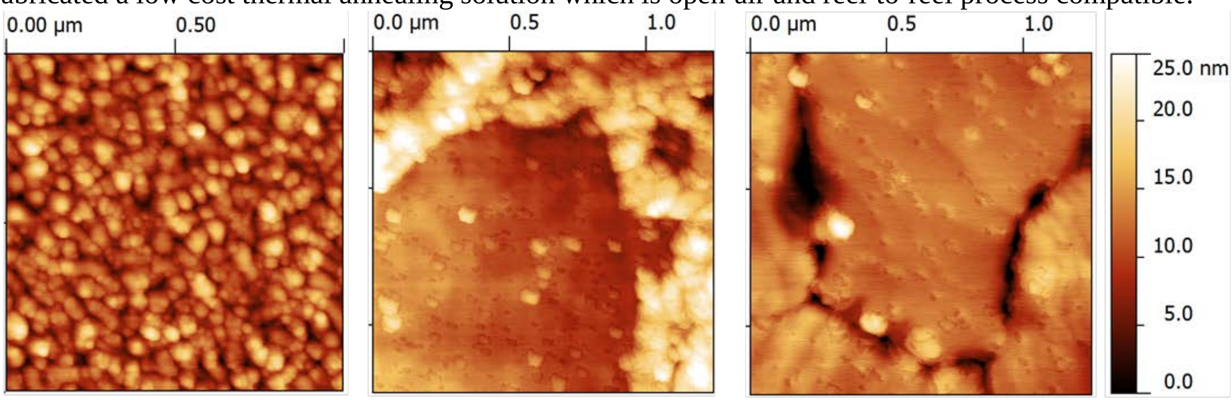
The results were compared with a standard zener diode which is a pure semiconducting p-n junction diode. As can be observed in Fig. 3, the NiO device outputs a higher signal when excited with radiation compared to the commercial Zener diode. The sensitivity of the device was also measured by biasing it at the turn on voltage and exciting the device with a 2V pulse. The device sensitivity was low since the area was not optimized, but it will be in future measurements.

The device also responded well to UV light when it was pulsed in 1 second intervals. The sharp rise and fall of the peak shows that the device switch speed is very fast. NiO/ZnO tunnel junctions show great promise as very fast switching diodes that can be used for sensing and detection and ultimately for energy harvesting.

TASK 1B. Self-assembled organic monolayer based MIM junctions

This study aims to produce near atomically-flat metallic films for the purpose of self-assembled monolayer growth. Self-assembled monolayers (SAMs) are formed from organic molecules which spontaneously chemisorb onto (in the case of thiol chemistry) noble metal surfaces. Films are exactly one monolayer and thus very thin—typically on the order of 1 – 2 nm. Because nearest neighbor interactions contribute greatly to the uniformity and tightness of packing, substrate roughness should be well below these thickness values.

Conventional microfabrication toolsets typically employ e-beam or thermal evaporation for the deposition of metal thin films. While these techniques are fast and relatively low cost, the roughness of the metal is unacceptable for the desired application (Fig. 4, shown below)). We have designed and fabricated a low cost thermal annealing solution which is open-air and reel-to-reel process compatible.



Above – (Left) Atomic Force Microscope image of thermally evaporated gold showing roughness. **(Center)** In-progress annealing shows "lakes" of annealed metal. **(Right)** Large near atomically flat planes following annealing.

Thermal evaporation of 15 nm of Chromium as an adhesion layer and 250 nm of Gold were applied to offer a baseline rough metal surface (above at left). Subsequently, the wafer was diced into 10mm x 10mm dies for small scale experiments. Initially, annealing was performed by using a high temperature flame (right) with the sample held in an inert gas purged glass envelope. Following this an electric heat annealing setup was devised utilizing a PID controller for more accurate ramp and hold temperature profiles. Annealing temperatures and times varied from 550 – 650°C and 60 – 240 s, respectively.

Roughness analysis of stripped Au surfaces

	10x Mag	50x Mag
Hexane 500hrs	13.66 nm	20.45 nm
Water 500hrs	20.99 nm	31.25 nm
Acetone 500hrs	51.99 nm	40.30 nm
Ethanol 500hrs	16.3 nm	11.36 nm
Air (Control)	3.13 nm	*0.69 nm
Evaporated Film	(AFM)	2.61 nm
Annealed Film	(AFM)	0.76 nm

Long term aging of above described films and template stripped films are summarized in the table at left reporting roughness in nanometers. We see that after immersion in various environments for 500 hours at 20°C, the roughness is reported and better understanding of process damage is gained.

Exploration into a soft top contact for the delicate self-assembled monolayer has lead to innovations in printing of conductive nanoparticles and conductive polymers. Conductivity of these AuNP (Gold Nanoparticles), AgNP (Silver Nanoparticles), and polyaniline was tested using interdigitated electrodes (Figure 5). The quantity of material deposited was then studied via an optical profiler and electrical measurements. A formulation of AuNP and AgNP was created for printing with off the shelf, low-cost inkjet printers. The top contacts were deposited at room temperature and ambient conditions. Furthermore, workup using electroless plating solution can permit a "hard shell" to be formed following the loose deposition of nanoparticles resulting in a more durable and stable contact.

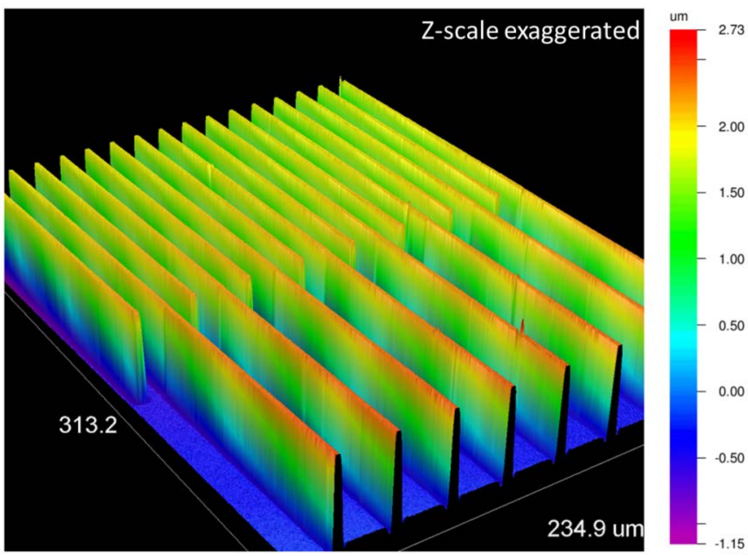


Figure 5 – Optical profiler z-height study of unpopulated interdigitated electrodes upon which conductivity studies were carried out.

Here we also report experimentation using the previously described setup consisting of a liquid metal contact. Using porphyrin molecules as the tunnel barrier, we were able to realize a hybrid organic-inorganic tunnel junction which had improved rectification ratio and very consistent performance (Figure 6). The hybrid junction results in a sharper turn-on inflection at around 1.2V when negatively biased.

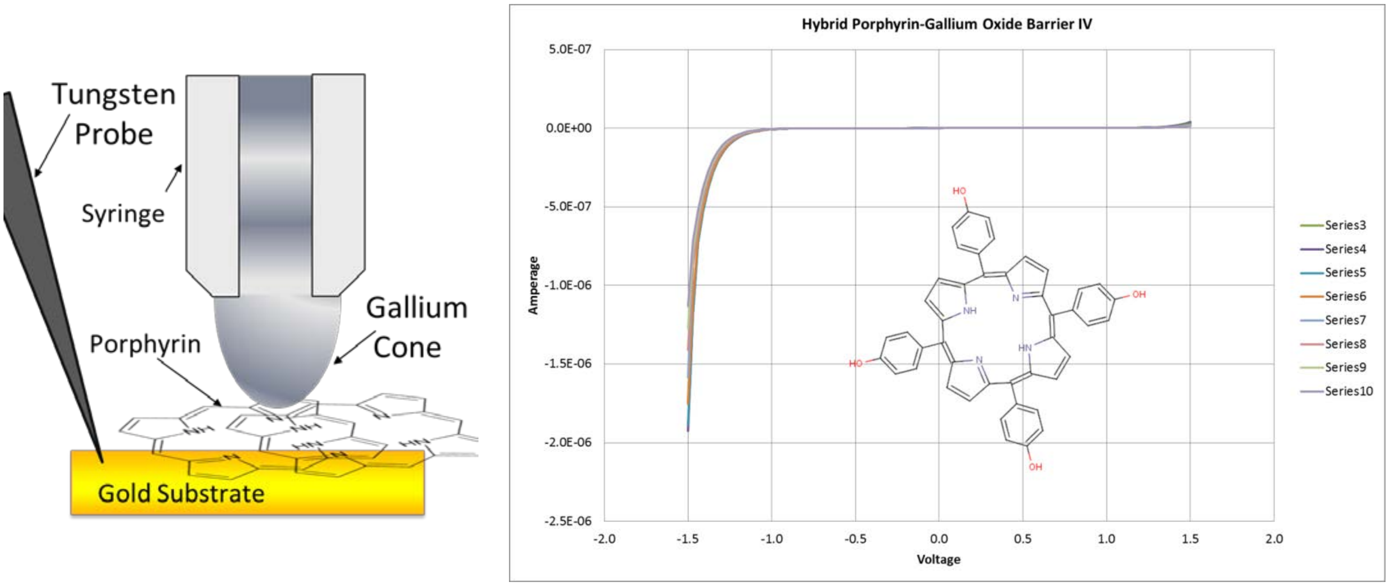


Figure 6 – Liquid metal contact resulting in hybrid organic-inorganic tunnel barrier and the resultant current-voltage response

TASK 2. Plasmonic infrared emitter

The main objectives of Task 2 are: (a) Fabrication of a plasmonic emitter and measurements of its infrared radiation spectrum; and (b) Characterization of dimensions, choice of substrate, and surface metal layer for the emitter to achieve optimum concentrated infrared radiation over a narrow frequency range

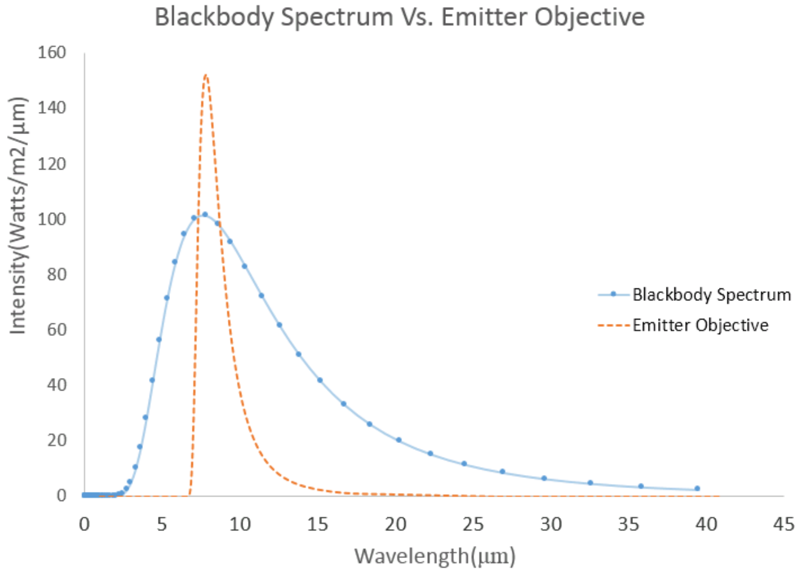
Description

The infrared spectrum of the patterned emitter is shown in Fig. 7. We expect to observe a narrow band, high intensity response when using plasmon excitation. This concentrated radiation subsequently can be fed into the antenna and later the coupled electromagnetic radiation at the antenna site can be rectified.

Figure 7. Black body and plasmonic emitter radiation spectra.

Results:

Fabrication of the plasmonic emitter involved nanoscale processing techniques such as lithography and deep reactive ion etching (DRIE). A variety of dimensions for the pattern was



used in the design of the photomask in order to be able to analyze the effect of pitch and etch depth of the microstructure on the resulting IR spectrum.

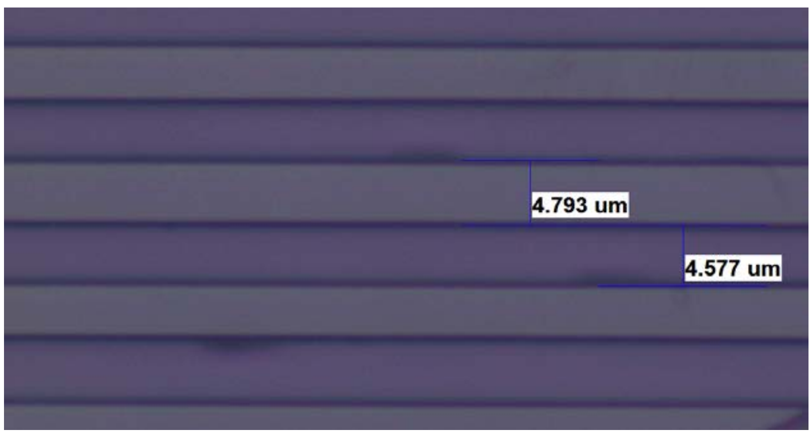


Figure 8. A micrograph of the fabricated plasmonic emitter with a depth of 2.7 microns and grating pitch of 9.3 microns.

An experimental setup as shown in Fig. 9 was used in order to gather the spectral results for our fabricated emitter as a source of infrared radiation .

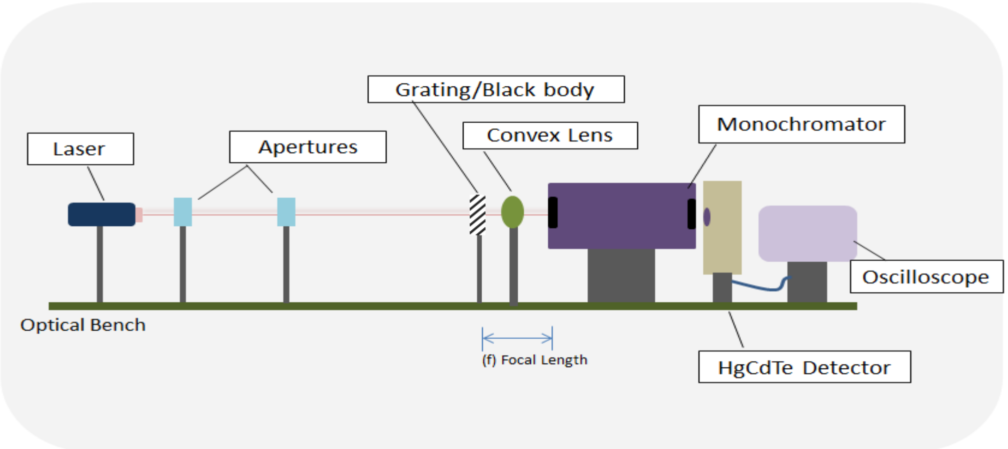


Figure 9: Experimental setup for the detection and measurement of the Infrared Spectrum.

A Graseby HgCdTe detector was used for the detection of incoming radiation. The setup (as shown above) was mounted on an optical bench to ensure linearity and focus of the beam radiated from the heated emitter. Weaker radiation from the edges of the sample emitter (weaker radiation because of differential heating across its surface) had to be masked off using a cold Aluminum sheet while recording the spectral response.

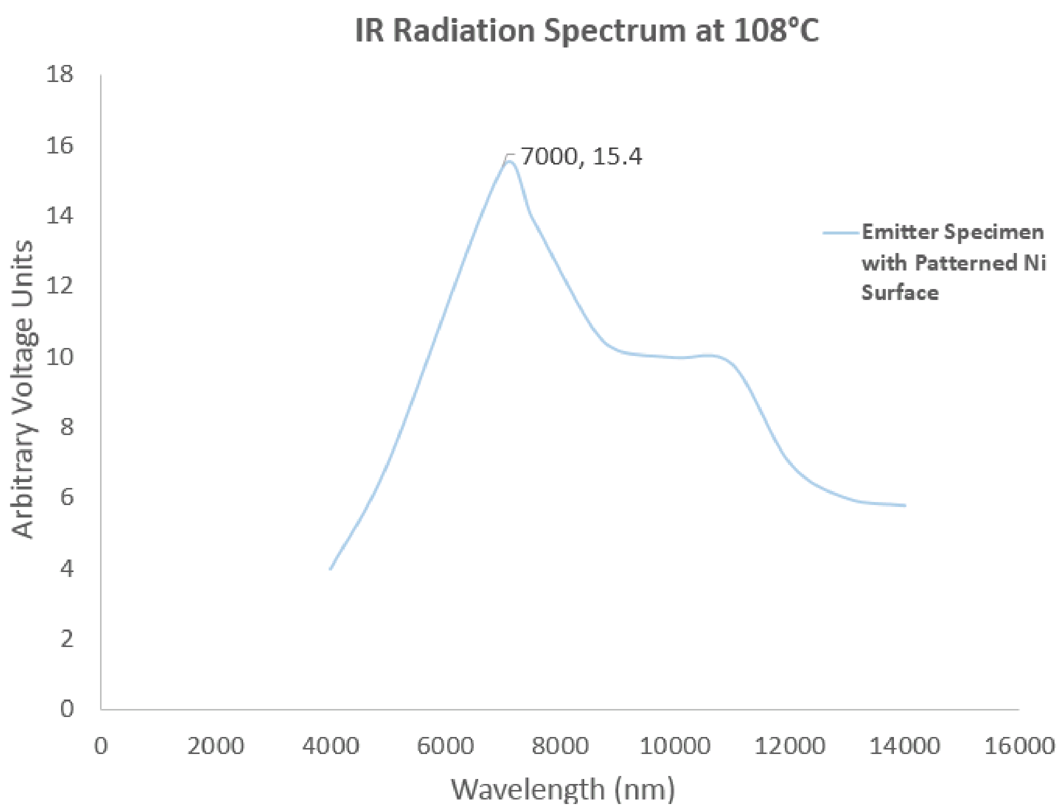


Figure 10: IR spectrum with patterned Ni Surface at 108°C

A narrow peak IR spectrum was observed for the patterned silicon sample with Nickel deposition on the surface but the desired concentration is yet to be achieved with further experimentation.

In a number of experiments the expected behavior of the emitter (with a high intensity emission at certain wavelengths) was not observed. The cause of this discrepancy was found to be imperfect duty cycle, an example of which is shown below:

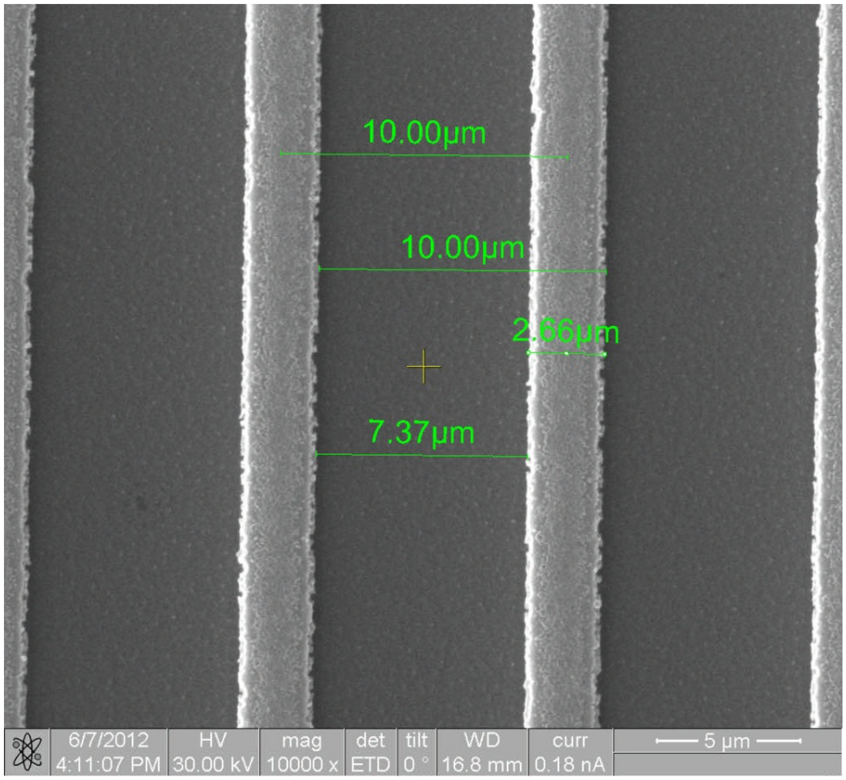


Figure 11. High Resolution image using Focused Ion Beam technique to show microstructures on emitter surface with inappropriately high duty cycle.

Funds leveraged/new partnerships created

We are currently collaborating with Bhabha Atomic Research Center, India in developing an organic based tunnel junction. Proposals are also under development for additional funding from federal agencies.

Journal and Conference publications:

1. M. Celestin, S. Krishnan, E. Stefanakos, Y. Goswami, S. Bhansali, "A review of Alkanethiol Self-Assembled Monolayers for Low Cost Nano Rectenna Energy Harvesting," Progress in Energy and Combustion Science, 2012. (Under Review)

2. M. Celestin, S. Koiry, S, Krishnan, Y. Goswami, "Metal Thin-film Roughness Mitigation Through Thermal Annealing for Self-Assembled Monolyaer Growth" USF Research Day, 2011.

University of South Florida

Fresh Water Using low Grade Heat and Alternative Energy
(Formerly titled: Clean Drinking Water using Advanced Solar Energy Technologies)

PI: E.K.Stefanakos **Co-PIs:** Yogi Goswami
Students: Chennan Li (PhD), Yangyang Zhang(PhD)

Description: This project is being pursued by means of two tasks: Task 1: Water desalination by the use of optimized thermodynamic systems; and Task 2: Design of a photocatalytic reactor for air purification.

Budget: $326,756
Universities: USF

Progress Summary

Water Desalination

Water and energy crises have forced researchers to seek alternative water and energy sources. Seawater desalination can contribute towards meeting the increasing demand for fresh water using alternative energy sources like low-grade heat. Industrial waste heat, geothermal, solar thermal, could help to ease the energy crisis. Unfortunately, the efficiency of the conventional power cycle becomes uneconomically low with low-grade heat sources, while, at the same time, seawater desalination requires more energy than a conventional water treatment process. However, heat discarded from low-grade heat power cycles could be used as part of desalination energy sources with seawater being used as coolant for the power cycles. Therefore a study of desalination using low-grade heat is of great significance.

This research has comprehensively reviewed the current literature and proposes two systems that use low-grade heat for desalination applications or even desalination/power cogeneration. The results suggest two cogeneration systems, that is, a supercritical Rankine cycle-type coupled with a reverse osmosis (RO) membrane desalination process, and a power cycle with an ejector coupled with a multi-effect distillation desalination system. The first configuration provides the advantages of making full use of heat sources and is suitable for hybrid systems. The second system has several advantages, such as handling highly concentrated brine without external electricity input as well as the potential of water/power cogeneration when it is not used to treat concentrated brine. Compared to different stand-alone power cycles, the proposed systems could use seawater as coolant to reject low-grade heat from the power cycle to reduce thermal pollution.

Photocatalytic Reactor
Description
This study focuses on the enhancement of the effectiveness of the photocatalytic process by the introduction of artificial roughness on the interior reactor surface in a photocatalytic system. Artificial roughness elements on the catalytic surface could enhance the turbulence intensity close to the catalytic surface. The enhanced turbulence intensity would translate to an increase in the mass transfer of airborne contaminants to the catalyst surface, improving the efficiency of photocatalysis. For maximum enhancement of the turbulence intensity (or mass transfer or reactor performance) in the photoreactor channel, different shapes, sizes, and arrangements of roughness elements have been numerically investigated. A model reactor was fabricated to carry out the experimental study for air purification. The experimental results compare well with simulations.

Table 1. Summary of the optimum parameters for different roughness arrangements

		Continuous rib roughness			
	Smooth	Transverse	Inclined	V shape	Mesh
Pitch ratio (p/e)	----	10	10	10	10
Relative height (e/h)	----	0.05	0.05	0.05	0.05
Flow attack angle (α)	----	----	75	75	75
Turbulence intensity	7.95%	9.78%	10.49%	10.54%	10.26%

- ❖ The order of the increased turbulence intensity in reactor channel (or the possible reactor performance) is: V shape > inclined > mesh > transverse > smooth.

Experimental study

The purpose of the experiment was to clean contaminated air in a closed chamber by a model reactor. 1ppm toluene was used as the representative air contaminant. The samples were analyzed by GC/FID.

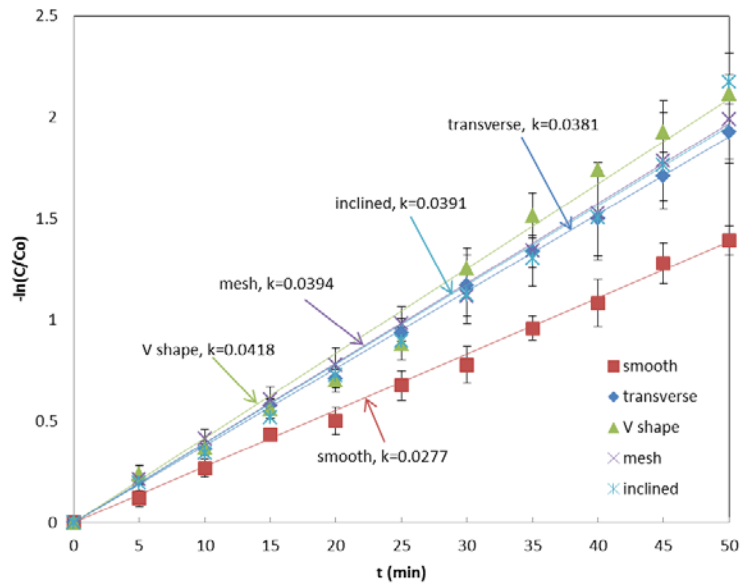


Figure 1. Comparison of toluene photocatalytic oxidation of the reactor with various rough catalyst plates in terms of $-\ln(C/C_0)$

- ❖ The order of the reactor performance with various rough catalyst surfaces could be V shape > mesh > inclined > transverse > smooth.

Conclusions

- The optimum pitch ratio (p/e) of roughness was determined equal to 10.
- The optimal flow attack angle (α) would be 75^{o} for inclined, V shape and mesh roughness pattern.
- The order of the reactor performance for various rough catalyst surfaces could be V shape > mesh > inclined > transverse > smooth.
- The ideal could also be used in water application.

Publications

1. Yangyang Zhang, Manoj K. Ram, Elias K. Stefanakos, and D. Yogi Goswami, Synthesis, Characterization, and Applications of ZnO nanowires. *Journal of Nanomaterials* 2012 (published)

2. Yangyang Zhang, Elias K. Stefanakos, and D. Yogi Goswami, Effect of photocatalytic surface roughness on reactors effectiveness for indoor air cleaning. *Atmospheric Environment* 2012 (Under review)

3. Yangyang Zhang, Elias K. Stefanakos, and D. Yogi Goswami, Optimum photocatalytic reactor performance with surface roughness arrangement for indoor air cleaning. *Atmospheric Environment* 2012 (finished)

4. Yangyang Zhang, Elias K. Stefanakos, and D. Yogi Goswami, Design of an efficient photocatalytic reactor with artificial surface roughness for air purification. *Atmospheric Environment* 2012 (finished)

University of South Florida

Creation of Carbon Sequestration Data, Technologies and Professional Cohorts for Florida

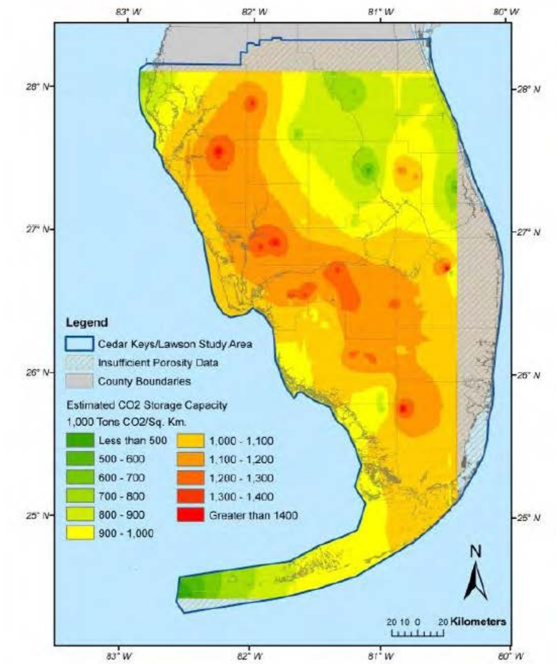
PI: Mark Stewart **Co-PIs:** Jeffrey Cunningham, Maya Trotz
Students: Arlin Briley, PhD, Mark Thomas, PhD

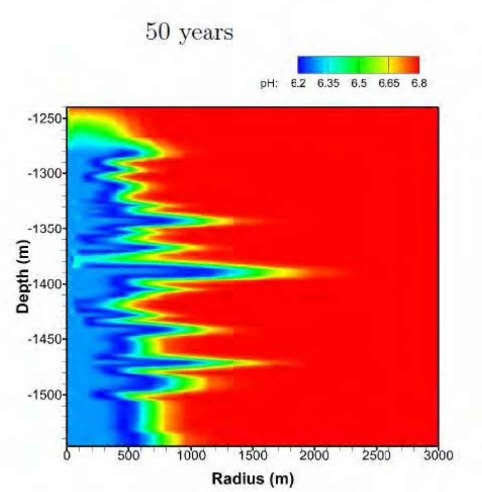
Description: Rising concerns over increasing levels of greenhouse gases, especially carbon dioxide, have led to suggestions to capture carbon dioxide at fixed sources, such as fossil fuel power plants, and sequester the carbon for millennia by injecting it underground. Florida overlies many thousands of feet of carbonate rocks which may be suitable for geologic sequestration of carbon dioxide. This project is investigating the potential for geologic sequestration of carbon dioxide in Florida, the physical and chemical changes that may occur as a result of injection, assess the potential for escape of injected carbon dioxide, determine the risk, if any, to aquifer systems used for water supplies, develop methodologies for Florida utilities to predict the performance and risks of proposed sequestration projects, and educate a cohort of geologic sequestration professionals to create a carbon sequestration industry in Florida. This project has graduated two PhD students, Tina Roberts-Ashby, US Geological Survey, and Roland Okwen, Illinois State Geological Survey, one post-doctoral student, Anwar Shadab, Missouri University of Science and Technology, and currently supports two PhD students.

Budget: $479,640
Universities: USF
External Collaborators: TECO, RTI, ECT, DOE

Progress Summary

Progress continued on the collaboration with Tampa Electric Co, DOE and RTI on the carbon sequestration and wastewater injection pilot project at the Polk Power Station (PPS). The total DOE funding for this project is $171 million. USF is responsible for the mathematical modeling of the pilot carbon sequestration and wastewater injection project at the PPS. In conjunction with this project, USF had a grant in 2011-2012 through Tampa Electric/ECT Inc that supported two PhD students. Four refereed publications on carbon sequestration appeared in print in 2012, one is in press, and one is in review. Four presentations/posters on research results were given at national and regional meetings by faculty members and graduate students. A proposal was submitted to DOE to investigate an innovative and potentially very important conjunctive injection of carbon dioxide and wastewater and is in review. This proposed project would provide a new source of potable water, help municipalities deal with wastewater disposal, increase the efficiency and safety of carbon sequestration, and reduce costs through shared facilities. This proposal would leverage current Federal funding at the PPS project. Two USF GCS PhD students, Tina Roberts-Ashby, USGS, Washington, DC, and Roland Okwen, Illinois State Geological Survey/Univ Illinois, are continuing to collaborate with the USF Carbon Sequestration Group on GCS research. The USF GCS group has achieved international recognition through its refereed publications in international journals and presentations at national meetings. As a result of USF GCS Group work, Florida was selected for one of the few DOE funded carbon capture/sequestration pilot projects in the US. The USF GCS group will continue to attempt to leverage the existing funding at PPS to further funded research and graduate training in carbon sequestration. The expertise and technology for physical and geochemical modeling of co-injection of reverse-osmosis reject water, supercritical carbon dioxide and industrial process water developed by USF GCS at the Polk Power Station has resulted in a new project transferring the technology to a facility operated by the Mosaic phosphate company. This expertise may have wide applicability for safely treating and reusing of municipal wastewater, reducing industrial demands on potable water supplies, and providing a safe disposal method for industrial process waters.





Funds leveraged/new partnerships created:

During 2012 the USF Geological Carbon Sequestration (GCS) group had a continuing collaborative relationship with Tampa Electric and DOE to provide mathematical modeling expertise for the DOE-funded carbon sequestration and wastewater injection project at the Polk Power Station in Polk County, Florida. This collaboration provided research funding and training for two PhD students, Arlin Briley and Mark Thomas. This project was used as leverage for a proposal submitted to DOE in April, 2012, to investigate the conjunctive injection of wastewater from a reverse osmosis plant and CO2 captured at the Polk Power Station. Municipal wastewater from the City of Lakeland will be treated to potable water standards in a reverse osmosis plant. Ninety percent of the original wastewater will become potable water, and the 10% reject water from the RO plant will be injected in a deep well after CO2 injection. Preliminary modeling suggests that the waste water injection transfers the CO2 from a supercritical gas phase to a dissolved phase, safely sequestering it for millennia. This process could provide for efficient wastewater reuse, safe CO2 sequestration, and lowered costs through shared facilities. The technology and expertise developed during this project has resulted in a new grant from the Mosaic company to investigate the potential for a similar injection project at a phosphate chemical plant. This expertise and technology has the potential to be widely used in Florida.

2012 Annual Report

Progress continued on the collaboration with Tampa Electric Co, DOE and RTI on the carbon sequestration and wastewater injection pilot project at the Polk Power Station (PPS). The total DOE funding for this project is $171 million. USF was responsible for the mathematical modeling of the pilot carbon sequestration and wastewater injection project at the PPS. In conjunction with this project, USF had a grant through Tampa Electric/ECT Inc that supported two PhD students. Four refereed publications on carbon sequestration appeared in print in 2012. Four presentations on research results were given at national and regional meetings by faculty members and graduate students. A proposal was submitted to DOE to investigate an innovative and potentially very important conjunctive injection of carbon dioxide and wastewater and is in review. This proposed project would provide a new source of potable water, help municipalities deal with wastewater disposal, increase the efficiency and safety of carbon sequestration, and reduce costs through shared facilities. This proposal would leverage current Federal funding at the PPS project. Two USF GCS PhD students, Tina Roberts-Ashby, USGS, Washington, DC, and Roland Okwen, Illinois State Geological Survey/Univ Illinois, are continuing to collaborate with the USF Carbon Sequestration Group on GCS research. The USF GCS group has achieved international recognition through its refereed publications in international journals and presentations at national meetings. As a result of USF GCS Group work, Florida was selected for one of the few DOE funded carbon sequestration pilot projects in the US. The USF GCS group will continue to attempt to leverage the existing funding at PPS to further funded research and graduate training in carbon sequestration. This investigation has resulted in two grants, one with Tampa Electric and one with Mosaic phosphate, an accepted publication in the journal of the National Academy of Inventors, and a proposal submitted to the US Department of Energy. This technology holds promise for increasing the availability of potable water supplies for wastewater reuse, safer and more efficient geologic sequestration of carbon dioxide, and reduced waste disposal costs for Florida industries such as power utilities and phosphate companies.

Active Grants:

Tampa Electric/ECT Inc, 2010-2012, Numerical modeling of carbon sequestration and waste water injection at the Polk Power Station, Polk County, Florida, approximately $60,000 in 2012.

Grants Submitted:

Numerical and geochemical modeling of conjunctive injection of reverse osmosis reject water and industrial process water, Mosaic/ECT Inc, 10/12, awarded.

Evaluation of Wastewater Flooding on the Efficiency and Safety of Geologic Sequestration of Carbon Dioxide, US DOE, $760,000, 4/12, pending.

Refereed Publications:

Roland T. Okwen, Mark T. Stewart, Jeffery A. Cunningham, 2012. An Analytical model for screening potential CO2 repositories, Computational Geosciences ,05/2012; 15(4):755-770. DOI:10.1007/s10596-011-9246-2

Roland Okwen, Mark Stewart, Jeffrey Cunningham, 2012. Effect of Well Orientation (Vertical vs. Horizontal) and Well Length on the Injection of CO2 in Deep Saline Aquifers Transport in Porous Media, 05/2012; 90(1):219-232. DOI:10.1007/s11242-010-9686-5

Roland T. Okwen, Mark Thomas, Mark T. Stewart, Maya Trotz, Jeffrey A. Cunningham, 2012. Conjunctive Injection of CO2 and Wastewater in a

Heterogenous Porous Formation, Technology and Innovation, National Academy of Inventors, DOI: http://dx.doi.org/10.3727/194982412X13462021397778.

Tina Roberts-Ashby, Mark Stewart, 2012. Potential for carbon dioxide sequestration in the Lower Cretaceous Sunniland Formation within the Sunniland Trend of the South Florida Basin, U.S., International Journal of Greenhouse Gas Control, doi:10.1016/j.ijggc.2011.11.009

Presentations and Poster Sessions:

Roland T. Okwen, Mark Thomas, Mark T. Stewart, Maya Trotz, Jeffrey A. Cunningham, 2012. Conjunctive Injection of CO2 and Wastewater in a Heterogenous Porous Formation American Geophysical Fall Meeting, San Francisco, 12/11

Geochemical Modeling of CO2 Sequestration in Deep, Saline, Dolomitic Limestone Aquifers: Sensitivity to Physico-Chemical Conditions. Participants: M. W Thomas, M. Stewart, M. A Trotz, and J. Cunningham, Florida Energy Summit August 15-17, 2012

At the University of South Florida 4th Annual College of Engineering Research Day, Engineering II (ENB), First Floor, Thursday, November 17, 2011:
Simulation of Alternating Wastewater/CO2 Injection into a Deep Saline Aquifer. Mark Thomas, Roland Okwen, Arlin Briley, Mark Stewart, Maya Trotz, Jeffrey Cunningham University of South Florida 4th Annual College of Engineering Research Day, 10/2012.

Funded research:

Project 1: : Physical and geochemical modeling of geologic sequestration of carbon dioxide and RO reject water at the Polk Power Station (PPS), Polk County.
Principal Investigators: M Stewart (USF), J Cunningham(USF), M Trotz(USF), R Okwen(ISGS)
Students: Arlin Briley (CEE, PhD), Mark Thomas (CEE, PhD)
Grantors and Collaborators: Tampa Electric Company, ECT Inc.
Funding: Funding was provided on a continuing and as needed basis, for specific tasks. 2012funding was about $40,000-$50,000. Funds provided research support for faculty members Cunningham, Trotz, and Stewart, a sub-contract with Dr Roland Okwen (USF PhD) of the Illinois State Geological Survey, licenses for advanced modeling software, and support for two PhD students, Arlin Briley and Mark Thomas in CEE.
Description: This project is part of a >$160,000,000 project funded by DOE and the SWFWMD. SWFWMD funded two deep injection wells at PPS to dispose of reverse osmosis reject water from a RO plant that will process City of Lakeland wastewater. The potable water from the RO plant will replace Floridan Aquifer water currently used by Tampa Electric at the PPS. The existence of a suitable deep injection zone was confirmed by earlier USF research. As a result of the availability of deep injection wells and the integrated coal gasification-combined cycle (IGCC) power plant at PPS, the PPS was selected by DOE for a pilot project for hot-gas clean up, carbon capture, and carbon sequestration. USF is responsible for modeling the physical and chemical behavior of both the injected carbon dioxide that will be captured by the CCS pilot plant and the reject water from the RO plant. This project provided a unique research opportunity, as it is the only CCS project where injection of CO2 will can be followed by wastewater injection. The majority of the refereed publications and meeting presentations of the USF Carbon Sequestration group have been based on research results from this project.
Project lifespan: The DOE has put the sequestration project on hold, but the wastewater injection will start in 2014 and continue indefinitely.

Project 2: Monitoring of carbon sequestration using InSAR

Principal Investigator: Tim Dixon (USF)
Grantor: DOE
Funding: This is part of a larger grant from DOE held by Tim Dixon. Funding on the FESC project is probably about $50,000
Project description: This project will use the carbon dioxide and wastewater injection projects at the Polk Power Station (PPS) to investigate the use of radar interferometry to monitor the progress of CO2 injection at CCS sites. Dixon has received permission to include the PPS site as one of the investigative sites for this DOE grant.

Proposals submitted:

1**:** The current CCS and wastewater injection project at the Polk Power Station (PPS) provides a unique research opportunity. As the principal purpose of the deep wells is disposal of RO plant reject water and waste streams from PPS facilities, wastewater will be injected into the deep disposal well after possible injection of supercritical CO2. Preliminary modeling (see figures below) suggests that the carbon dioxide sequestered as a supercritical gas phase will dissolve in the injected waste water. This will convert the CO2 from a very buoyant supercritical gas to a more dense dissolved phase. This nearly eliminates the buoyancy effect of sequestered CO2, greatly reducing the importance of caprock continuity and sequestering the CO2 in a chemically stable form. The proposed project will create predictive geochemical models for the conjunctive injection of CO2 and wastewater, calibrated to monitoring data from the PPS.
Submission: A proposal was submitted to DOE in April, 2012. Funding would be about $760,000 for three years, 2013-2016

2**:** Numerical and geochemical modeling of conjunctive injection of reverse osmosis reject water and industrial process water, Mosaic, submitted 9/2012.

UNIVERSITY OF SOUTH FLORIDA

Design, Construction and Operation of CSP Solar Thermal Power Plants in Florida

PI: D. Yogi Goswami **Co-PIs**: Elias Stefanakos, Muhammad M. Rahman, Sunol Aydin, Robert Reedy
Students: Gokmen Demirkaya (Ph.D.); Ricardo Vasquez Padilla (Ph.D.);
Huijuan Chen (Ph.D.); Jamie Trahan (Ph.D.)

Description:
Florida utilities are mandated to achieve 20% renewable energy contribution to their generation mix by 2020. While technologically feasible with solar energy, the capital costs are high – presently, capital costs range from $6,000-$7,000/kW for PV and $3,500-$4,000/kW for concentrating solar thermal power. This project targets the development of solar thermal power technology for bulk power and distributed generation, which will diversify energy resources in Florida and reduce greenhouse emissions by utilizing renewable sources. Also, there will be economic impacts with the establishment of new power industry in Florida, which will help the electrical utilities of the state to meet the renewable portfolio standards. The project has three main tasks; the first one is to develop design methodologies and standards for the proven solar thermal power technologies in combination with bio or fossil fuels based on Florida conditions and resources. Secondly, the project aims to set up demonstration and test facilities for these technologies for optimization for Florida conditions, and the final task is to develop and commercialize innovative technologies based on new thermodynamic cycles.

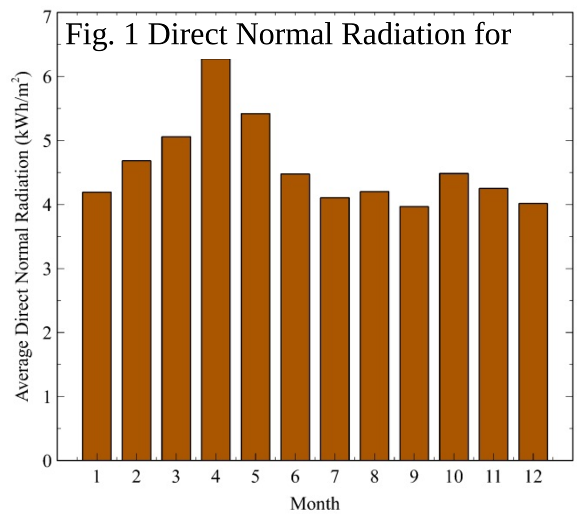


Fig. 1 Direct Normal Radiation for

Budget: $882,000
Universities: USF, UF, UCF
External Colaborators: Sopogy Corporation

Progress Summary

Research Objectives for Current Reporting Period:

The main research objectives for the current reporting period include the development of a test facility and pilot demonstration systems based on parabolic trough technology.

Progress Made Toward Objectives during Reporting Period

Daily integration (DI) approach was used to obtain the average direct normal solar radiation for the location of the pilot demonstration solar plant (USF, Tampa, Fl). The direct normal solar radiation obtained for Tampa is shown in Fig. 1. The annual average for this location is 4.6 kWh/m^2-day. These solar radiation values and the solar shading analysis for solar collector rows were used for the solar field calculation. The solar field layout proposed for 50 kW$_e$ is shown is Fig. 2. The Soponova 4.0 (Sopogy Inc.) parabolic trough collectors will be used in the solar field for providing 430 W/m^2 of thermal energy after losses. The solar field is being designed to work in conjunction with a thermal energy storage system which will use phase change material (PCM) as a storage material.

The remaining thermal energy will be provided by a natural gas boiler, which will work in series with the solar field and supply thermal energy to the power block when the solar energy is not available.

The power block that will convert the thermal energy to electricity is based on Organic Rankine Cycle. This power block will have a nominal capacity of 120 kW_e. A preliminary study on condensation methods for solar thermal plants is also conducted and more research will be devoted to the development of cost effective dry cooling technology.

Research activities for the next reporting period will focus on the modeling of heat transfer losses through the solar receiver and field piping, pressure drops and pumping requirement and thermal energy storage system design.

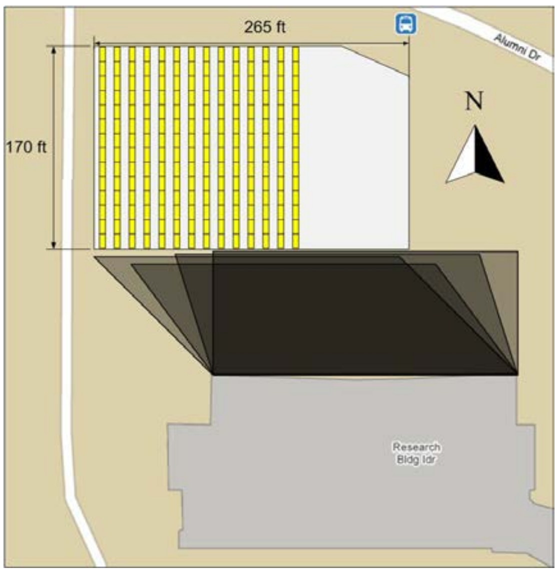


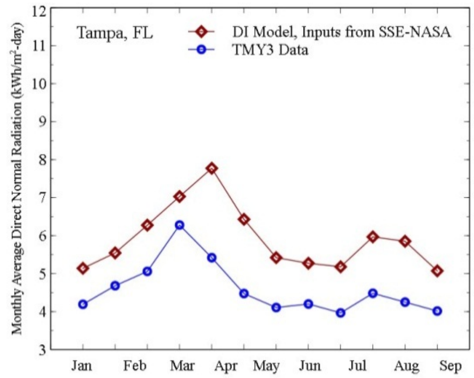
Fig.2 The solar field layout proposed for 50 kW_e

Task 1: Development of simulation and design methodology for parabolic trough and parabolic dish

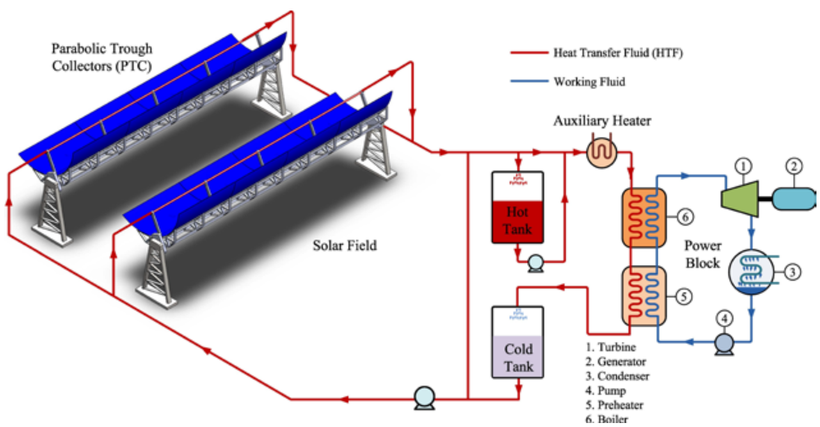
The objective of the task one is to develop a simulation and design methodology for the parabolic trough and parabolic dish based technologies for Florida conditions. Solar radiation, solar collector and thermal storage topics are the subtasks, and following progresses have been made during the period.

Parabolic trough solar systems are currently one of the most mature and prominent applications of solar energy for production of electricity. Compared to conventional power plants, parabolic trough solar power plants produce significantly lower levels of emissions and carbon dioxide. Thermal simulations and cost analysis of the system are used to evaluate the economic feasibility. Complex models and components are integrated to emulate real operating conditions, such as: Solar Radiation Model, Solar Thermal Collector, Thermal Energy Storage, Solar Field Piping, Power Block, Cost Analysis, and Integration of all Systems. This progress report presents a preliminary design method to calculate solar radiation data and thermal collector efficiency which are used to determine the size and the cost of solar field.

Fig. Comparison of two models



An hourly solar radiation model is necessary to calculate the energy input that come from the sun, since the solar collector performance changes during the whole day. The inputs for the hourly solar radiation model are the long term average values of total horizontal and diffuse radiation, which can be obtained by ground or satellite measurements. Satellite data provide information about solar radiation and meteorological conditions in locations where ground measurement data are not available. Gueymard developed a Daily integration approach model to predict the monthly-average hourly global irradiation by using a large dataset of 135 stations with diverse geographic locations (82.58N to 67.68S) and climates. The results showed that the daily integration model is most accurate than previous hourly models.



The second part of this report is about the numerical heat transfer model. The receiver consists of an absorber surrounded by a glass envelope. The absorber is typically stainless steel tube with a selective absorber surface. The glass envelope is an antireflective evacuated glass tube which protects the absorber from degradation and reduces heat losses. The Solar receiver uses conventional glass to metal seals and bellows to achieve the necessary vacuum enclosure and for thermal expansion.

The heat transfer model is based on an energy balance between the heat transfer fluid and the surroundings (atmosphere and sky). A comprehensive radiation model between the absorber and the envelope is included in this study. The results showed that the new model has lower RMSE than the NREL Model (0.985% and 1.382% respectively). The numerical heat transfer model integrated with the solar radiation model can be used for evaluating the performance of solar collectors for any location.

Task 2: Development of a test facility and pilot demonstration

The second task targets the development of a test facility and pilot demonstration systems based on parabolic trough and dish technologies. The experimental combined power and cooling setup will be used as a preliminary study of the demonstration system that will be developed.

1.1 PERFORMANCE ANALYSIS OF A RANKINE-GOSWAMI COMBINED CYCLE

Improving the efficiency of thermodynamic cycles plays a fundamental role for the development of solar power plants. These plants work normally with Rankine cycles which present some disadvantages due to the thermodynamic behavior of steam at low pressures. These disadvantages can be reduced by introducing alternatives such as combined cycles which combine the best features of each cycle. In the present study a combined Rankine-Goswami cycle is proposed and a thermodynamic analysis is conducted. The Goswami cycle, used as a bottoming cycle, uses ammonia-water mixture as the working fluid and produces power and refrigeration while power is the primary goal. Figure 5 shows a schematic of the Rankine-Goswami cycle.

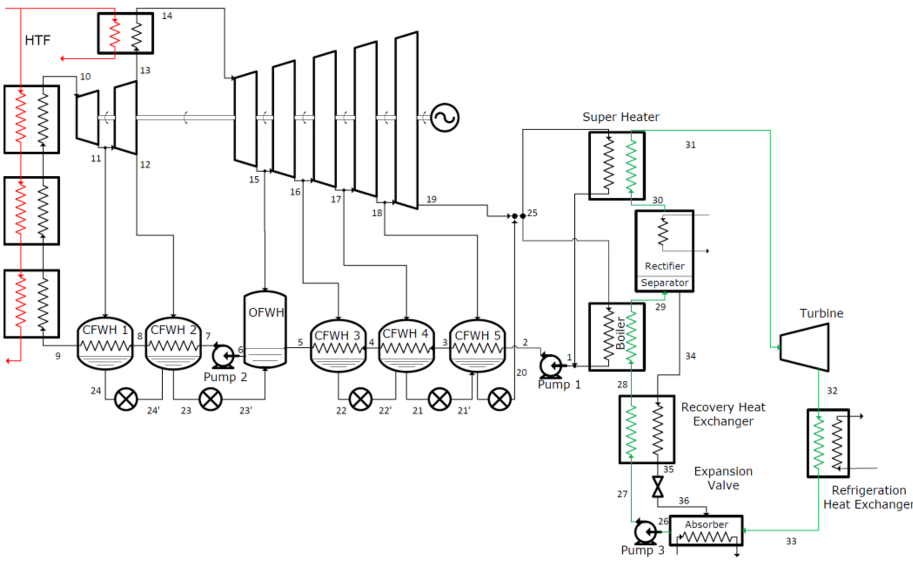
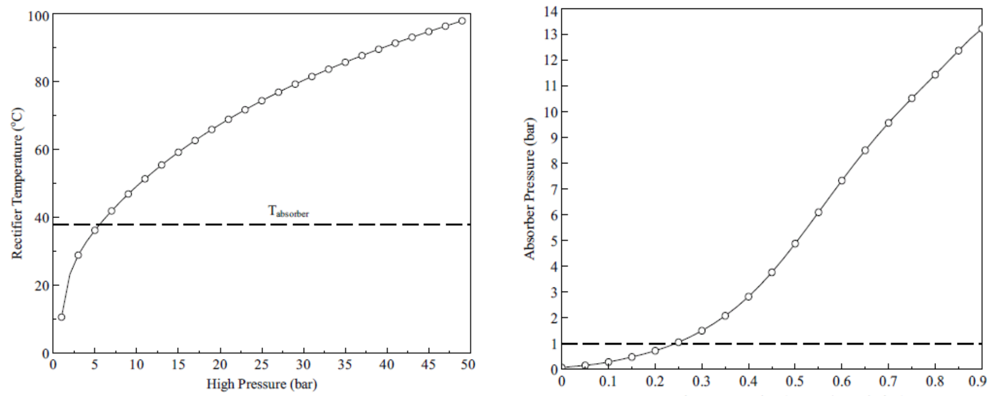


Fig.5

The detailed explanation about the parameters that were used for simulation is given in the paper. Different cases were also considered for parametric studies which are shown below.

Case	Rectifier	Superheater	Controlled Parameter
R	Yes	No	$x_{rectifier} = 0.995$ $T_{superheater} = T_{rectifier}$
R+S	Yes	Yes	$x_{rectifier} = 0.98$ $T_{superheater} = T_{boiler}$
B (Base)	No	No	Saturated vapor condition at the boiler exit

The thermodynamic properties of water and steam were implemented in Python 2.6 by using the international-standard IAPWS-IF97 steam tables. For the Goswami cycle, the properties of ammonia water were obtained from a Gibbs free energy formulation given by Xu and Goswami. In this study the amount of the electric work obtained from the topping cycle was held constant at 50 MWe while for the bottoming cycle the turbine work was considered as an output parameter. Figure 6 shows the effect of the high pressure side on the rectifier temperature and absorber concentration, In this case, the ammonia concentration range was selected such as the absorber was kept at least under atmospheric pressure.



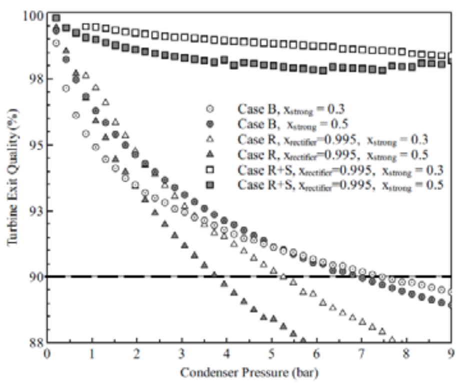
(a) Rectifier Tempearture, $x_{rectifier} = 0.995$

(b) Absorber Pressure, $T_{absorber} = 38.3°C$

+

Fig 6

Figure 7 shows the effect of the condenser pressure on the Goswami bottoming cycle exit quality for different cases and ammonia mass fraction. Moreover, Figure 8 shows the effect of the variations of the net -work with the condenser pressure for ammonia mass concentration of 0.3, in all the studied cases.



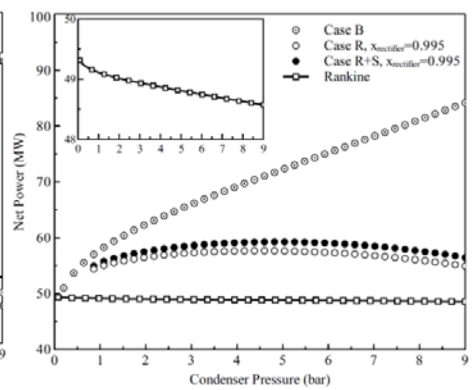


Fig.7 Fig. 8

The effect of condenser pressure on the effective First Law efficiency is also illustrated in Figure 9 while the cooling capacity of the Goswami bottoming cycle is presented in Figure 10. The effective exergy efficiency in the cycle as a function of the condenser pressure and ammonia mass fraction is also presented in Fig.11.

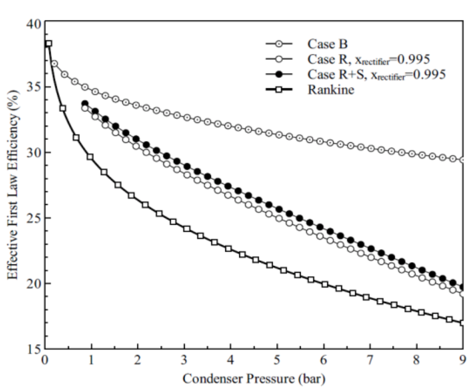


Fig. 9

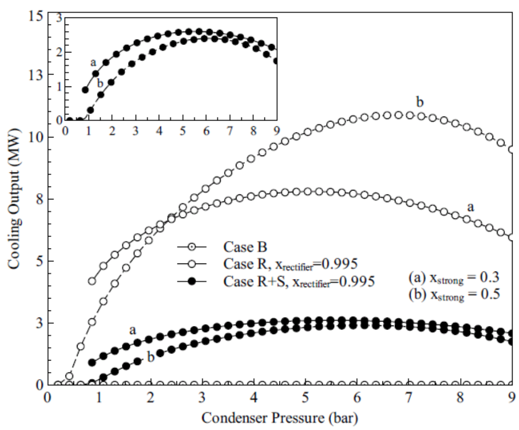


Fig. 10

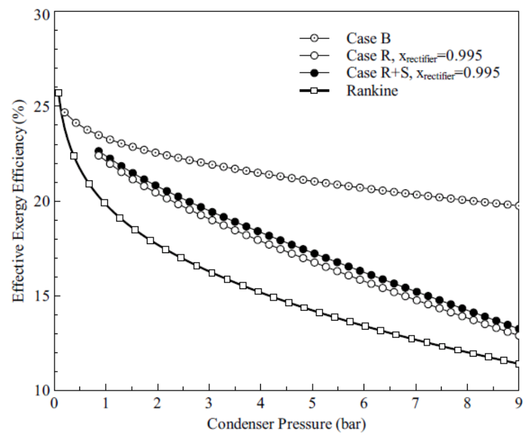
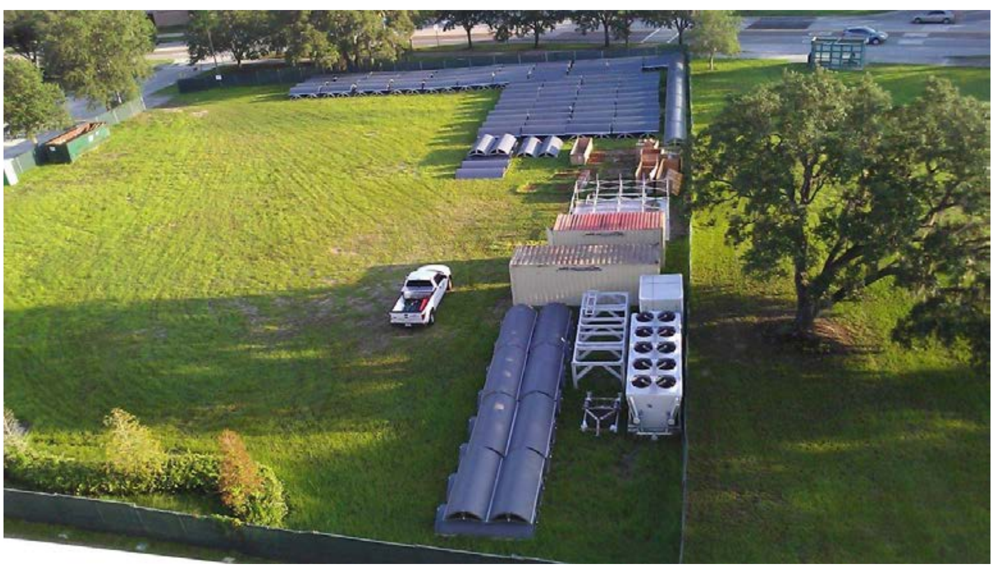


Fig. 11

Task 3. Installation and Operation of 50kWe Solar Power Plant

Sopogy Inc. Honolulu Hawai is the main contractor for installation and operation of 50kWe Solar Power Plant at USF. We have received all the parabolic concentrators (Soponova 4.0) from Sopogy Inc. All these collectors have been assembled and are ready for installation. We have also received Green Machine Elite 4000 manufactured by Electratherm and air-cooled condenser. Picture below shows the assembled concentrators, Green machine and air-cooled condenser. It is expected that the commissioning and operation of this power plant will be completed sometime in the months of January or February 2013.



Task 4: Thermal Energy Storage

We are currently working on the development of low cost thermal energy storage (TES) systems. The objective is to research and develop a thermal energy storage system (operating range 300^{0}C – 450 ^{0}C) based on encapsulated phase change materials (PCM) that can meet the utility-scale base-load concentrated solar power plant requirements at much lower system costs compared to the existing TES concepts that cost about \$27/ kWh$_t$. The major focus of this study is to develop suitable encapsulation

methods for existing low-cost phase change materials that would provide a cost effective and reliable solution for thermal energy storage to be integrated in solar thermal power plants. This project proposes a TES system concept that will allow for an increase of the capacity factor of the present CSP technologies to 75% or greater and reduce the cost to less than $10/kWh_t$ to make it very competitive with fossil fuels.
We have successfully prepared porous pellets of phase change materials that will allow for the volumetric expansion during PCM melting and hence impose less stress on the encapsulating material. We have developed the encapsulation techniques and selected the low cost encapsulating material that will be used to encapsulate the PCM. Currently we are optimizing the process for encapsulating the PCM so that it can undergo at-least one thousand charge and discharge cycles without any deterioration of the encapsulation. We are also working on the development of numerical model that will help to design the thermal energy storage systems.