Supercritical Geothermal Cogeneration: Combining Leading-Edge, Highly-Efficient Energy and Materials Technologies in a Load-Following Renewable Power Generation Facility

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ABSTRACT

Geothermal power must contribute much more to the supply of clean renewable energy. Electricity generated from wind and solar power is intermittent and cannot alone balance the demands of the grid. Geothermal power provides baseload generation. The geothermal industry needs to both improve its return on investment and increase its flexibility in supplying electricity to the grid. A recent development that has great promise occurred last year, when the Iceland Deep Drilling Project successfully drilled a well into a supercritical geothermal reservoir. This breakthrough has the potential to offset the high front-end costs and risks of geothermal power by allowing high enthalpy production from supercritical wells. Such wells are expected to produce an order of magnitude increase in power output relative to conventional, subcritical geothermal systems, as discussed by Elders et al. (this volume).

In addition to greater power output, supercritical resources cause dramatic changes in important properties of water. As a result, supercritical geothermal cogeneration (SGC) can produce electricity and create hydrogen with high efficiency and low costs using a flexible and thermally integrated energy plant combining: (1) a Brayton-cycle turbine generator using supercritical CO_2 as its working fluid; (2) electrolysis cells using ceramic proton-conducting membranes; (3) extraction of metals and minerals; and (4) desalination by switchable polarity solvent forward osmosis to supply deionized water required for brine processing, electrolysis and electrical power generation. The results will enable exploitation of new geothermal resources, and provide

a flexible source of grid balancing for more rapid increases of intermittent wind and solar power enabling 100% use of renewables for both electric power generation and transportation.

1. Introduction.

Supercritical geothermal cogeneration (SGC) will use very high-temperature geothermal resources to power a supercritical turbine generator that will balance the generation of electricity on the grid by load-following, produce hydrogen by electrolysis, extract metals and other valuable compounds, and use excess heat to produce pure water by desalination. The secondary goal is to enable the excess energy that is not needed to balance the grid to be used to reduce California's use of fossil fuels for transportation and resulting production of greenhouse gases, in accordance with the state's statutory energy goals. SGC will advance electrolysis to be performed using supercritical water, exploiting a number of special properties of supercritical water that will render such electrolysis much more efficient and less expensive, so that the goals described above will provide economic as well as environmental benefits. The combination of supercritical geothermal resources to generate electricity and to provide hydrogen very efficiently has been addressed previously (Elders, *et al*.; Shnell *et al*.). The objective of this paper is to present further developments in those technologies, and to add to SGC technologies relating to desalination, to support the generation and electrolysis functions, and the extraction of metals and minerals, to improve the returns on geothermal investment and to ameliorate scaling and other negative issues caused by metals and minerals. Waste heat will become a worthwhile resource by providing the heat to replace electricity in desalination and thereby reduce the cost of clean water. Clean water is needed for general brine processing, electrolysis, so it helps to create revenue, and it also reduces the cost of using cooling towers or other heat sinks to dispose of the waste heat. Using SGC, load following could, under appropriate conditions, be achieved more economically and effectively by using geothermal resources to (a) generate electricity for sale and for electrolysis to produce hydrogen as a non-polluting fuel (eligible for carbon credits for transportation and for microgrids), and (b) to preheat the feedwater for electrolysis. Because power generation and electrolysis of water are more efficient at high temperature, the best environment to test this concept involves supercritical geothermal reservoirs. In Iceland, the Iceland Deep Drilling Project (IDDP) is investigating such supercritical geothermal conditions. In 2009, Phase 1 of the IDDP created the hottest geothermal well in the world (450°C) but it was too shallow to reach supercritical pressures. In 2017, Phase 2, a well was drilled to greater depth and reached supercritical pressure and temperature. In California, the Salton Sea, Coso and Geysers geothermal fields all exhibit very high temperatures at commercially drillable depths. In fact, in some parts of the Salton Sea geothermal field, reservoir temperatures exceeding the critical temperature for pure water occur at depths of only 2 km (Hulen et al., 2002) and in some parts of The Geysers geothermal field, reservoir temperatures exceeding the critical temperature appear to occur at about 4.0 km depth. This creates the possibility of providing baseload energy using supercritical temperatures, and therefore efficiently and inexpensively, without using batteries or other storage of electricity, and producing large volumes of clean hydrogen to alleviate the serious levels of greenhouse gas and air pollution produced by combustion of fossil fuels in Southern California, as reported in recent studies of current high levels of pollution in Southern California. See the web page of the California Air Resources Board describing its

research program on the health effects associated with air pollution effects at https://ww2.arb.ca.gov/research/research-health-effects-air-pollution .

The greatest potential worldwide for SGC, however, is along the 65,000 kilometers of rift zones around the world in the ocean floor that produce supercritical geothermal resources (including touching land in Iceland and the Salton Sea geothermal field and including the Gorda Rift Zone that parallels the coast of northern California and southern Oregon about 200 miles to the west). The geothermal energy under the ocean floor, a vast, high-temperature resource which has never before been accessed to generate electricity, could provide enough baseload energy to reverse climate change. This resource will power a self-contained, submersible, remote-controlled SGC station that will sit on the ocean floor at depths of 2,000 meters or more, where it can access geothermal resources at supercritical pressures and temperatures over 500°C.

2. Supercritical CO_2 Turbine Generator.

Supercritical geothermal resources will enable the generation of electricity on an efficient, economical and highly reliable basis through the use of turbine generators that will supply both the grid's demand for electricity and, by operating during off-peak hours, the power needed to replace existing transportation fuels. These stations will incorporate a further innovation, the use of turbines powered by supercritical CO_2 (sCO_2) as the working fluid, which is still in the development stage for nuclear power plants and has not previously been considered for geothermal plants. These advancements in geothermal technology will develop a very high-temperature and therefore very efficient form of geothermal generation. Supercritical CO_2 in a closed-loop recompression Brayton cycle can achieve a plant efficiency of 50%. This advance will make geothermal energy (already highly reliable, with availability factors over 90%, and very friendly to the environment, with negligible impacts on the land surface or the atmosphere) more affordable, by reducing the levelized cost of geothermal power.

This sCO_2 turbine coupled to a generator, and the rest of the SGC, can operate in a self-contained, submersible, remote-controlled geothermal-powered electric generating station. The station can be built on a barge, which can be towed by a tug to the ocean surface above the geothermal wells, then submerged and lowered by winches on the installation vessel to the site on the ocean floor prepared for the station. There, by remote control, with the assistance (to the extent needed) of a remotely operable submersible vehicle operated from the tug, the station is coupled to the wellheads for the geothermal production wells and to the wellhead for the injection well. The station uses the production from more than one well, each of which is started in close proximity to the others but accesses different geothermal reservoirs, or different areas of the same reservoir, using directional drilling. The station is also connected to a remote control cable that enables control of the station from a facility on land, and to an undersea high voltage direct current transmission cable that delivers the electricity to the electrical grid on land. The station is detachable from the wellheads and the cables by remote control, so that the station can be retrieved by a tug, raised to the surface and towed to shore every three to five years for maintenance and overhaul. These regular overhauls, combined with the very cold water and the low levels of oxygen in the water at such depths, will avert the corrosion of the station by salt water.

3. Electrolysis Using Ceramic Proton-Conducting Membranes.

Supercritical geothermal resources will, by operating during off-peak hours, supply the power needed to replace existing transportation fuels, whether by charging the batteries of electric cars or by providing hydrogen through electrolysis, which can be performed advantageously on the ocean floor by making direct use of the supercritical geothermal resources together with the excess off-peak electricity from the baseload geothermal generation of the supercritical CO_2 turbine generator discussed above. The nuclear industry has promoted the development of solid oxide electrolysis cells for high-temperature electrolysis, but they require temperatures of 800°-900°C to achieve maximum efficiency, and recent tests have observed long-term performance degradation rates of 3.2% to 4.6% per thousand hours of operation, which is considered unacceptable (O'Brien, 2010; Zhang, *et al*., 2012). It was noted, however, even before the development of solid oxide electrolysis cells, that supercritical water has properties that render electrolysis significantly more efficient than at standard temperature and pressure. (Franck, 1970; Flarsheim *et al*., 1986) Electrolysis stations can make direct use of supercritical geothermal resources to heat water above critical temperature. Electrolysis of water becomes more efficient when done at supercritical temperatures, in part because at high temperatures the additional heat replaces some of the electricity that is otherwise required for electrolysis, as shown in Figure 1 (from Mougin, 2015).

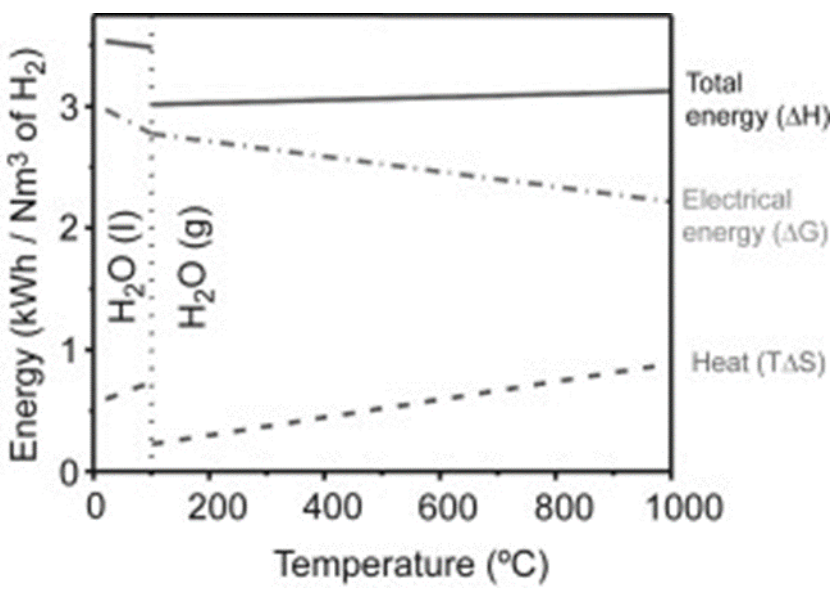
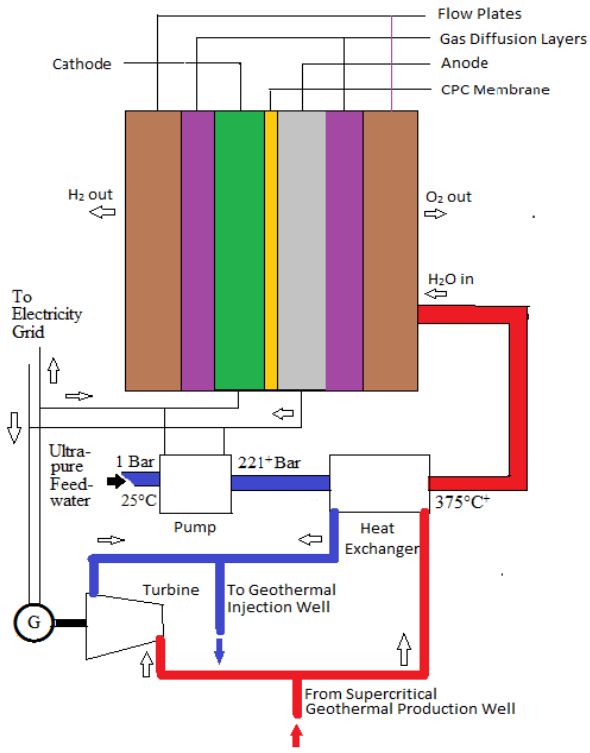


Figure 1- Effect of temperature on the thermodynamic parameters of water electrolysis

Much of the new power replacing baseload coal and nuclear power is wind and solar power, requiring load following to achieve grid balancing, which is increasingly provided by natural gas-fueled generation that produces greenhouse gas. Geothermal energy is baseload, but geothermal power generation using current technology is not sufficient to balance the grid; supercritical resources are needed. Also, further curtailment of greenhouse gases will require renewable energy to replace the fossil fuels now used for transportation fuels. Hydrogen could

replace fossil fuels, but over 90% of hydrogen is now produced from fossil fuels, producing greenhouse gases. This can be avoided by generating electricity from renewable resources to produce hydrogen by electrolysis. SGC will produce vast amounts of clean electricity cheaply and will perform electrolysis efficiently and on a large scale using a ceramic proton conducting membrane (CPCM).

SGC is transformational because the properties of water under supercritical conditions change in unique ways that make both electricity generation and electrolysis more efficient. The supercritical temperature is sufficient for high proton conductivity of the CPCM so that the protons pass more easily and efficiently (which may be further advanced by the effects of supercritical pressure) and the properties of water change to make both electricity generation and electrolysis more efficient. It is anticipated that the concept will use electrolysis, and its flexibility, to expand greatly the scope and effect of virtually unlimited geothermal resources by opening major markets for geothermal and other renewable energy relating to balancing the electrical grid and to replacing current transportation fuels with hydrogen. To the extent that the grid needs balancing, baseload geothermal can do so without disruption of the grid, but it will disrupt the providers of coal, nuclear, natural gas and battery power that would otherwise be used for balancing. To the extent that electricity is not needed to balance the electricity grid, it can be used in electrolysis to create hydrogen for the transportation sector, disrupting and ultimately replacing oil, natural gas and other polluting fuels. When electricity is needed for balancing the grid, the amount used for CPCM electrolysis can be reduced accordingly in two seconds, and the power sent to the grid.



CPCM in Supercritical Geothermal Cogeneration System (*not to scale*)

Figure 2

SGC makes dual use of geothermal resources at temperatures above the critical temperature of water to power both electricity generation and electrolysis (Figure 2). The feedstock for the electrolysis can be water that is purified using excess low-grade geothermal heat (which would otherwise require "heat sinks" to dispose of it) and pressurized above 221 bar before being heated above 374°C in a heat exchanger using the supercritical resource. Electricity from geothermal power using current technologies, recently estimated by the Energy Information Agency to cost $50 per MWh, is cost competitive with other forms of generation. (U.S. Energy Information Administration, 2015) SGC will use geothermal resources at supercritical temperatures and pressures, more efficient than the current technology, so the cost of electricity from the proposed approach is projected to be 20% lower. This approach will use stranded energy resources such as Salton Sea and ocean rift zone geothermal, with potential to cogenerate with solar and offshore wind resources, and reduce the use of coal, petroleum, natural gas and nuclear energy while providing hydrogen (without producing greenhouse gas or other pollution) as a flexible, balancing fuel for microgrids and other backup power. It will enable utility-scale production of hydrogen for grid resiliency, energy storage and energy security around the world.

The efficiency of standard electrolysis is decreased by activation, ohmic, and concentration overpotential, which is alleviated by changes in the properties of water as it goes from a liquid to a supercritical state. (Franck, E. U., 1970; McDonald, A. C., et al., 1986) Some of the changes which are important to electrolysis are related to the loss of polarity in supercritical water. These changes include: the loss of surface tension and drop in viscosity by a factor of 10 to 20 (depending on pressure), increase in diffusivity and self-ionization, lower relative permittivity by an order of magnitude and higher specific conductance by an order of magnitude or more. ***See*** the Table below.

PROPERTY	**LIQUID WATER**	**SUPERCRITICAL**
Self-Ionization	pK_w14 @25°C	pK_w15
Dynamic Viscosity	890µPas	41.79µPas
Surface Tension	72mNm^2 @25°C	0
Relative Permittivity	78.54 @25°C	5.9 @400C°
Specific Conductance	.055 µS/cm^2	1.17 µS/cm2

Moreover, the concept combines supercritical electrolysis with recent developments in proton exchange electrolysis using a CPCM, instead of a polymer membrane. The CPCM will withstand the higher temperature and produce purer hydrogen. If the costs of electrolysis cell stacks follow those of equivalent fuel cell stacks, the low operating temperature of the CPCM may enable it to mimic the protonic ceramic fuel cell (PCFC): PCFC production costs are 27% to 37% lower than SOFC production costs; (b) PCFC balance-of-plant hardware costs are lower than SOFC balance-of-plant hardware costs; and (c) PCFCs are more durable than SOFCs. (Dubois, A., S.) The lower costs and higher durability due to lower temperatures are not lost due to the pressure of SGC; current "ultra-supercritical" power plants, which operate at pressures of 292 bar and at

temperatures of 623°C, use ferritic and austenitic stainless steel, which are in the same class of materials now used in PCFCs. (Marion, J.)

4. Desalination.

Water systems are typically energy-intensive. The energy sector withdraws nearly half of all water in the U.S. and the water sector accounts for over 12% of all U.S. energy consumption. Treating, moving, and distributing water account for a major energy cost in the water use cycle. Large energy-efficiency gains are possible through water efficiency improvements or through source switching (e.g., use of advanced water treatment technologies accessing nontraditional sources). However, as more nontraditional types of water are used, such as oil- and gas-produced waters, saline aquifers, brackish groundwater, and brines, the associated energy requirements generally increase (e.g., desalination can be 100 times as energy intensive as treatment of surface fresh water). Novel water treatment technologies can enhance energy efficiency of water systems and enable the productive and safe use of non-traditional water resources for energy and non-energy applications.

So far, renewable energy has played only a minor part in desalination (NRC 2008). The earth is a huge reservoir of geothermal energy, that when accessible can be used in many applications. When collocated with saline or brackish water sources, geothermal thermal energy can enable new and/or alternative desalination technologies such as multistage flash distillation, multi-effect distillation, and forward osmosis (FO) (Chung et al., 2012; Zhao et al., 2012). Prior work has utilized lower temperature geothermal fluids as the thermal energy source for multi-effect distillation, and multistage flash distillation (Goosen, 2010), as well as other distillation systems (Bourouni and Chaibi, 2005). The amount of treated water recovered from saline waters using these technologies was low relative to reverse osmosis (RO). The thermally driven FO technologies described in this proposal have the potential to recover more water while using less electricity than is accomplished with RO.

The use of geothermal energy to desalt saline water depends on its competitiveness with other sources of energy. SGC will be competitive by using an innovative, energy-efficient FO desalination technique that will be powered using geothermal heat that, having initially been supercritical, has expended some of that thermal energy in SGC but still retains a comparatively high temperature. The waters produced will add economic value to the geothermal facility by producing water.

Forward osmosis (FO) is a membrane-based separation process that uses the osmotic pressure gradient between a concentrated draw solution and a feed stream to drive water flux across a semi-permeable membrane (i.e., passively with the gradient, as opposed to RO which requires energy to pump against the gradient; Cath et al., 2006; Shaffer et al., 2015). The primary requirement for draw solutions is to find a mixture with enough osmotic potential to power the trans-membrane transfer. Other challenges include selecting a draw solute that may be easily and economically removed and re-generated. While FO has achieved some market success, substantial R&D work remains in order for this method to compete with RO and traditional thermal desalination techniques.

The foregoing includes a novel approach to FO water purification, each using the ionic liquids class of thermally sensitive draw solutes. Phase separation between ionic liquid (IL) and water has been of great interest for fundamental research as well as potential industrial applications (Kohno and Ohno, 2012). SGC will use the dynamic shifts of IL/water mixtures between a homogeneous mixture and separate IL and water phases for FO desalination applications. Most IL/water mixtures exhibit an upper critical solution temperature phase change (i.e., miscibility of IL with water generally increases upon heating). Interestingly, some ILs undergo a lower critical solution temperature phase transition with water in which the separated IL and water phases become miscible upon cooling. As the phase transition of IL/water mixtures can occur at ambient conditions within a few degrees ILs can be used as solvents in a highly energy efficient FO desalination process (Cai et al., 2015).

SGC can utilize lower temperature geothermal resources to provide the energy necessary for FO water treatment. SGC can provide all the thermal energy necessary for the FO treatment using geothermal fluids having temperatures of 150°C or less, while recovering more water from the feed stream than could be accomplished using reverse osmosis (RO) technologies.

ILs are expected to be effective draw solutes for FO given their ability to reach high concentrations. The driving force for this separation is the natural osmotic pressure gradient between IL draw solution and saline water feed solution, which will force a net flow of water through the membrane, thus effectively separating the feed water from its solutes at temperatures that corresponds to formation of a homogeneous IL/water phase. A small amount of the waste heat can be used to split the homogeneous IL/water phase into an IL phase and an aqueous phase. The rate of phase change between the homogeneous mixture and the separated IL/water biphasic mixture upon heating or cooling should be rapid but may require facilitation. This scheme could radically reduce the energy-intensity of water purification.

The miscibility of ILs with water depends strongly on the character of the ionic species. Physico-chemical analysis of hydrophobic ILs that undergo a phase separation after mixing with water showed that there is a particular range of “hydrophilicity” of the ampiphilic ILs within which the phase transition is possible. IL/water phase changes can phase separation upon heating from 20° to 25°C. Since the hydrophilicity of ILs depends on the chemical structure and composition of the ion species, the phase behavior of the IL-water systems can be controlled by specific molecular design of IL ions (e.g., [P_{4444}][TMBS] and/or mixing ILs with different hydrophilicity, or hydrophobic [P_{4448}]CF_3COO mixed with hydrophilic [P_{4448}]CH_3SO_3). The design and testing of different IL-water schemes for FO will be the primary focus at the beginning of the planning of this scheme.

The barrier for widespread application of ILs in technologies at large scale is their high cost. Therefore, an ILs-based desalination system that uses large reactors filled with large volumes of ILs and operated via consecutive phase change cycles would be impractical and economically prohibitive. Therefore, we envision developing a novel approach to desalination in which the reactor comprises two horizontal membranes with a thin layer of IL in between and small temperature gradient applied across the IL gap. The FO membrane at the bottom of the reactor will perform the main function of extracting water from the saline feed stream and moving it into the IL phase on the other side of the membrane. The FO membrane will be held below the temperature that corresponds to formation of the homogeneous phase IL/water phase, which will assure full miscibility of IL and water in the vicinity of the FO membrane. The slightly warmer

water permeable membrane at the upper end of the reactor will perform dual function of warming the IL/water phase thus inducing separation of water and IL phases and allowing water through the membrane into the pure water stream. This reactor design could assure a continuous operation of the system, minimize the volume of the IL draw solution and allow use of low grade waste heat from geothermal power plant to drive and control the process. In for some reason FO does not work as expected, SGC could still operate by using RO for desalination, but producing less water and using more electricity.

5. Extraction of Metals and Minerals.

The SGC will extract metals and other valuable compounds from geothermal brine, creating an additional source of revenue. The potential to exploit the high concentrations of metals in geothermal brine was a focus of the earliest investigations at the Salton Sea (Werner, 1970; Hornburg, 1975; McKibben et al, 1989). However, the deleterious effects of amorphous silica precipitation and scaling, and corrosion due to high chloride concentration, hindered initial attempts to process the brine for power generation (Hoffman, 1975; Featherstone et al., 1979), and is a continued impediment to metals extraction (Harrison, 2014).

A number of studies have been performed regarding the recovery of minerals and metals from geothermal fluids (Bakane, 2013.) A number of attempts have been made at commercializing such recovery. At the Salton Sea, metals extraction has primarily focused on silica, zinc, manganese and lithium. Amorphous silica is currently extracted from the brine at all Salton Sea power plants to prevent scaling in injection pipelines and wells, but is disposed as waste due to low purity. BHP investigated zinc, lead and silver extraction at the Salton Sea (U.S. Patent 5,229,003), but later ceded efforts to CalEnergy (U.S. Patent 6,458,184). From 2000-2004, CalEnergy extracted and produced commercial quantities of High Grade zinc from Salton Sea geothermal brine using solid-liquid ion exchange; the plant was decommissioned due to a combination of technical difficulties and poor market conditions. CalEnergy also produced manganese at the pilot scale using liquid-liquid solvent extraction but did not attempt to commercialize the process (U.S. Patent 6,682,644). Recent efforts have focused on lithium extraction due to rising market conditions related to electric vehicles and storage, and because power plants currently in operation at the Salton Sea process brine with an annual lithium flux valued in excess of $2B. Various methods for selectively extracting lithium that have been proposed or attempted include: (1) solid-liquid ion exchange, (2) liquid-liquid solvent extraction, (3) high temperature membrane filtration, (4) wholesale brine salt precipitation followed by off-site purification, (4) .

The viability of metals extraction from geothermal fluids will be improved in a commercial SGC facility. Whereas the currently operating Salton Sea geothermal plants are optimized for power generation, the SGC facility will include metals extraction in the integrated process design, allowing improved mitigation of unwanted amorphous silica precipitation, and extraction of the target metals at optimum temperature, pressure and other physico-chemical conditions.

6. Conclusion.

As a result of the success of the Iceland Deep Drilling Project in demonstrating the possibility of developing supercritical geothermal resources (as discussed by Elders et al. (this volume) which enable the development of supercritical geothermal generation of electricity and supercritical electrolysis of hydrogen, and the rest of the elements of SGC, unbounded opportunities have been opened for development of the geothermal industry, and the unification of the energy sector, in California and the U.S. and, ultimately, around the world.

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