2012 Presidential Green Chemistry Challenge Award Nomination Package

Project Title: Electrodialysis & Chromatographic Separation Technology Developed by NSR Technologies for Chlorine-Free Production of Potassium Hydroxide (KOH) and Hydrochloric Acid (HCl)

Nomination Date: December 31, 2011

Primary Sponsor(s): NSR Technologies, Inc. (www.nsr-tech.com) is self-nominating for this award and is not sponsored by any other entity.

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Contributors: NSR is an independently owned and operated corporation. However, its Founder and CEO, Kris N. Mani, Ph.D., developed numerous patents that formed the basis of NSR's technology. Dr. Mani developed these patents during his employment at Archer Daniels Midland Co. (ADM). NSR currently holds an exclusive, worldwide patent estate of Dr. Mani's research, which NSR licensed from ADM.[1] Dr. Mani's extensive research in the field of Electrodialysis & Ion-Exchange Chromatography began during his tenure with Allied Signal Corporation (now Honeywell, Inc.). These research patents also helped form the foundation of NSR's current technology base.[2]

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[1] (US Patent Nos.: 5,972,191; 6,110,342 ; 6,221,225; 6,224,731; 5,814,498; 6,123,823; 6,017,433; 6,294,066; 6,482,305; 6,627,061; 6,331,236 ; 6,755,951

[2] (US Patent Nos.: 4,082,835; 4,107,264; 4,107,015; 4,144,158; 4,168,297; 4,389,293; 4,390,402 ; 4,391,680; 4,504,373; 4,536,269; 4,584,077; 4,592,817; 4,608,141; 4,629,545; 4,636,289 ; 4,740,281; 4,976,838; 5,135,626; 4,995,956; 4,999,095; 5,139,632; 5,162,076; 5,200,046; 5,198,086; 5,228,962; 5,291,317; 5,352,345

Project Title: Electrodialysis & Chromatographic Separation Technology Developed by NSR Technologies for the Chlorine-Free Production of Potassium Hydroxide (KOH) and Hydrochloric Acid (HCl)

Short Description of Recent Milestone: NSR Technologies commercialized a new route to produce potassium hydroxide (45%-50%) and dilute hydrochloric acid. NSR's process utilizes NSR's newly developed and implemented electrodialysis cell design, which allows ion-exchange membranes to perform more reliably and operate at higher efficiency. This, coupled with a highly-selective ion-exchange chromatographic purification system, produces commercial grade KOH without environmental pollutants like Chlorine (Cl_2) and Mercury (Hg). The plant, constructed and operational in 2009, renewed long-term supply contracts with key customers like Archer Daniels Midland (ADM) in 2011 and operated reliably for 48/52 weeks in 2011.

Award Application & Focus Area: The nominated technology is eligible for the Small Business Award. NSR's primary focus area is greener reaction conditions. A secondary focus area is the design of greener chemicals.

U.S. Component Description: The Company researched, developed and commercialized all technology in Decatur, Illinois. The Company's production facility is also based in Decatur, Illinois.

Abstract: NSR commercialized a new technology process to manufacture 45%-50% Potassium Hydroxide (KOH) and 7% Hydrochloric Acid (HCl). The process uses NSR's novel electrodialysis IonSel™ stacks, which consist of specialty polymeric membranes and a novel design that allows the cells to operate at high efficiency, consume 40% less energy, and generate high-purity products. The process, which involves a rearrangement of ions in solution, is particularly suited to recycling salts in other applications, including recycling salts generated in pulp & paper industries and from environmental control systems in coal-fired power plants.

Currently NSR's plant is the first environmentally-friendly, cost-effective alternative to electrolysis (chlor-alkali) production in decades. NSR's process yields high purity, food-grade products ***without*** Hg (a health hazard to children) and oxidizing species like chlorate and hypochlorite. NSR's process also does not produce the hazardous air pollutant (HAP), chlorine (Cl_2). A major feature is significantly lower energy consumption per unit of product manufactured, which allows smaller profitable plants to produce equivalent amounts of acid and alkali. The smaller plant costs less, is built close to end-users, and reduces transportation hazards. The US consumes approximately 2 billion pounds of KOH/year.[3] NSR supplies food-grade 7% HCl to ADM via pipeline. This efficient transfer eliminates the unnecessary transport – and accidental release – of fuming 35% HCl.

NSR's process also does not produce Cl_2, and its single plant would eliminate the production of 10 million lbs/year of Cl_2. Competing processes at over 500 companies (at over 650 sites worldwide) produced 140 billion lbs of chlorine/year in producing KOH and NaOH.[4] Although the Cl_2 is recovered and sold, supply/demand imbalances can yield unnecessary Cl_2

[3] Suresh, Bala, Stefan Schlag and Kazuo Yagi. "Inorganic Potassium Chemicals." The Chemical Economics Handbook, SRI Consulting. 2004, p.7.
[4] Linak, Eric, Stefan Schlag and Kazuteru Yokose. "Chlorine & Sodium Hydroxide." The Chemical Economics Handbook, SRI Consulting. 2008, Abstract.

production, particularly due to reduced Cl_2 demand from the phase-out of halogenated ozone depleting materials.[5] Implementation of NSR's technology could eliminate billions of lbs of unnecessary Cl_2 production. (Words: 350)

NSR's innovations represent an original and dramatic advancement in scientific innovation with broad applications to many processes and industries. Part I of this paper will discuss the scientific innovation and technical merits of the technology. Part II will compare NSR's technology with existing technology and applications. Part III will discuss the applicability to other industries and applications. Finally, Part IV will provide an update on the future plans for the technology and current status of awards and recognition.

Part I: The Chemistry of NSR's Technology

ED Membrane Technology: The heart of NSR's process consists of its IonSel™electrodialysis (ED) cell technology, which includes a layer of cation-selective, anion-selective, and bipolar-selective membranes.

Electrodialysis is a technology with enormous potential in numerous areas, including bio-processing, because any ionic product, such as inorganic acids and bases, organic and amino acids, can potentially be separated. Electrodialysis has the potential to convert salts to their acids, eliminate salt waste streams generated when done conventionally, and can be used to replace ion exchange processes used in removing ions from a wide variety of products, including dextrose, fructose and corn syrup. These applications can eliminate tons of waste byproduct salts generated using current technologies. NSR has expanded electrodialysis to an even wider application by using it to manufacture a high value, specialty chemical product (Potassium Hydroxide). This has never been done before.

The key basis of NSR's technology is the deployment of bipolar ion exchange (BPIX) membranes within an electrodialysis cell (ED Cell) to effect the forced dissociation of water molecules (H_2O) to hydrogen (H^+) and hydroxyl (OH^-) ions, and concentrating these ions to levels that are attractive for commercial applications using a direct current (DC current) driving force. The H^+ and OH^- ions are the components for acid and base (alkali) products respectively. Within the ED cell, each bipolar membrane is coupled with an anion exchange membrane (AM) and a cation exchange membrane (CM) that separate the feed salt such as sodium chloride (NaCl) or potassium chloride (KCl) into their components, namely sodium or potassium ions (Na^+ or K^+) and the chloride ions (Cl^-) using the same DC current driving force. The net result within the ED cell is the conversion of a salt (NaCl or KCl) into acid and base products; in this particular case, Hydrochloric Acid (HCl) and Potassium Hydroxide (KOH). The same principles apply for NaOH production. The process can be represented schematically as follows:

$$KCl + H_2O = KOH + HCl \qquad \text{(Equation 1)}$$
$$NaCl + H_2O = NaOH + HCl \qquad \text{(Equation 2)}$$

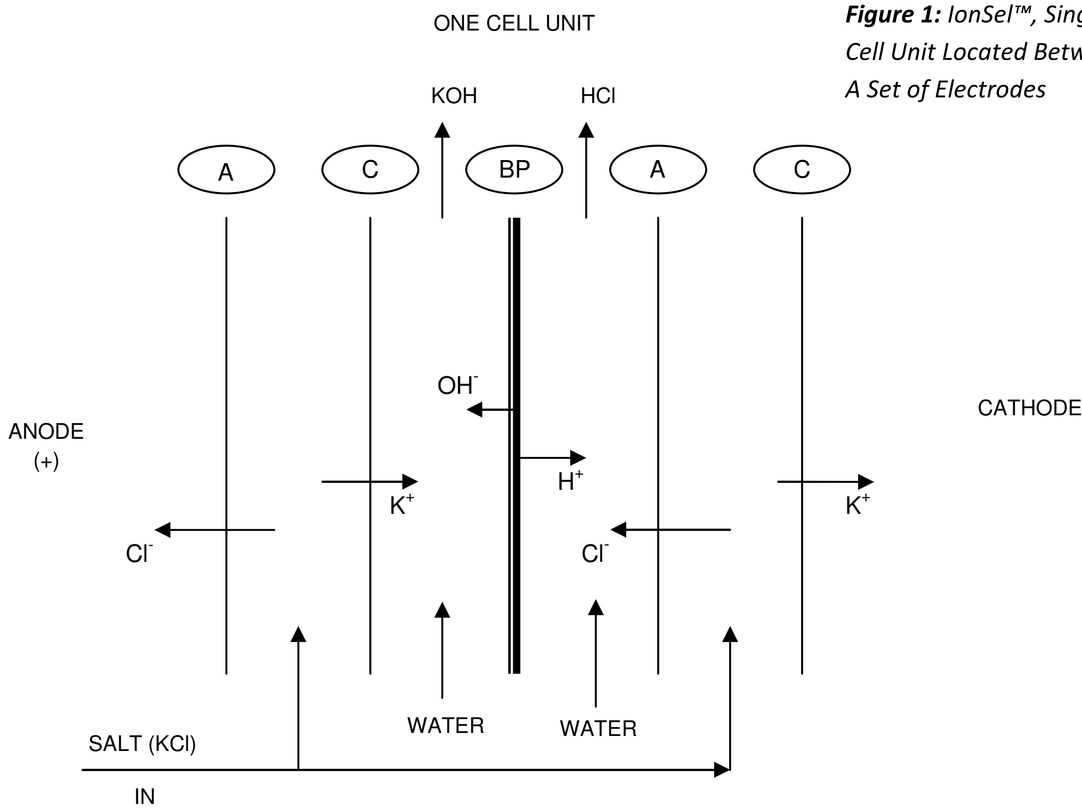
In contrast, the chlor-alkali production involves an oxidation-reduction reaction that produces Cl_2 as a byproduct. Equation 3 illustrates this reaction to produce KOH. Equation 4 illustrates NaOH production:

[5] Linak, Eric, Stefan Schlag and Kazuteru Yokose. "Chlorine & Sodium Hydroxide." The Chemical Economics Handbook, SRI Consulting, 2008, Abstract.

$$2KCl + 2H_2O = Cl_2 + H_2 + 2KOH \quad \text{(Equation 3)}$$
$$2NaCl + 2H_2O = Cl_2 + H_2 + 2NaOH \quad \text{(Equation 4)}$$

Figure 1 shows a single cell unit located between a set of electrodes. The commercial IonSel™ cell stack contains 160 cell units that are assembled between a single set of electrodes, which form the compact commercial electrodialysis cell ("Cell Stack").

***Figure 1:** IonSel™, Single Cell Unit Located Between A Set of Electrodes*



Electrodialysis (ED) achieves a significant energy advantage when compared with chlor-alkali production. The minimum electrical potential for achieving the separation process used by NSR is approximately 0.83V; which translates to approximately 500 kWh/short ton of NaOH or ~360 kWh/short ton for KOH. The chlor-alkali process, however, involves chemical conversion using oxidation/reduction steps at the electrodes. The minimum electrical potential for achieving this is about 2.1 V. The energy usage per ton of KOH is typically 1800-2000 kWh/ton of KOH when produced via chlor-alkali production.

The key factor behind the commercialization of NSR's technology has been the development and availability of specialty ion exchange (IX) membranes that have the desirable electrical properties, ion selectivity and long life at the commercial operating conditions. Additionally the cell design and construction is critical to ensure that the membranes are performing optimally. The capabilities of the NSR process are as follows:

***High Selectivity**:* The cell can operate at a high efficiency and generate high-purity product. The bipolar membrane selectivity is >98%, and anion/cation membrane selectivity >80% for producing 7% HCl and 12-20% KOH/NaOH.

Lower Power Consumption: The bipolar membrane has a voltage drop of ~1 volt at an operating current density of 100A/ft^2. The cation and anion exchange membranes have voltage drops of 0.3-0.4V each. The overall voltage drop including that for the circulating solutions is ~2-2.1V/cell; while the overall power consumption would be ~1200 kW/ton of NaOH.

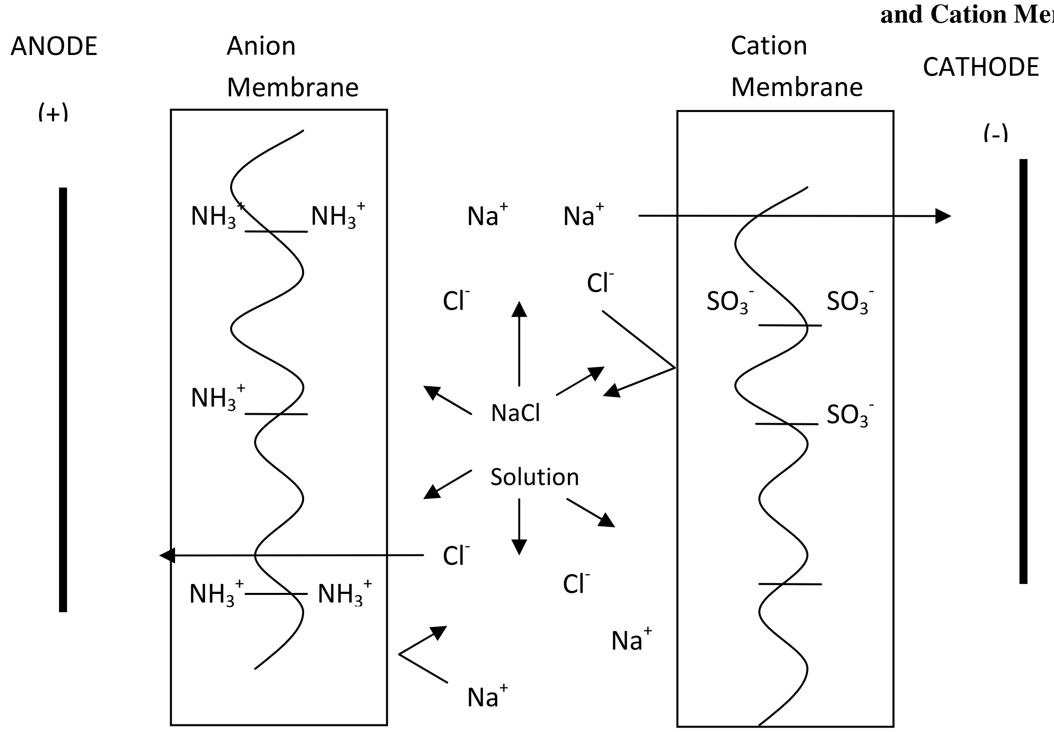
Novel Cell Design: NSR has developed and implemented a novel design that allows the membranes to perform reliably and at high efficiency. The design of the cell reduces electrical shunt losses, reduces fluid recirculation requirements and ensures reliable long-term performance for the membranes.

Extended Membrane Life: The ion exchange membranes are specialty polymers and are relatively expensive, when compared to, say, nylon or polyethylene. The long-term stability and durability of the membranes and cell stacks are therefore critically important to the commercial viability of the technology. To date, membranes in the NSR process have operated for > 3 years without exhibiting a loss in the performance. We believe that our cell design will allow the membranes to operate for a considerably longer time period. In time we also expect the membrane prices to decrease, which will allow us to expand capacity and address many other environmentally beneficial applications for our technology.

Specialty polymeric membranes: The membranes are made of hydrocarbon polymers (styrene polymers) to which ion exchange groups have been incorporated in order to make them selective to the specific ions:

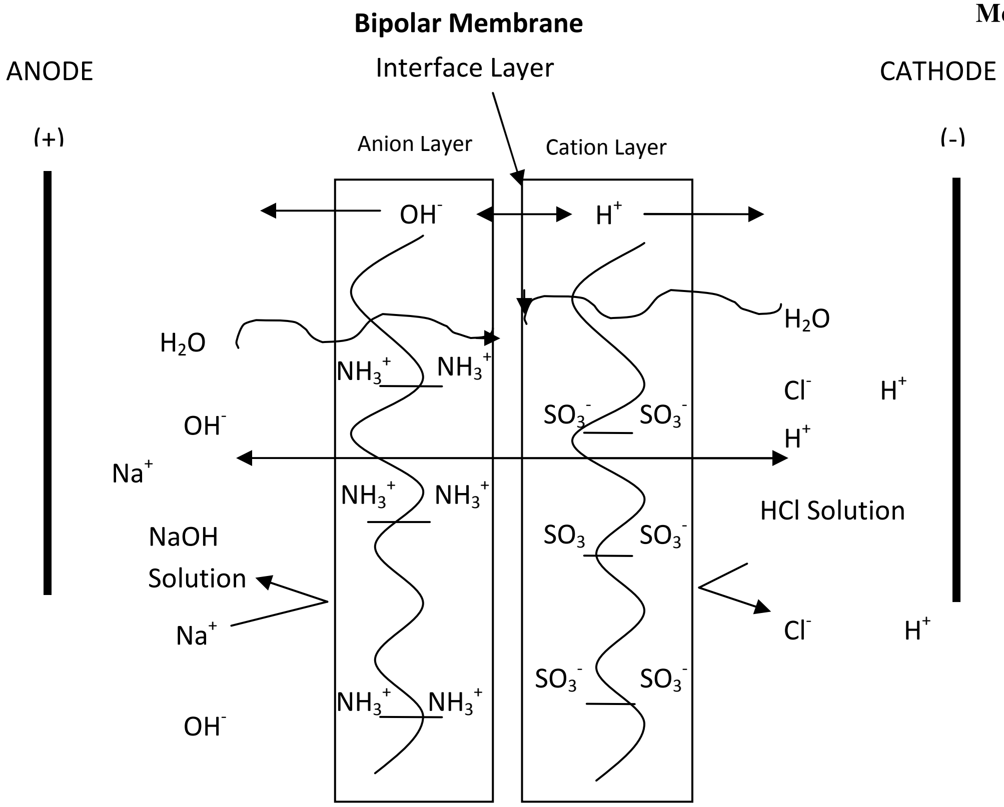
- The cation exchange membrane has negatively charged sulfonic-acid groups that exclude the negatively charged chloride ions (Donnan exclusion) and allow, under an electrical gradient, the positively charged cation (Na^+ or K^+) to transport across it.
- The anion exchange membrane has positively charged quarternary ammonium ions (or tertiary ammonium ions that become positively charged in an acidic-HCl -environment) that exclude the positively charged cation and allow the negatively charged chloride (Cl^-) ion to transport across it.

Figure 2 : Ionic Separation across Anion and Cation Membranes



- The bipolar membrane is a composite membrane that has a cation layer on one side and an anion layer on the other side. The two layers are sandwiched between a third (so called interface) layer comprised of an amine polymer or transition metal ions that catalyze the dissociation of water to hydrogen (H^+) and hydroxyl (OH^-) ions. When the membrane is positioned in a cell with the cation selective side facing the cathode electrode the bipolar membrane substantially excludes the transport of the salt ions (Na^+, K^+, Cl^-). As a result electrical conduction is achieved from the forced dissociation of the water molecules and the concurrent transport of the H^+ and the OH^- ions out of the membrane and into the adjoining acid and base compartments.

Figure 3 : Ionic Separation across Bipolar Membranes



Chromatographic Purification of Caustic (KOH, NaOH)

As mentioned in an earlier paragraph, the bipolar membrane selectivity is typically 98-99%. This means 1-2% of the current is carried by the counter-ion, which is chloride ion for the caustic product. This, plus any internal leaks in the cell stacks, results in chloride levels of >1,000 ppm in the 12-15 wt% caustic product out of the cell stacks. This level is deemed too high, particularly for the KOH product.

Chromatography has been found to be an effective method for reducing the chloride level in KOH. Under optimum operating conditions chromatography has been found to remove 98-99.5+% of the chloride contaminant. The purification is achieved using a specialty ion exchange resin. The resin is amphoteric in nature; i.e., it has both cation and anion functionalities within the resin structure. The so-called cage structure of the resin has a greater affinity for the salt molecule vis-a-vis the caustic. When the caustic solution containing the chloride salt is passed through a column packed with the resin, the chloride salt moves slower than KOH; in effect, the salt movement is retarded.

The NSR design takes this particular property of the resin to purify the KOH product. In the process, a certain volume of the KOH solution containing the chloride is passed within an 8 feet long column of the resin. Subsequent to this, water is injected into the column and travels in the same direction as the feed KOH solution. The resin retains the salt contaminant for a period of time, allowing the purified KOH solution to be eluted and collected first. The chloride containing solution is released thereafter by the action of additional water to the resin. The purified KOH solution is typically 10-12 wt% strength and contains 0-50 ppm chloride. This is then concentrated in a triple-effect evaporator to obtain the 45-50% KOH product for sale. The chloride containing solution from the chromatography column is recycled to the process for pH adjustment of the feed to the cell stacks.

Part II: Comparison of NSR's Technology with Existing Technology

Traditionally, these chemicals have been made via the chlor-alkali (or the electrolysis) process. This process, like the NSR's process, is also electrically driven. Separation of the sodium or potassium ion in solution is achieved via a membrane, diaphragm or a mercury amalgam formation. However the conversion to the acid, base values takes place at the metal electrode surfaces, instead of the bipolar membrane, and results in the generation of chlorine (Cl_2) gas at the anode electrode and hydrogen gas (H_2) at the cathode. The chlorine then has to be burned with the hydrogen gas (H_2) to produce the HCl product. The process can be represented schematically as follows for NaCl conversion. (The process for KCl conversion is similar):

$$2NaCl + 2H_2O \rightarrow 2NaOH + H_2 + Cl_2$$

$$H_2 + Cl_2 \rightarrow 2HCl$$

In addition to the generation of chlorine, the required energy input is greater than that for the membrane process. The minimum voltage requirement is ~2.1V, which translates to ~1,265 kWh/ton of NaOH. The actual usage is higher; 3.5-4V, and ~2200-2500 kWh/ton.

NSR's production route, in contrast, uses less energy and does not produce Cl_2. ***In 2011, NSR's technology process resulted in an absence of 2 million lbs/year of Cl_2 production. At full capacity, its single plant would eliminate producing 10 million lbs/year of Cl_2.***

Part III: Technology Features and Applications

NSR's membrane technology is a general purpose unit operation that has wide ranging applications, particularly in environmental and pollution control areas. There are no oxidation/reduction problems like the ones encountered in electrolysis. The process involves only a rearrangement of ions in solution and is particularly suited to recycling salts that are generated in pulp and paper industries and from environmental control systems in coal fired power plants.

Controlling emissions from coal fired boilers:

The recently proposed emission regulations for SO_x, NO_x control provide important opportunities for the broader application of the technology and provide valuable health benefits for the community at large. The application involves scrubbing the flue gases from the boiler with a soluble alkali such as sodium hydroxide/sodium sulfite or potassium hydroxide/potassium sulfite. The conventional lime ($Ca(OH)_2$) scrubbing removes only 70-85% of the harmful emissions and generates significant amounts of solid waste that needs placement in landfills. In comparison the soluble alkalis can remove >98% of the harmful emissions. Additionally, with the incorporation of a novel scrubber design one can remove additional amounts of the particulates that are not removed by the upstream electrostatic precipitators.

Using NSR's technology, the spent soluble alkali solution from the scrubber can be substantially regenerated and recycled back to the scrubber. In one scenario the power plant gases will be scrubbed in an absorber using potassium sulfite/potassium hydroxide solution. The recovered solution comprising the potassium salts, namely, the bisulfite/ nitrate/sulfate solution can then be processed in the bipolar membrane cell stack to recover the SO_2 values and the sulfite/hydroxide for recycle. The NO_x and the sulfate values (resulting from secondary oxidation reactions in the scrubber) can be recovered separately and sold in the fertilizer market.

In terms of commercial readiness, we have a proven cell design and are presently employing it in the production of KOH, while the SO_x recovery from spent bisulfite solutions has been demonstrated earlier on a 0.5MWe scale using the sodium system.

Part IV: Technology Features and Applications

Awards & Recognition: Media, technical publications and other organizations have recognized NSR for its innovations. In 2011, Chemical Engineering(C&E) Magazine awarded NSR an Honor Award in the Magazine's biennial competition that honors outstanding chemical engineering innovations (November 2011). ICIS, the international chemical business industry magazine, short listed NSR Technologies as a finalist in its 2010 Innovation Awards. NSR was selected in the category of "Innovation with the Best Environmental Benefit" (July 2011).

In 2010, R&D Magazine awarded NSR its R&D 100 Award, which recognizes the 100 most technologically significant achievements to reach the marketplace in 2010; (November 2010); Chemical Engineering (C&E) Magazine awarded Dr. Kris Mani its 2010 Personal Achievement Award and named him as a green chemistry pioneer who has helped advance the field of chemical engineering; (November 2010)[6] ; NSR was named a finalist in the Green Jobs Award, which recognized entrepreneurial companies that are creating Green Jobs, by SJF Advisory Board (October 2010).

NSR's Future Plans: NSR plans to continue to expand its existing facility. The production continues to operate reliably and steadily, and is in the process of expanding to full capacity amidst a tough economic climate and capital constraints. NSR is also in the process beginning technology sales to other companies in need of efficient separations and recovery processes. NSR's entire technology estate is geared toward EPA mandated pollution control and eliminating the production of harmful products. Global applications include the production of additional chemical compounds and pollution control applications as discussed earlier in this paper using NSR's proprietary technology suite.

[6] "CE Personal Achievement Award: The Winners are Waste Management Expert Tom McGowan and Green Chemistry Pioneer Kris Mani." Chemical Engineering. November 2010, p. 17-22. (link: http://accessintelligence.imirus.com/Mpowered/book/vche1/i9/p1)