

## ***Carbon sequestration using carbonation***

S. K. Saxena, Professor and Director,  
Center for the Study of Matter at Extreme Conditions,  
College of Engineering & Computing,  
Florida International University

### **About The Author**

#### **Surendra K. Saxena**

##### **Current:**

Professor and Director, Center for the Study of Matter at Extreme Conditions,  
College of Engineering & Computing, Florida International University,  
Miami, FL 33199, USA

Tel: 305-348-3030 (direct 0540) Cell:305-338-0615

*Member of the Royal Swedish Academy of Sciences, 1994.* (The academy is the home of several committees which award many prestigious prizes, including the Nobel Prize).

*La Laurea Ad Honorem in Scienze Geologiche, Padova University, Italy, 2001.*

*Recipient of the Rudbeck Medal of Excellence in Science, Uppsala University, Sweden 2007.*

**Education:** Ph.D. 1964 Mineral-chemistry, geophysics, D.Sc., Thermodynamics 1967, Uppsala University, Sweden

##### **Professional:**

Research fellow, Uppsala University; 1964-1967 Doctoral research;

1967-1968 Assistant Professor, Institute of Mineralogy and Geology, Uppsala;

1968-1969 Research scientist, Institute of Mineralogy and Geology, Uppsala;

1969-1971 Senior Research Associate, National Academy of Science, at Goddard Space Flight Center, Greenbelt, Maryland;

1971-1972 Research associate, Virginia Polytechnic Institute and State University;

1973-1976 Associate Professor, Brooklyn College, City University of New York;

1977- 1996 Professor, Brooklyn College, City University of New York; 1983- 1996 Professor, Graduate Center of the City University of New York;

1989- 2001 Professor, University of Uppsala, Sweden.

2001- Emeritus Professor, Uppsala University, Sweden

1999- Professor, Florida International University, Miami, USA  
Director, Center for the Study of Matter at Extreme Conditions (CeSMEC)

### **Publications:**

Author of 300 papers in international scientific journals

### **Books**

1. *Thermodynamics of rock-forming crystalline solutions*, Springer-Verlag, New York, 1973.

*Published in Russian by MIR publications, 1975, Ed. L.L.Perchuk., Translated into Chinese, 1979.*

2. *Chemical Petrology: with applications to terrestrial planets and meteorites*, R. F. Mueller and S. K. Saxena. Springer-Verlag, New York, 1977., *Translated in Russian by MIR publishers in 1979. Translated into Chinese in 1983.*

3. *Mixtures and Mineral Reactions*. J.Ganguly and S.K.Saxena; Springer-Verlag, 1987.

4. *Thermodynamic data on oxides and silicates*. S.K.Saxena, N. Chatterjee, Y. Fei and G. Shen. Springer Verlag, 1994.

5. *Thermodynamic data on oxides in the Fe-Mg-Si-O system*. O.Fabrichnaya, S.K.Saxena, Pascal Richet and E. Westrun. Springer Verlag, 2004.

### **Editor**

Energetics of Geological Processes: Hans Ramberg Volume, Edit. Saxena and Bhattacharji. Springer-Verlag, 1977.

*Advances in Physical Geochemistry; Series editor: S.K.Saxena,*

Springer-Verlag,(beginning with volume 1, 1981).

*APG Series Volumes edited by S. K. Saxena:*

Volume 2. Fe-Mg order-disorder in silicates and other topics,1982.

Volume 3. Kinetics and equilibrium in mineral reactions,1983.

Volume 6. Chemistry and Physics of Terrestrial Planets,1986.

Volume 10. Thermodynamic Data Systematics, Springer Verlag, 1992.

Inhomogeneous and strongly correlated materials and the study of matter at extreme conditions. Proc of the conference SMEC2003 (eds: Saini, Saxena and Bansil) J.Phys. Chem. Solids, 65, 0022-3697, 2004.

### **Synergistic Activities:**

Reviewer of articles for several journals (Solid State Chemistry, Applied Physics Letters, NSF proposals and books.

Organizer of many international meetings. Participant in many European projects.

Chairman, Working Group on Thermodynamics of minerals. 1991-95

Chairman of the CODATA Task Group on Geothermodynamic Data, Paris, France. 1979-96

Member of the Joint European Thermodynamic Database for Environmental Modeling committee, 2004-2007,

Member, French Nuclear Agency Technical Database.

### **Patents:**

“Production of silicon from silicates” Provisional 2005-5

“Production of Silicon” Patent applied 2008

“Hydrogen production with carbon sequestration” US Patent files

(PCT/US08/55586)

“Synthesis of Metal Hydrides for Vehicular Use “ Patent pending

**Collaborators (International):** Marcelle Gaune-Escard: Ecole Polytechnique, Marsielles France, B. Sundmann: Royal Institute of Technology, Sweden, Arthur Pelton: Ecole Polytechnique, Montreal Canada, Peter Lazor, Uppsala University, Sweden, R. Ahuja, Uppsala University, Sweden, G.Grimwall, Royal Technical University, Stockholm, Sweden, Giulio Ottonello, University of Genoa, Italy, Gunnar Eriksson, GTT, Aachen, Germany, M. Krisch: ESRF, Grenoble, France, A. K. Singh, National Physical Lab, Bangalore, India, Josu M. Igartua Aldamiz, Fisika Aplikatua II Saila, Zientzia Fakultatea, Bilbao, Spain, Gonzalo Gutierrez, U.Santiago, Chile, W. Orellana, U. Santiago, Chile, M. Zinkevich, S. Geupel, F. Aldinger, Max-Planck-Institut für Metallforschung Stuttgart, Germany, M. Tkacz, Polish Academy of Sc., Warsaw, Poland.

**Collaborators (National):** A.Davydov (NIST), M. Barsoum (Drexel), H.K.Mao (CIW, DC and HPCAT, Argonne National Laboratory), J. Ganguly, U. Arizona, Tucson, Z. Wang, Cornell, G. Shen, HPCAT, Argonne National Lab, Jingzhu Hu, Brookhaven National Lab., Hans-Peter Liermann, HPCAT, Argonne National Lab.

**Ph.D. Graduates (20):** To mention some: Y. Fei, Staff member, Geophysical Laboratory, Carnegie Inst of Washington; Peter Laazor, Professor, Uppsala University, Sweden; S. Reki, Scientist, Brookhaven National Laboratory; Z. Wang, Scientist CHESS, Cornell University;; J.Zhang, Scientist Los Alamos; G. Shen, Senior Scientist, Argonne National Laboratory; M. Bokreta, Dean, University of Pennsylvania, Philadelphia, P.F.Shi, Scientist, Thermo-calc AB, Stockholm; N. Chatterjee, MIT, Cambridge. N.Phatak, EasyLab, U.K., S. Kulkarni, EasyLab, U.K. G. Subrahmanyam, Utah State University, Lyci George, StonyBrook.

**Master’s** Over 30.

**Post-doctoral Fellows:** Leonid Dubrovinsky, 1995-1999. Professor, Bayreuth Geophysical Laboratory, Bayreuth, Germany; A. Belonoshko, 1990-1995. Research Associate, Royal Technical University, Stockholm, Sweden; .Hans-Peter Liermann; 2001-2004. Scientist, Argonne National Laboratory; B. Manoun, Professor, Morocco. F. Zhang, Research Associate, University of Michigan., A. Durygin, FIU., V. Drozd, FIU., S.V.Raju, U of California, Berkeley. J. Sowerby, Miami.

## **Abstract**

It is contended that by producing sodium hydroxide from electrolysis of brine and then converting the hydroxide to a bicarbonate ( $\text{NaOH} + \text{CO}_2 = \text{NaHCO}_3$ ), we will be able to get rid of  $\text{CO}_2$  from fossil-fuel burning plants [1]. Salt which occurs in abundance can be used to produce sodium hydroxide, chlorine and a little hydrogen (the chlor-alkali process); sodium hydroxide reacted with  $\text{CO}_2$  would form sodium carbonate or bicarbonate. The problem is both the high energy cost and the violation of the “chlor-alkali balance”; the latter term is explained as follows. The reaction to produce sodium hydroxide ( $\text{NaOH}$ ) is:



Thus for each mole (40 grams) of  $\text{NaOH}$ , there is 0.5 mole (39 grams) of chlorine produced. Depending on the market, either sodium hydroxide or chlorine can be byproduct. It is obvious that sodium hydroxide cannot be produced in such quantities, that chlorine becomes surplus because it is more than what industry can use. When that happens, we will have the problem of chlorine storage which will be worse than the problem of  $\text{CO}_2$  storage. Chlorine is a poisonous gas. Similarly the baking soda produced from one plant may exceed the needs of the industry by several million tons.

Sodium hydroxide may be used on a smaller scale if procured as a byproduct of chlorine production from existing chlor-alkali plants to sequester  $\text{CO}_2$  and produce hydrogen. The process is highly profitable and is the only process (other than electrolysis from alternate energy) to produce carbon-emission free hydrogen [2].

## **Introduction**

The problem of carbon emissions from our fossil fuel burning plants of various kinds (power, steel, cement, gasifiers) has become so critical as to threaten our very survival. There are a number of possible solutions that have been explored over the last several decades but a viable solution is still at large (Lackner et al [3]). Most likely there is no one single solution but perhaps multitude solutions have to emerge, each doing its bid in curtailing the carbon emission.

Carbonation is a method by which we can lock the gases such as carbon dioxide or carbon monoxide into solid stable carbonates and as long as these carbonates are not reused in high temperature or acidic applications, the gases will be locked permanently and safely. In this paper, we provide briefly a review of the current practice and then focus on a specific carbonate which

is being favored in some projects. The review is brief to put the carbonation theme in proper context. The paper by Lackner et al [3] gives a detailed review of the carbonation methods.

### Carbonation reactions

Mineral sequestration was first mentioned by Seifritz [4] and discussed further by Dunsmore [5]. However, Lackner *et al.* [3] were the first to provide the details and foundation for today's research efforts. Here we present a brief review.

A carbonation reaction may be represented by



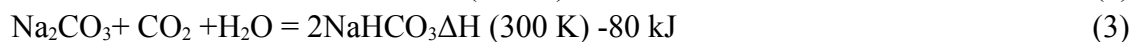
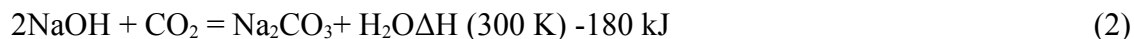
where M can be any metal such as (Ca or Mg). To qualify for this application, the metal oxide has to be

- abundant in the earth's crust
- must react with CO<sub>2</sub> at low temperatures
- must have a reaction kinetics appropriate for the low temperature equilibrium
- must form a carbonate that is stable in the environment at ambient conditions.

Unfortunately, although we live on an oxidized crust of a planet, there are no oxides that occur in abundance that fulfill the requirements as outlined above.

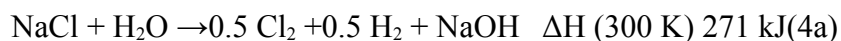
### The sodium carbonate as carbon storage

It is well known that sodium hydroxide would react with CO<sub>2</sub> to produce sodium carbonate or sodium bicarbonate:

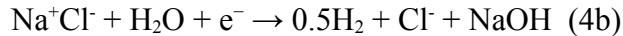


Both the reactions are exothermic and proceed rapidly to completion. Sodium carbonate would then seem an ideal candidate for the storage. It has, indeed, been adopted and promoted by some [1,2].

The sequestration of CO<sub>2</sub> in sodium carbonate will depend on the availability of sodium hydroxide. Industrially sodium hydroxide is produced by the electrolysis of brine as (the chlor-alkali reaction):



More accurately:



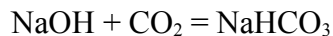
The reaction produces chlorine and NaOH in approximately equal amounts. Depending on which demand is dominant, either chlorine or NaOH can be regarded as a by-product and the price varies accordingly. To produce NaOH it is necessary to prevent reaction of the NaOH with the chlorine. This is typically done in several ways, of which the *membrane cell process* is economically the most viable requiring lowest consumption of electric energy and the amount of steam needed for concentration of the caustic is relatively small (less than one metric ton per metric ton of sodium hydroxide). It would then appear that the global warming problem can be solved simply by using salt and water which we have plenty in our oceans.

The chlor-alkali process is very energy intensive. It requires 1873.84 kWh per metric ton of NaOH. Note that this energy is the energy required for the reaction (4) and is independent of whether we employ a diaphragm method or the membrane technique.

If we can have enough supply of the sodium hydroxide, we can sequester carbon gases safely by combining reaction (4) with reactions (2) and (3) as suggested by some [1,2]. There is little doubt that such a method will work but we must consider how effective this could be as a global solution. To understand this better, let us take the example of the Kingston fossil plant in Tennessee. The plant consumes some 12,700 metric tons of coal a day when operating at full power which equals 530 metric tons/hour. The material balance is as follows:

Reaction	$\text{C} + \text{O}_2 = \text{CO}_2$				
Metric tons	12	32	44		
Reaction (4)	$2\text{NaCl} + 2\text{H}_2\text{O} \rightarrow \text{Cl}_2 + \text{H}_2 + 2\text{NaOH}$				
Metric tons	117	36	71	2	80
Reaction (2)	$2\text{NaOH} + \text{CO}_2 = \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$				
Metric tons	80	44	106		18
Reaction (3)	$\text{Na}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} = 2\text{NaHCO}_3$				
Metric tons	106	44	18		168

Let us now consider the material consequences the method which will combine reactions (2) to (4) for carbon sequestration. For bicarbonate reaction

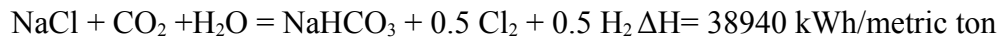


Each metric ton of NaOH sequesters 1.1 metric tons of  $\text{CO}_2$ ; if we consider a plant of the size of the Kingston plant, we are generating 1943 metric tons of  $\text{CO}_2$  per hour (17 million metric tons; the Kingston Plant is capturing  $\text{CO}_2$  and they have reduced the emission to 2.16 million tons in 2009) requiring 1766 metric tons of NaOH and 3.31 MWh energy. If this energy is to come from burning coal (starting with energy density of coal 6.67 kW•h/kg and taking into account 30%

efficiency of power burning plant we get 2000 kWh/metric tons of coal)), we need to burn 1655 metric tons of coal, which would release 6068metric tons of CO<sub>2</sub> per hour. *Depending on the energy value of the coal, the carbon emission could be less but it will be few times more than what will be sequestered.*

To ensure that there is no mistake in using the numbers, let us quote directly from US Energy Information Administration [7]: “Coal with a carbon content of 78 percent and a heating value of 14,000 Btu per pound emits about 204.3 pounds of carbon dioxide per million Btu when completely burned.” However, average Btu per pound of coal used in US is even lower 10,000 [7]. This gives us the following: to produce 106 Btu (293. KWh), 71.43 lbs (32.43 kg) of coal is needed and 204.3 lbs (92.75 kg) CO<sub>2</sub> is emitted. If we take as an example 1GW coal power plant with average efficiency of 34% [7], to produce 1GW of electricity 325.47 tons/h of coal is needed and 930.85 tons/h of CO<sub>2</sub> is generated. To sequester this amount of carbon dioxide in the form of sodium bicarbonate 846.22 tons/h of NaOH will be needed. If production of 1 ton of NaOH requires 1873.84 kW of electricity, 1.59 GW of electricity will be needed to sequester all CO<sub>2</sub> emitted by 1GW power plant!

We may consider the simplified process (assuming that energy is conserved in various reactions):



Mass balance/Metric tons 58.5 44 18 84 35.5 1

Table: Mass balance for sequestering CO<sub>2</sub>.

	Metric ton (1 GW plant)	5 GW Plant	Total US production	#Plants (1 GW) that can be built
NaCl	9,882,905	49,414,525	40,300,300	4.1
NaOH	6,764,480	33,822,400	11,025,000	1.62
Cl <sub>2</sub>	5,995,527	29,977,638	12,600,000	2.1
NaHCO <sub>3</sub>	14,205,408	71,027,040	100,000	0.007
CO <sub>2</sub> carbonated	7,440,928	37,204,640		

The annual production of chlorine from one plant will be 13.7 million metric tons or 15 million short ton. *According to The Chlorine Institute statistics, in 2008, the U.S. chlor-alkali industry produced 11.5 million short tons of chlorine and 12.1 million short tons of caustic soda (sodium hydroxide).* Therefore chlorine from one plant will flood the market and will lose its market value and create new and formidable problem of sequestration of a toxic gas.

The baking soda production annually will amount to 33 million metric tons. At the turn of the twentieth century, 53,000 tons (48,071 metric tons) of baking soda were sold annually. While the population increased dramatically, sales by 1990 were down to about 32,000 tons (29,024 metric tons) per year. If a truck carries 13 tons per trip, the salt to be carried would require 198 trucks of salt per hour and they will transport out 285 truck load of baking soda. This will be an impossible traffic to handle.

## Conclusions

In conclusion, it is clear that carbonation using NaOH is not a practical method for carbon sequestration when such NaOH is to be produced specifically for carbonation. Such is the method proposed by Jones [1] which will result in market saturation with chlorine after the method is used in one or two medium sized power plants. The industry has to maintain the chlor-alkali balance for a stable market and not produce chlorine more than what the industry can use. Within the limits of chlor-alkali balance, we may use the byproduct NaOH produced by the already existing chlor-alkali plants. By using the method as proposed by Saxena et al. [2,8], we help the environment by reducing some percent of carbon emission created by the currently operating chlor-alkali plants and reap a substantial economic benefit

## References

1. Jones, J.D. Removing carbon dioxide from waste streams through co-generation of carbonate and/or bicarbonate. U.S. Patent No. 727374 B2, June (2010).
2. S.K. Saxena, V. Drozd, A. Durygin, A fossil-fuel based recipe for clean energy. *Int. J. Hydrogen Energy* 33(14),3625-3631(2008).
3. Lackner K.S., C.H. Wendt, D.P. Butt, E.L. Joyce and D.H. Sharp, "Carbon Dioxide Disposalin Carbonate Minerals," *Energy*, 20, 1153-1170 (1995).
4. Seifritz W., "CO<sub>2</sub> disposal by means of silicates," *Nature* 345, 486 (1990).
5. Dunsmore H.E., "A Geological Perspective on Global Warming and The Possibility of Carbon Dioxide Removal as Calcium Carbonate Mineral," *Energy Convers. Mgmt*, 33 (5-8),565-572 (1992).
6. Lu Gao, Nigel Paterson, Paul Fennell, Denis Dugwell, and Rafael Kandiyoti, The Zero Emission Carbon Concept (ZECA): Extents of Reaction with Different Coals in Steam/Hydrogen, Tar Formation and Residual Char Reactivity *Energy & Fuels* 22, 2504–2511 (2008).
7. U.S. Department of Energy  
([http://www.eia.doe.gov/cneaf/coal/quarterly/co2\\_article/co2.html#N\\_5](http://www.eia.doe.gov/cneaf/coal/quarterly/co2_article/co2.html#N_5));  
(<http://www.eia.doe.gov/cneaf/electricity/epa/epat3p7.html> ).

8. S. K. Saxena, Hydrogen Production and Carbon Sequestration in Coal and Natural Gas-Burning power plants, Publication No.US-2010 -002824-1A.