

High Resolution NISSAR-Satellite Study of Multiple Stressors in Arctic Marine Systems to Correlate Ocean-Atmosphere-Cryosphere Interactions with Climate Variability and Environmental Pollution using Nanomaterials and Developing 'Arctic-Ocean Climate Predicting Models' (AOCPM)

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Abstract

The present study endeavours to develop innovative technologies to depollute water and environmental pollution by using the nanomaterials and conventional technologies by employing Physicochemical and Spectroscopic methods to characterize the in-situ chemical speciation of the inorganic contaminants. Next, it aims to use Nanotechnology and Nanomaterials for remediation of Water Pollution by using Catalytic Oxidants of first row of transition metal oxides in the Water Treatment Processes and to entrap toxins, by employing High Affinity Toxin Receptors (HART). Also, Nanotechnology and Nanomaterials would be applied to study Chemical Reaction Kinetics to assess water contaminant transformation. High Resolution NISAR- Satellite Data would be used to study multiple stressors in Arctic marine systems to correlate Ocean-Atmosphere-Cryosphere (OAC) interactions with Climate Variability and Environmental Pollution to evaluate the correlation between the impacts of multiple stressors on the ocean and the associated risks of abrupt state shift, rising of sea level, melting of the glaciers, vis-à-vis climate variability. Also, it aims to study regional climate dynamics, and the Correlation of Arctic- Ocean-Atmospheric-Cryosphere Variability Mechanism, Sub-Mesoscale Dynamics & its impact on, Climate Variability, and the large-scale kinematic and thermodynamic behaviour of selected mesoscale convective systems. Next, the oxidation process would be employed in remediation of subsurface cum above-ground water treatment systems involving the regeneration of Granular Activated Carbon (GAC). To treat groundwater contaminants, the chemical oxidants viz. hydrogen peroxide, persulfate, permanganate and ozone causing chemical destruction of toxic organic chemicals would be used. Also, the physicochemical and spectroscopic methods would be developed to characterize in situ chemical speciation of the inorganic contaminants and in developing 'Catalytic Chemical Processes' (CCPs) for remediation of water and environmental pollution as well as to investigate process fundamentals for the assessment of contaminant transformation through Chemical Reaction Kinetics. The study aims to investigate whether Nano-Oxidants can be used to Control Global Warming by converting GHG (Methane) to ethanol by catalytic processes and in developing hybrid fuels like bioethanol and biodiesel and go for electricity from biomass. Also, by using cooling technologies like 'Magnetic Refrigeration Technology' (VG-MRT), developed by the author in the past, can be employed to replace Chlorofluorocarbons in the refrigeration and air-conditioning; to Control Global Warming vis-à-vis Climate change.

Keywords: High Affinity Toxin Receptors (HART), Nanomaterials, Granular Activated Carbon (GAC), Reaction Kinetics, Ocean-Atmosphere-Cryosphere (Arctic), High Resolution NISSAR-Satellite Data, 'Catalytic Chemical Processes' (CCPs) and 'Magnetic Refrigeration Technology' (VG-MRT).

Introduction

There are places on Earth that are so cold that water is frozen solid. These areas of snow or ice compose the cryosphere. The term “cryosphere” comes from the Greek word, “krios,” which means cold e.g. Arctic, Greenland & Antarctica regions. The understanding of impacts of multiple stressors on the ocean and the associated risks of abrupt state shifts can be explored through the comprehensive studies of Ocean Systems Interactions, Risks, Instabilities and Synergies (OSIRIS). The role of chemical oxidants in subsurface remediation and above-ground water treatment systems dependent on the few site-specific conditions e.g., locating the source(s) of contamination, delivery of oxidant to the contaminated zones, background oxidant demand and competing reactions, reaction rate kinetics, reaction by-products, and attenuation of reaction by-products. Assessments of water quality and efforts to restore contaminated waters depend strongly on a fundamental understanding of geochemical processes involving reactions with mineral surfaces and substrates. Such processes include weathering reactions that contribute dissolved chemicals, sorption that removes aqueous species, and electron transfer mechanisms that establish redox conditions [1].

Water gets polluted due to toxins & toxic gases. There are generally four types of toxic entities: chemical, biological, physical and radiation. Chemical toxicants include inorganic substances such as, lead, mercury, hydrofluoric acid, and chlorine gas, and organic compounds such as methyl alcohol.

Groundwater Contaminants can be oxidized utilizing various chemical oxidants viz. hydrogen peroxide, persulfate, permanganate & Ozone. These oxidants have been able to cause the rapid and complete chemical destruction of many toxic organic chemicals; other organics are amenable to partial degradation as an aid to subsequent bioremediation. In general, the oxidants have been capable of achieving high treatment efficiencies (e.g., > 90 percent) for unsaturated aliphatic (e.g., trichloroethylene [TCE]) and aromatic compounds (e.g., benzene), with very fast reaction rates (90 percent destruction in minutes). Ozone gas oxidizes contaminants directly or through the formation of hydroxyl radicals. Oxidation using liquid hydrogen peroxide (H₂O₂) in the presence of native or supplemental ferrous iron (Fe⁺²) produces Fenton's Reagent which yields free hydroxyl radicals (OH⁻). In case of Permanganate there is a slower rate of oxidation reactions. There is an interaction between chemical oxidants with chemical species associated with soil and aquifer materials as well as with target and nontarget contaminants during water treatment processes. The oxidation process would be employed to treat Groundwater contaminants by making use of the chemical oxidants viz. hydrogen peroxide, persulfate, permanganate & ozone [2].

Types of Chemical Contaminants

Chemical Contaminants can be separated into eight contaminant groups as follows:

- *Nonhalogenated volatile organic compounds (VOCs).
- *Halogenated volatile organic compounds.
- *Nonhalogenated semi volatile organic compounds (SVOCs).
- *Halogenated semi volatile organic compounds
- *Fuels. Inorganics.
- *Radionuclides, and *Explosives.

The contaminated water not only give rise to water borne diseases but, also results Climate change is altering our environment affecting agriculture, water availability, and sea-levels. It's increasing the intensity of natural disasters like Tsunami, Cyclonic Storms, droughts, floods, species extinction particularly marine life & diseases, and Rise of Sea level due to Global Warming i.e. Climate Change [3].

Introduction to Nanotechnology and Nanomaterials

Nanotechnology encompasses the nanomaterials or nanoparticles (NPs) having the nano sized dimension ranging between 1 and 100 nanometres (nm), and these are capable to enhance not only their physical and chemical characteristics but biological effectiveness as well. These Nanomaterials contain larger surface area per unit volume with respect to their macro-counterpart, and hence do have higher catalytic activity, higher rate of reaction kinetics due to higher chemisorption/absorption properties and be useful in detoxification of toxic gases and absorbing Green House Gases (GHS) responsible for Global Warming vis-a-vis Climate change [4].

The interaction of these nanoparticles is much better with other materials and are good transporters of clean energy. Also, these have been proved to be good nano fertilizers, nano-pesticides in agriculture resulting better productivity and maintaining ecological balance. Nanotechnology vis-à-vis Nanomaterials cover wide spectra of its utility in almost all the fields like medicine, health, environment (Land, Ocean, ice), food, material, planetary, Geological, Chemical, Physical sciences and even creating nanotechnological tools for the diagnosis and treatment of diseases. For example, Nano sensors play key roles in the detection of agroclimatic conditions for food crops and supervision other parameters related to, pesticides, herbicides, fertilizers while the nano biosensors are used in food packaging [5].

Moreover, nanostructure materials e.g. nanocomposites, nano catalysts, nano-coatings, nano lubricants etc. are environmental friendly in comparison to their conventional counterparts. The oxygen, nano catalyst helps in complete combustion of fuels, and especially in the REDOX reaction useful not control Global Warming by chemical processes by reducing the greenhouse gas emission. Similarly, nano lubricants and nanocoating's help to decrease friction in engine which significantly reduces CO₂ emission [6].

The Nanotechnology products/NPs are used in improving the efficiency of renewable energies (e.g., biofuels, solar and hydrogen fuel cells), and thereby, reducing the dependency on fossil fuels and thus controlling the Global Warming and Environmental pollution occurring in the Oceanic, Atmospheric and Cryosphere regions. Also, the Nanomaterials may be used to control degradation of dyes and other colourless pollutants in wastewater streams as well as producing nanostructured materials involved in green architecture in the form of nanocomposites, nano coatings, nano glass, carbonic nanotubes, nano silica, and polymeric structures in roof, windows, wall coatings, insulation, energy storage, solar cells, and a refrigerant free cooling for energy efficient sustainable constructions/buildings and the nontoxic-environment [7].

Types of Nanomaterials

Nanomaterials/nanoparticles/nanostructures are of nano size (approximately 1–100 nm) exhibit extraordinary physical, chemical and biological properties and on the other hand Nanotechnology deals with the design, production, manipulation and application of nano structured materials/nanoparticles. These are categorized as advanced nanomaterials (viz. super, smart, active and swarms' nanomaterials) [8].

(a) **Super/nano Pure Nanomaterials:** In these each atom is at its perfect geometry, strong and defects free that could be further improved using nano engineering e.g. wings of aircraft and diamond bolts.

(b) **Smart Nanomaterials:** These can respond to any signal/command and can change size, shape, colour, density or any physical property like refraction of light by rearranging the atoms.

(c) **Active Nanomaterials:** consist of sensors, actuators and computers and are capable to check out its environment, tract a change and respond.

(d) **Swarms' Nanomaterials:** These are active nanomaterials composed of various nanomachines that work collectively to fulfil a specific goal.

Objectives i.e. Statement of Problem

The present study is of hexagonal objectives comprising firstly, to develop 'Arctic-Ocean Climate Predicting Models (AOC-PM)' by inculcating sea –land- ice & ocean-atmosphere-land interactions. Investigation would be made through diverse processes involving physical and biochemical modification of water masses, their communication between shelves and deep basins in the Arctic Ocean, and with the sub-polar seas, to understand regional climate dynamics, air-sea-ice interactions and their effects on Global Warming and its polar amplification.

Secondly, to evolve innovative technologies to control Water and Environmental pollution resulting due to toxin, toxic gases, Green House Gases (GHG), by using Catalytic oxides of first row transition metal oxides, to save marine(under-water) life by inhibiting the water contamination through remediation of Water treatment process. Also, to employ oxidation process to treat Groundwater contaminants by making use of the chemical oxidant s viz. hydrogen peroxide, persulfate, permanganate & ozone.

Thirdly, to correlate Physicochemical properties of these catalytic oxidants with water contaminants in subsurface systems, ground water treatment systems involving chemical oxidation regeneration of Granular Activated carbon (GAC) [9].

Also, to develop innovative methods to entrap water contaminants, toxins through High Affinity Toxin Receptors (HART), Catalyst – Absorption – Beds (CAB), 'Carbon sinks', Cobalt Oxide Catalyst Converters (Co O-CC), etc., for limiting Green House Gases (CO₂, CH₄, CO, H₂, N₂O, SF₆, 14CO₂) and inhibit the generation and widespread release of toxic chemical substances/Contaminants in waterbodies.

Next, efforts would be made to develop Correlational Predictive Model of Chemical Reaction Kinetics (MCRK) to investigate process fundamentals and assess contaminant transformation. Fourthly, It would be endeavoured to develop innovative tech-

nologies to depollute water and environmental pollution by using the nanomaterials and conventional technologies by employing Physicochemical and Spectroscopic methods to characterize the in-situ chemical speciation of the inorganic contaminants, studying Chemical Reaction Kinetics, and develop 'Catalytic Chemical Processes'(CCPs) for remediation of water and environmental pollution [10].

Fifthly, High Resolution NISAR- Satellite Data would be used to study multiple stressors in Arctic marine systems to correlate Ocean-Atmosphere-Cryosphere (OAC) interactions with Climate Variability and Environmental Pollution to evaluate the correlation between the impacts of multiple stressors on the ocean and the associated risks of abrupt state shift, rising of sea level, melting of the glaciers, vis-à-vis climate variability. Also, it aims to study regional climate dynamics, and the Correlation of Arctic- Ocean-Atmospheric-Cryosphere Variability Mechanism, Sub-Mesoscale Dynamics and its impact on, Climate Variability.

Sixthly, it aims to investigate whether Nano-Oxidants can be used to Control Global Warming by converting GHG (Methane) to ethanol using catalytic processes and developing hybrid fuels like bioethanol and biodiesel to go for electricity from biomass. Also, by using cooling technologies like 'Magnetic Refrigeration Technology'(VG-MRT), developed by the author in the past, the Chlorofluorocarbons would be replaced in the refrigeration and air-conditioning; to Control Global Warming vis-à-vis Climate change [11].

Background and Relevance to Previous Work

(i) Researchers in University of Washington, in (Feb'17) USA, and the University of Edinburgh found that the pools underneath the glacier, Thwaites, are draining out at an unprecedented rate and emptying themselves. This unstoppably melting of the glacier into the ocean mainly because of warmer seawater lapping at its underside. Prof. Peter Clark, OSU attributed that the Glacier retreat was due to rising levels of Carbon Dioxide and other GHG, as opposed to other types of forces. If, this continues then the most of Glaciers would disappear in the next few centuries & the Glaciers loss in future will contributing to rising sea levels & environmental pollution. This ocean- atmosphere cryosphere (OAC) interaction is more evident on North pole i.e., Arctic regions as the temp raised above freezing point on 20 Dec'15.

(i) Researchers in University of Washington, in (Feb'17) USA, and the University of Edinburgh

(ii) (Canadian Scientist 01/01/2016-HindustanTimes), studied over Antarctic & Southern Ocean regions resulting the significant changes in Climate parameters.

(iii) Lately, Research HT (Hindustan Times 29Apr'17) reported that nanoparticles in air and water pollution are associated with cardiovascular disease, leading to premature death. The tiny particles in polluted air and dissolved in polluted water can travel from the lungs into our bloodstream and increase the risk of a heart attack or stroke.

(iv) Hindustan Times Dtd.24 May'16: reported that German Researchers in Bonn have found that average temperature would climb up to 9.5 deg. C-five times the cap on GW set at Climate talks in Paris in Dec'15 if, burning of all fossil fuels are not stopped. This unstopped rise of temperature would also affect marine life resulting water contamination, floods due to sea level

rise resulting contamination into ground water [12].

(v) The 13% Global Warming has been Reported by the Troposphere O₃ during 1980-1990. The estimation shows that a 50% increase in tropo-spheric Ozone would increase the global surface temperature by 0.3deg.C. This is due to the growing use of petroleum fuel. The absorption capacity of O₃ per mole is approximately 2000 times than that of CO₂.The meteorological and resource survey satellites have led that potential Global Warming would result the rise in Sea level and important environmental change in the coastal and low- lying regions of the earth.

(vi) Hindustan Times dtd.23 Aug'15 reported: that the Glacier retreat was due to rising levels of Carbon Dioxide and other GHG, as opposed to other types of forces. Also, the Glaciers loss in future will contributing to rising sea levels and, in some cases have an impact on local water supplies as well as give rise to Water Pollution as per my presumptions.

Effects of Global Warming vis-à-vis Climate Change

Global Warming vis-à-vis Climate variability has impacted almost all sectors of human's life spanning from environmental, agriculture, health and by can be realised as entirely altered the climatic system and weather patterns of our earth in form of increase of warmer land, warming air, warmer ocean, changing ocean currents, ocean acidification, rising sea levels, changes in hydrological cycle, flooding, melting glaciers and sea ice and extreme adverse weather conditions in terms of intensity and frequency. Not only that, the climate change due to Global warming causing effect on health and the economy of Nations [13].

The Health Effects induced by Climate Change are Shown in Fig. 1.Below (C.f. Google Search). Ref.(vii)

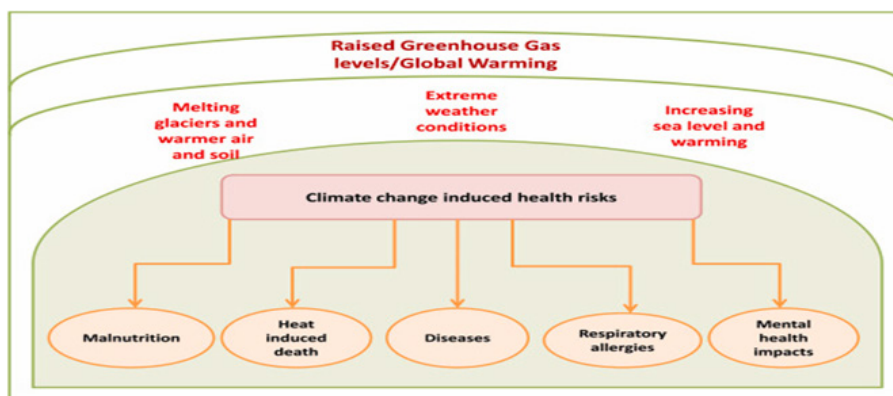


Figure 1

NISAR-Satellite Data: Ref.(viii), <Space.com30July25> reported the launch of NISAR-Satellite and released the launch-video as well. NISAR (NASA-ISRO) Satellite launched by ISRO-Geosynchronous Satellite Launch Vehicle (GSLV) on 30th Jul'25, is a joint effort between NASA and ISRO. It aims to study Earth planet in detail from orbit for at least five years using Synthetic Aperture Radar (SAR), capable to gather data in all weather and lighting conditions.

In the Word of ISRO Officials, "NISAR will image the global land and ice-covered surfaces, including islands, sea ice and selected oceans every 12 days," .NISAR's "primary object land and ice deformation, land ecosystems and oceanic regions in areas of common interest to the U.S. and Indian science communities," they added.

The NISAR Launch is the 18th liftoff to date for the GSLV, an expendable three-stage rocket that stands 169.6 feet (51.7 meters) tall , 5,300-pound (2,400-kilogram) in weight deployed

into orbit about 18.5 minutes after liftoff on 30thJuly 2025. It would work from a circular orbit 464 miles (747 kilometres) above Earth that takes it over the planet's poles [14].

Also, NISAR is a Dual-Frequency Band Radar. The L-band radar, which transmits microwaves between 1 and 2 gigahertz (GHz), was built by NASA's Jet Propulsion Laboratory (JPL) in Southern California, while ISRO provided the S-band radar operating between 2 to 4 GHz. The S-band is sensitive to vegetation and foliage, whereas the L-band can see through the trees to monitor the bare surface, be that rock or ice.

The Synthetic Aperture Radar SAR Technique gives NISAR powers of high resolution, and it takes advantage of the moving capacity of the NISAR wherein; spacecraft beams down radar pulses while flying along, the area on the ground covered by each radar beam while switched on is about 10 kilometres (6 miles) long.



Figure 2: The Synthetic Aperture Radar (SAR).

The NASA-ISRO Synthetic Aperture Radar is capable to scan Earth planet and provide detailed map of the ground or ice creeping by degrees of less than a centimetre helping to avert, or minimize, the effects of natural disasters e.g. Earthquakes, Volcanoes, land subsidence, swelling, and the movement, deformation of melting of ice sheets, glaciers, and tracking of wildfires and floods.

This would help to Predict Earthquakes in particular, by tracking the smallest shifts in the landscape as the precursor to a major disaster. For example, the "slow" landslides in mountainside or cliff move by just a few centimetres per day, before reaching a tipping point and crashing down would be observed by NISAR enabling to see that slow creep/subtle movement of tectonic plates, and forecast the when and where the disaster would take place.



Figure 3: The GSLV rocket carrying the U.S.-Indian NISAR Earth-observing satellite rolls out to the launch pad on July 24, 2025. (Image credit: ISRO).

General Methodology and Procedure to be Followed

It's imperative to investigate sub mesoscale dynamics of Arctic ice sheet stability, ice and bedrock coring, ice sheet modelling, and ice sheet processes viz. physical, chemical, and biological oceanographic for climate modelling study through the computation of Correlation of Cryosphere Ice Sheet Stability with Sea-level Variability Mechanism, Sub-Mesoscale Dynamics and Climate variability by developing Ocean Systems Interactions, Risks, Instabilities and Synergies (OSIRIS) & Arctic-Ocean Climate Predicting Models (AOCPM). The kinematic features of the mesoscale convective systems over Arctic- Ocean regions would be correlated with ocean-atmosphere-cryosphere variability on time & Space Scales; at the local, regional and global levels through the extracted Sea Surface Temperature (SSTs) over the grid box, attributing the regional change to natural and anthropogenic radiative forcing agents to bring out the few optimum values of these to develop Ocean Systems Interactions, Risks, Instabilities and Synergies (OSIRIS) & Arctic Ocean Climate Predicting Models (AOCPM), by using High Resolution Satellite imageries, data access, assimilation; HPC and cloud computing for real-time analysis [15].

Remediation of Water Treatment Process (WTP)

In remediation of Water treatment process by making use of catalytic chemical oxidants, it has been observed that matching the oxidant and in situ delivery system to the contaminants of concern (COCs) and the site conditions is the key to successful implementation and achieving best results in Water treatment process. In situ treatments the ground water is treated without being brought to the surface. These processes are slower but economical. The general methods and procedures to be followed for remediation of Water treatment processes are:

Physical/Chemical Remediation Water Treatment Technologies. (PRT & CRT): The Physical Remediation Technology (PRT) involves the use of physical properties of the contaminants and separation of contamination. In Chemical Remediation Technology (CRT); the contaminated medium is destroyed

by chemical conversion (i.e., chemically convert). The Chemically convert may involve use of chemical oxidant and Catalytic Oxidants to either separate the contaminants or destroy the contamination. This investigation intends to employ the following well tested PRTs & CRTs as regards ground water, surface water, and leachate i.e.

air sparging, # bio slurping, # directional wells # dual phase extraction.# thermal treatment # hydrofracturing, # in-well air stripping # passive/reactive treatment walls.

The Rate and Extent of Degradation of a Target Contaminants of Concern (COC)

These are dictated by the properties of the chemical itself and its susceptibility to oxidative degradation, and the matrix conditions e.g. pH, temperature, the concentration of oxidant, and the concentration of other oxidant-consuming substances (e.g. organic matter, reduced minerals, carbonate and other free radical scavengers.).

In these processes, Oxidant delivery systems often employ vertical or horizontal injection wells and sparge points with forced advection to rapidly move the oxidant into the subsurface.

Ozone Oxidation: Ozone gas oxidizes contaminants directly or through the formation of hydroxyl radicals e.g. peroxide. ozone oxidation reactions are most effective in systems with acidic pH. Ozone oxidation reaction proceeds with extremely fast, pseudo first order kinetics. In situ decomposition of the ozone can lead to beneficial oxygenation and bio stimulation.

Peroxide Oxidation i.e. Fenton's Reagent oxidation: Oxidation using liquid hydrogen peroxide (H_2O_2) in the presence of native or supplemental ferrous iron (Fe^{+2}) produces Fenton's Reagent which yields free hydroxyl radicals ($OH\cdot$). These strong, nonspecific oxidants can rapidly degrade a variety of organic compounds. Fenton's Reagent oxidation is most effective under very acidic pH (e.g., pH 2 to 4) and becomes ineffective

under moderate to strongly alkaline conditions. The reactions are extremely rapid and follow second-order kinetics.

Second Order Permanganate Reactions

The reaction stoichiometry of permanganate (liquid or solid KMnO_4 , or in Na, Ca, or Mg salts) in natural systems is complex. Due to its multiple valence states and mineral forms, Mn can participate in numerous reactions. The reactions proceed at a somewhat slower rate than the previous two reactions, according to second order kinetics. Depending on pH, the reaction can include destruction by direct electron transfer or free radical advanced oxidation—permanganate reactions are effective over a pH range of 3.5 to 12. Permanganate is relatively more stable and relatively more persistent in the subsurface and migrate by diffusive processes. All oxidation reactions can decrease the pH if the system is not buffered effectively.

Other Potential Oxidation-Induced Effects Include colloid genesis leading to reduced permeability; mobilization of redox-sensitive and exchangeable sorbed metals; possible formation of toxic by-products evolution of heat and gas, and biological perturbation.

Remediation of Environmental Pollution (REP)

Ref.(ix).@ May 03, 2010, NASA, ARC's Scientists; Lee, Francisco et.al. have developed strategies to minimize the environmental impact of GHG on Global Warming. They discovered that several fluorinated compounds tend to be stronger greenhouse gases than compounds containing chlorine and-or hydrogen.

Ref.(x)@Ph.D. Thesis. @Goswami V.K et. al. have shown that the few oxides of first row of transition metals viz. Cobalt Oxides : Co O (CoO I , CoO II , Co O I, II), CO_2O_3 ; CO_3O_4 with high values of Magnetic Susceptibility, high Surface area ,highest activation energy & high Catalytic activity exhibits dramatic heating and cooling when a magnetic field is applied and removed, at normal conditions by providing highly efficient cooling at room temp., and does not loose efficiency when the cooling cycle is repeated time after time.

These results were found after employing the rigorous Research methodology to conduct Magnetic Susceptibility measurements using the said Cobalt Oxides Catalysts and designing Magnetic

Balance/Reactor at the Indian Institute of Technology, Kharagpur, by Virendra Goswami, B. Ghosh, Dr. S.K. Duttaroy and Dr. KS De. The investigations were carried on to Study of the relationship between the physicochemical characterization and catalytic activity of catalysts having the same electronic configuration, such as Co O(I) , Co O(II) and Co O (I, II) ; to find out which of the two structures 3d6 or 3d7 of the oxides is the more active configuration for catalytic reactions involving hydrogen and /or hydrocarbons.

Method of Characterization of the Catalysts:

The oxide, prepared either by decomposing nitrates /oxalates or by heating the lower oxides in oxygen, were characterized by (I) X-ray diffraction pattern (II) differential thermal analysis (III) magnetic susceptibility measurements (IV) surface area determination and (V) chemical analysis.

(i) **X-ray diffraction:** The X-ray diffraction pattern has been used to identify the crystalline nature and structure of the oxides by calculating the lattice parameter in some cases. Differential Thermal Analysis (DTA) Differential thermal analysis was carried out with the help of a manual unit.

(ii) Differential Thermal Analysis (DTA):

By using DTA, Goswami VK et.al found that Co O (II) transforms noticeably to Co O (I) at about 300deg.C, giving Co O (I, II) – a mixture of form I and II. Also, it was investigated which of the two forms of cobaltous oxide is mainly responsible for catalytic activity, through a study of the physical properties of the two forms and their catalytic activities.

Experimental: Co O (II) , Co O (I) , Co O (I, II) have been prepared following the methods described by Ok and Mullen. Ref.(xi). In addition to this, Co O(I) and Co O(I,II) have also been prepared by a second method. The DTA measurements on Co O (II) in the temperature region 300deg – 850degK in vacuum and Ar. Atmosphere were done in sealed Pyrex glass ampoule by using the conventional DTA apparatus. (fig.4) below.

Differential Thermal Analysis (DTA): Prior to the measurement, Co O (II) was prepared was placed in one of the ampoules of the specially designed Sample -Holder and in the adjacent ampoule, the thermally inert reference substance (calcined -alumina) was placed. The ampoules were sealed in vacuum and mounted on the porcelain support. (Fig.4)

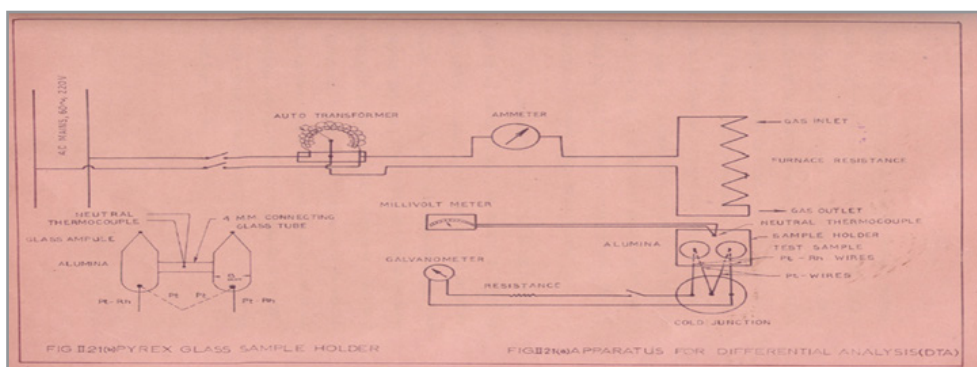


Figure 4: DTA-Apparatus. <c. f. (Ph. D Thesis Submitted by Dr. Virendra Goswami)>

In the case of other Cobalt Oxides, the samples were packed in one of the two holes of the nickel specimen holder, the other being filled with reference substance. The system was calibrated

with known substances. The sample-holder was positioned in the furnace, and the rate of the heating was maintained constant at $10 \pm 1 \text{ deg.C /min}$. The required air/nitrogen/hydrogen)

was maintained and the galvanometer reading noted down. The 'thermogram' has been plotted in the form of continuous curves correlating galvanometer deflection, which is a function of differential temperature of the furnace (T), represented as the abscissa, such that the exothermal peaks upwards with respect to the base line $\Delta T = 0$.

(iii) Magnetic Susceptibility:

Magnetic Susceptibility: was studied by the specially designed and fabricated Magnetic Balance at IIT Kharagpur (Fig.5). The specimen to be studied was tightly packed in a small round Pyrex glass ampoule, seated under vacuum and was suspended from one end of the balance beam by means of a tungsten fibre. The beam of the balance was then made horizontal by placing suitable counterpoising weight on the beam. The position of the phototubes was adjusted, so that the spot of light reflected from the mirror say M, illuminated the cathodes equally. Then the balance assembly was enclosed in a brass case provided with a glass window and the entire system was evacuated to avoid convection disturbances. When the vacuum was of the order of 10-5 mm of mercury, initial deflection in the output galvanom-

eter was noted, and on switching the magnetic field, the galvanometer spot was observed to move away. The current in the compensating coil was switched on, and it was adjusted by using various controls until the galvanometer spot comes back to the original position. The potential drop across a standard 10 Ohm resistance was measured by means of micro potentiometer. The temperature was measured by copper-constantan thermocouple kept very close to the sample.

Computation of Magnetic-Susceptibility

The following expression was used for the calculation of mass susceptibility.

$$\chi = \frac{I}{I_s} \frac{m_s}{m} (\chi_s - k \frac{P}{T}) \frac{V}{V_s}$$

where, k_a = volume susceptibility of air at T deg. K and P, P_s are the densities of sample and standard sample respectively. I and I_s are the currents required to compensate the torque on the sample and standard sample of mass susceptibilities χ , χ_s of mass m, m_s respectively.

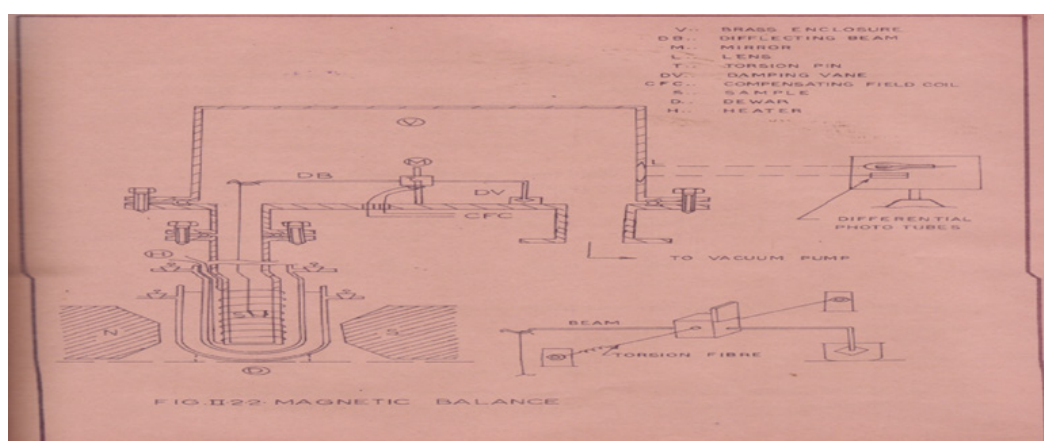


Figure 5: Specially Designed and fabricated Magnetic Balance at IIT Kharagpur.

(iv) Surface Area Measurement

Since heterogeneous catalysis is a surface phenomenon, the determination of catalyst surface area is necessary in the reproducible preparation^[1] and the systematic composition of Physicochemical properties and catalytic activity of catalysts. A high surface area is an important characteristic of all good catalysts. Brun Auer, Emmett and Teller (B.E.T.) method was used for the determination of surface area of oxide catalysts.

Research Methodology to Study of Catalytic Activity and Reaction Kinetics by Dehydrogenation and Hydrogenation Reactions under High Pressure

The Dehydrogenation of Cyclohexane and Hydrogenation of Ethylene Reactions: were selected to study the Reaction Kinetics and Catalytic Activity of the First row of Transition metal oxides e.g. Cobalt Oxides, comprising all the five types of viz. Co O, Co OI, Co O II, Co OI-II & Co₂O₃. The experiments were done in a batch (static) system under High Pressure following the procedure as detailed below.

The experiment set up along with High Pressure Reactors was designed and fabricated at IIT Kharagpur by the author (Shown Below in Figure-6).

(i) Setting the Apparatus: At first all the high-pressure valves, reactor and pre- heater were thoroughly cleaned with water, followed by solvent oil and finally dried to remove the last traces of cleansing liquids.

(ii) Charging of Reactor and Preheater: The powered catalyst was taken, weighed accurately and smeared on the perforated ring (catalyst-seat). A layer of fine glass wool was then placed over the catalyst seat in such a way as to cover the space between the catalyst and the orifice in the topknobs of the reactor, when the bottom stud is fixed in its position. The reactor was next connected in turn to the precision gauge, pre-heater, vacuum. line and product release assembly through the high pressure Amico four-way connector. The outlet of the reactor was closed.

(iii) The Entry of Inert Gas: when necessary was regulated by spindle Valve. A known amount of purified cyclohexane was taken into the preheater by opening the stud of the reactant inlet at the top nut and finally tightening it well with an adjustable spanner. The amount of cyclohexane fed into the reactor could be known either from the amount of cyclohexane left over in the preheater or from the observed pressure, temperature and known volume (available space) of the reactor.

(iv) Reaction Study: The whole unit was finally connected with a high vacuum system through spindle of the valve, keeping the other parts isolated by the spindle of valve and spindle of valve. The simultaneous evacuation and degassing of the catalyst were done at a temperature. higher than the maximum reaction temperature depending upon the nature of the catalyst. This operation was carried out for four-six hours, which was. found sufficient for obtaining reproducible results. (Ref.(x)).

The Catalytic Activity of Cobalt oxide catalyst Co O (Co O I,

CoOII, Co O I, II,) CO₂O₃; CO₃O₄] were studied through the reaction kinetics of Dehydrogenation of Cyclohexane and Hydrogenation of Ethylene by Goswami V.K et.al.

The Dehydrogenation of Cyclohexane

The experiments were done in a batch (static) system and the procedure as detailed below as follows. The experiment set up along with High Pressure Reactors was designed and fabricated at IIT Kharagpur by the author.(Fog.6).

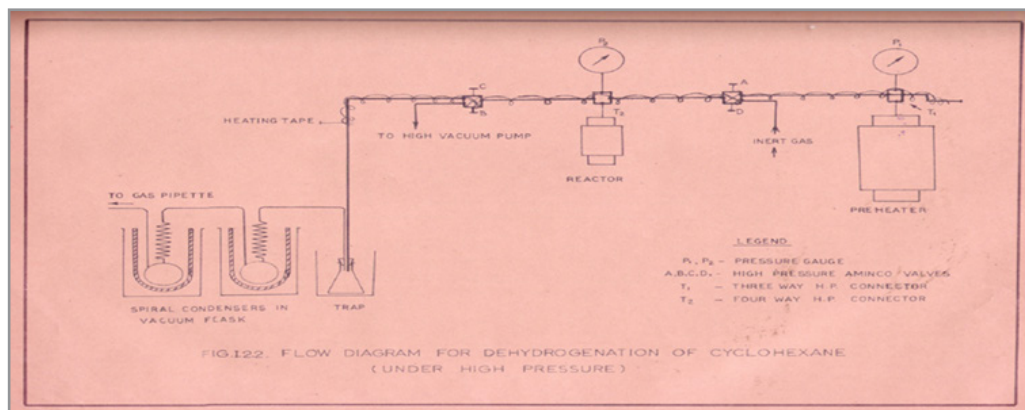


Figure 6: Flow Diagram for Dehydrogenation of Cyclohexane & Hydrogenation of Ethylene under High Pressure, IIT Kharagpur <c. f. (Ph. D Thesis Submitted by Dr. Virendra Kumar Goswami (Author).

(v) After evaluation, the high-pressure unit was disconnected from the vacuum unit by closing the spindle of valve. The reactor temperature was then brought down and maintained at the reaction temperature by regulating the voltage. The preheater was then heated so that cyclohexane (in vapor form) may be taken into the reactor at reaction temperature. When the requisite pressure of cyclohexane (about 300 psi) developed in the pre-heater & was opened and cyclohexane vapours were let into the reactor.

(vi) The Pressure of the Cyclohexane was Adjusted by the Spindle of Valve

The connecting tubes were heated electrically by using a heating tube to avoid any condensation cyclohexane vapor. After attainment of the desired initial pressure (100 psi) in the reactor system, the spindle of valve was closed to disconnect the pre-heater. At this stage, all the high-pressure valves closed, and the reactor system was an isolated system. The pressure change (ΔP) was noted by means of precision pressure gauge, and course of the reaction was followed by noting the change in pressure (ΔP) at regular interval of time. It was confirmed experimentally during blank runs that the reaction and the properties of the catalyst used were unaffected by glass wool.

(vii) Collection of the Products

The product was released at desired intervals (residence period) through the outlet and collected in the spiral condensers immersed in ice-bath. The gaseous product incompressible in the ice-bath (viz. hydrogen gas), was collected in the gas pipette. Finally, the spindle valve was opened very slowly, and pure argon gas was passed into the system to transfer the remaining product from the reactor system to the spiral condensers. This flushing of the unit was carried out for five to ten minutes. The gas pipette was disconnected during the flushing operation.

(viii) Analysis of the Product

(a) Gas analysis: Gaseous products whenever collected were analysed by modified Fisher gas analysis apparatus fitted with both slow and high combustion units. Only hydrogen could be detected.

(ix) Analysis of the Condensate: The condensed products in the spiral condenser were analysed by vapor phase chromatograph (Perkin Elmer Model 154) by using the requisite columns. No product other than benzene and unreacted cyclohexane could be detected. Generally, the amount of benzene was found to be approximately one third of the gaseous product.

(x) The Chromatographic Analysis of the product was done Vapor Phase Chromatograph (VPC), using Perkin-Elmer VPC-Chromatogram [8].

(xi) Calculation of the Rate Constant:

The rate constant k' for the reaction $C_6H_{12} = C_6H_6 + 3H_2$ Was determined by the following expression $K' = \Delta p / \Delta t \cdot p >$. Where, Δt = contact time in seconds i.e. the interval of time after which the product was released

n = order of reaction (found to be 1 in this case)
 P_i = Initial pressure of cyclohexane, (100 psi) in all experiments.
 Δp = The change in partial pressure of cyclohexane due to the reaction.

Results & Discussions

The results of magnetic susceptibility measurement and DTA are shown in figure 7 & 8 respectively.

The Magnetic Susceptibility data of the two forms of Co O and the mixture show that Co O(II) has got the highest magnetic susceptibility value at room temperature (5231 x 10⁶ grams/mole), in comparison to the room temperature susceptibility values of

Co O(I) (4684 x 106 grams per mole) and Co O (I, II) (4762 x 106 grams/mole). This arises from the low density of Co O(II) compared to Co O(I) and Co O (I, II).

Along with the temperature dependence of magnetic susceptibility of Co O (I, II), Co O(I) and Co O(II), the magnetic susceptibility data of La Blanche Tais has also been shown in figure 1. The sample-to-sample variation in the region 300deg – 600deg K indicates that the magnetic susceptibility depends profoundly on the sample preparation. The plot of χ_m^{-1} vs T in Co O (I, II) follows a linear relationship whereas Co O(I) shows a slight curvature, increasing in the case of Co O(II).

Further, in Co O(II) the susceptibility shows an anomalous behavior in the temperature region 550deg – 600degK; indicating that in this temperature range Co O(II) slowly passes into Co O(I). Beyond the transition region all the samples show a similar behavior. This result is in conformity with the Mossbauer data.

The transition observed in Co O(II) is not of magnetic origin since the sample is paramagnetic both below and above the transition temperature. But the large density difference between the two forms suggests that the transition is probably first order. The evaluation of exchange parameter appears difficult due to the magnetic anomaly in the region 300deg – 800 deg [9].

The DTA measurements on Co O(II) show that the endothermic pattern of thermograph changes at about 550 ± 50 deg. K, indicating a change in the form of Co O. Such a change might be due to contraction of the lattice.

Based on the observed differences in the physical properties of the two specimens of Co O, the catalytic activity has been investigated by Goswami VK et.al. Furthermore, D.T.A and temperature dependence of magnetic susceptibility of Co O(II) arises from a first order phase transition. The magnetic data of Co O(I) and Co O(II) have been correlated with a two sublattice model and exchange parameters evaluated.

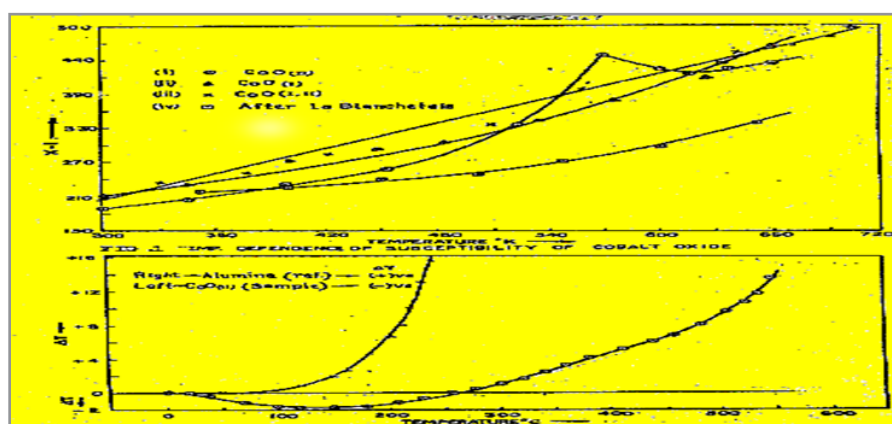


Figure 7 & 8: Differential Thermal Analysis (DTA) Results.

Mitigation of Emission of CO₂

- Plantation: plants are the best absorbent of CO₂. Each tree planted in the humid tropics absorbs 50 pounds (22 kg) of carbon dioxide every year for at least 40 years i.e. each tree will absorb 1 ton of CO₂ over its lifetime.
- Control Anthropogenic Activities GHG.
- Methane to Ethanol by Catalytic Processes.
- Non-Conventional Energy: (Nuclear, Electric, Wind, Water, & Solar energy). Reduce the use of fossil fuels, use energy efficiency devices and expand renewable and clean energy technologies viz. Power Generation from Biomass, reducing the use of Ozone Depleting Substances, reduce Carbon Emissions.
- Mitigation of Emission of CO₂: By pollution control devices e.g. Absorption – beds (Co O), ‘carbo sinks’, HART, Catalyst Converters, etc.,
- For limiting Green House Gases (active Catalyst-beds).
- Virendra Goswami-LUNAR COOLING: I’m of the view that Lunar Energy can be harnessed and used for Cooling and production of Lunar Ac and refrigeration as well. Lunar Cooling can be generated by either harnessing the Lunar energy through Lunar Panels alike Solar panels or developing the Lunar Concentrator by using a parabolic trough like machine, perhaps complete with methanol and activated Carbon attached on the top. Probably this proposed system of Lunar Concentrator comprising methanol and activated Carbon should minimize Green House effect, increasing the Cooling process [11].

Expected Results and their Significance

- Catalytic Activity:** While studying the Catalytic Activity of Cobalt oxide catalyst Co O (Co O I, CoOII, Co O I, II,) CO₂O₃; CO₃O₄] through the reaction kinetics of Dehydrogenation of Cyclohexane and Hydrogenation of ethylene by Goswami V.K et.al. It was observed that of the three oxides, Co O [$k = 1.16 \times 10^{-8}$ mole. sec.⁻¹ m.⁻² at 130deg.C], Co₃O₄ [$k = 2.27 \times 10^{-8}$ mole. sec.⁻¹ m.⁻² at 130deg.C], and CO₂O₃ [$k = 7.2 \times 10^{-8}$ mole. sec.⁻¹ m.⁻² at 130deg.C], CO₂O₃ has the highest activity. This trend in activity of the oxides is also reflected, though not significantly, in the activation energy values.
- Reaction Kinetics: Dehydrogenation & Hydrogenation Reactions**
A comparison of the activities of the different forms of cobaltous oxides for the Dehydrogenation reaction shows that Co O (II) has the highest activity [$k = 1.738 \times 10^{-8}$ mole. sec.⁻¹ m.⁻² at 130deg.C], compared to Co O(I) [$k = 0.572 \times 10^{-8}$ mole. sec.⁻¹ m.⁻² at 130deg.C], and the mixed form, Co O(I, II) [$k = 1.119 \times 10^{-8}$ mole. sec.⁻¹ m.⁻² at 130deg.C].
- Ethylene Hydrogenation.** Similar trend is also exhibited for ethylene hydrogenation. [k for Co O (II) = 3.28×10^{-7} mole. sec.⁻¹ m.⁻² at 130deg.C and k for Co O(I, II) = 1.29×10^{-7} mole. sec.⁻¹ m.⁻² at 130deg.C]. These observations have been discussed in the light of d-electron configuration of metal ions

of the oxides, and the possibility of 3d6 configuration having a higher activity than 3d7 arrangement has been suggested. (d) 'Carbon Sinks': Next, the present study plans to use this very technique of CO₂ Absorption from air to create 'Carbon Sinks' through the catalytic processes by making use of d- group transition metals particularly oxides with 3d6 & 3d7 structure due to their formation of bond to Carbon characteristics.

(e) Means to produce more O₃ by Catalytic Processes: Pure ozone can be obtained by fractional liquefaction of CO₂O₃ mixtures. producing elemental oxygen and by action of ultraviolet light on O₂.

Conclusion & Scope: Dr. V.K. Goswami et.al. concluded that the substance of high magnetic susceptibility value at room temperature ,high value of surface area, high value of metallic content and of low density exhibits dramatic heating and cooling when a magnetic field is applied and removed, and can operate in normal conditions without loss of efficiency when the cooling cycle is repeated time after time ;should be useful for the cooling application and manufacturing of Magnetic fridges* limiting the use of substances that are known as ozone depleting e.g. CFC .

Also, such catalytic oxidant with high catalytic activity and high activation energy are active chemical oxidant to inhibit water contamination and accelerate the water treatment process of remediation.

The results of above investigations comprising Physicochemical properties of solid Catalysts to predict parameters to Control Global Warming remediation of water contamination treatment & detoxification of toxins may be used to develop Correlation-Predictive Model of Chemical Reaction Kinetics (MCRK) in order to investigate process fundamentals & assess contaminant transformation [13].

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