SR III

UNIVERSITY GRANTS COMMISSION
SUPPORT FOR "SCIENCE RESERCH"
PROPOSAL FOR MAJOR RESEARCH PROJECT

1. Title of the research project (in Block letters):

PHOTOCHEMICAL SPLITTING OF WATER. ~~AND~~ FIXATION OF NITROGEN AND NITROGEN LOSS BY ORGANO-MOLYBDENUM MICRO-STRUCTURES, MODEL OF THE PROTOCELLS

2 (a) Principal Investigator and other members of research groups, if any:

A. PROF. KRISHNA BAHADUR M.Sc., D.Phil., D.Sc., D.I.C. (Lond.)

To be assisted by → B. PROF. (MRS) S. RANGANAYAKI D.Phil., D.Sc.

(b) Date of birth of Principal Investigator (financial Assistance is available upto the age of 65 years only)

A. 20 January, 1926

B. 17 June, 1930

(c) Department: CHEMISTRY

~~Department of Chemistry~~

(d). Institution and address:

University of Allahabad,
Allahabad - U.P., Pin 211 002

CO_2

3. Academic Experience:

(a) Research

A. ~~37~~ 40 years — {Nuffield fellow (1960), Exchange Scientist (1963), Canadian Commonwealth Research fellow (1968).

B. 36 years.

Research specialisation - Organic Chemistry, Plant Chemistry, Microbiology, fermentation, Enzymology, study of origin of life — Biopoesis, photochemical splitting of water and fixation of Nitrogen and of CO_2

(i) Scientific equipments

Purchase of carrier gas and other accessories	Rs. 40,000
Digital - pH meter	Rs. 15,000
Solarimeter	Rs. 30,000
Autoclave	Rs. 7,000
Xenon lamps (3)	Rs. 15,000
Clinical mercury vapour lamps (2)	Rs. 5,000
Optical microscope with phase contrast arrangement and camera	Rs. 1,30,000
Warburg's apparatus	Rs. 15,000

(b) Teaching

A. 36 years

B. 28 years

(c) Papers published : Give title of papers, name of authors, journals in which published and year of publication ~~(Separate sheet may be attached)~~.

Complete list of papers published by both the investigators attached as ENCLOSURE NO. .....

4. Please indicate whether the research work is :

(i) Basic ✓

(ii) Applied / R & D

(iii) Development / fabrication of equipment

5. Actual plan of work indicating briefly the objectives and importance of the work proposed ~~(Separate sheet may be attached)~~ Enclosure No. :

Brief plan of the proposed work is attached separately as ~~ANNEXURE~~ ENCLOSURE NO. .....

6. Duration of the project :

5 years.

7. Detailed estimates of the expenditure to be incurred on the project (for 3 years only)

(a) Non-recurring	Amount required
(i) Scientific equipments -	
Purchase of carrier gas and other accessories	Rs. 40,000
Digital pH meter	Rs. 15,000
Solarimeter	Rs. 30,000
(ii) Scientific journals and books.	Rs. 30,000
(iii) Strengthening of workshop facilities (repair of existing instruments)	Rs. 20,000

contd.→

Total Rs. ~~3,07,000~~ ~~2,07,000~~

No foreign exchange is required for the procurement of above items.

(b). Recurring (per annum) — Amount required

(i) Personnel.

A. Prof. ~~Krishna~~ Bahadur @ Rs. 5000/p.m. — Rs. 60,000

B. Prof. ~~(Smt.)~~ S. Ranganayaki @ Rs. 5,000/- p.m. — Rs. 60,000

(c) Research Associate (2) @ Rs. 2800/- p.m. — Rs. 67,200
(Rs. 100/- annual increment)

D. Senior Research Fellow (3) @ Rs 2100/- p.m. — Rs. 75,600
(fixed)

E. Junior Research Fellow (3) @ Rs. 1800/- p.m — Rs 64,800
(fixed)

F. Technical Assistant (2) @ Rs. 1500/p.m. — Rs. 36,000
(fixed)

Total ~~Rs.~~ 3,63,600

(ii) Contingency

A. Prof. K. Bahadur — ~~Rs.~~ 15,000

B. Prof. ~~(Smt.)~~ S. Ranganayaki — ~~Rs.~~ 15,000

C. Research Associates (2) — ~~Rs~~ 20,000

D. Senior Research Fellow (3) — ~~Rs~~ 30,000

E. Junior Research Fellow (3) — ~~Rs~~ 30,000

Total Rs. 1,10,000

(iii) Chemicals and consumables — Rs. 50,000

(iv) Computation work — Rs. 20,000

(v) Travel for field work, etc — Rs. 10,000

Total Rs. per annum — Rs. 5,53,600

Total recurring for the duration of project

I st year Rs. 5,53,600
II nd year Rs. 5,56,000
III rd year. Rs. 5,58,400
Rs. 16,68,000

Total non-recurring and recurring (for 3 years) Rs. ~~19,75,000~~ 19,75,000

Rupees Nineteen lakh Seventy Five Thousand

8. Please indicate research scheme already undertaken and inforce with funds from Commission or any other agencies : Not any

Name of the funding agency with reference number	Amount sanction (give detail)	Amount utilised	Progress made under the scheme

9. Please give names and address of three persons in other Universities / research institutes actively engaged in your area of research interest to whom a reference may be made, if necessary, regarding the research projet :

(i) Prof (Mrs.) Indra Kumari Verma
Department of Chemistry,
Indian Institute of Technology,
Hauz Khas, New Delhi

(ii) Prof. Vishnu Chandra
Department of Chemistry,
Gorakhpur University,
Gorakhpur

(iii) Prof. Ram Sajivan Pandey
Department of Biochemistry
National ~~Dairy~~ Dairy Research Institute, Karnal
~~Karnal~~.

10. Rules governing the scheme are acceptable to us and that the information given in the application form is correct to the best of our knowledge and belief.

KRISHNA BAHADUR S. RANGANAYAKI
(Signature of the applicants.)

CERTIFICATE FROM THE INSTITUTION

Certified that :

(a) General facilities required such as laboratories, equipments etc. are available in the department.

(b). The equipment / apparatus / chemicals / books etc. for which assistance is requested are not available for his / her research project.

(c) The research proposal is not being supported by any other agency.

(d). The Institution is fit to receive U.G.C. assistance.

facilities for research work will be provided to Prof. Krishna Bahadur and Prof. (Smt.) S. Rangamayalu in the University / College

(Signature of the principal of the College / Registrar of the University)

(Signature of the Head of the Department)

ITEM
~~ENCLOSURE~~ NO. 5 ENCLOSURE NO.

(1) Actual plan of the proposed work:

Double

Organo-molybdenum microstructures (OMM) were examined for their possible ferredoxin-like activity. It is because these OMM are prepared by the exposing of sterilised aqueous mixture of ammonium molybdate, diammonium hydrogen phosphate, biological minerals and formaldehyde to sunlight, have a distinct boundary wall and internal structures (1). D.O. Hall et al observed that these microstructures can be used in the place of ferredoxin in the system of chloroplast-ferredoxin-hydrogenase of algae which are capable of splitting water to hydrogen and oxygen in sunlight. In photolysis of water by green algae, ferredoxin is reduced to ferredoxin by electrons liberated from water through photosystems I and II. The electrons from ferredoxin are then transported to hydrogenase which produces H_2 from H^+ and the intact chloroplast membrane helps in charge separation. For a membrane acting in energy conserving manner, the flow of electrons must be towards the redox potential with high energy rather than from high to low redox level. The action of light is to provide a channel for dissociation of energy on existing redox potential along the membrane. OMM has characteristic membrane and this has an important role in its ability of photo-chemical splitting of water. The chloroplast-OMM-hydrogenase system does split water into hydrogen and oxygen and the ferredoxin-like material of OMM is not destroyed by

(2) light and/or oxygen, like natural ferredoxin (2).

Chemical nature of hydrogenase is not yet clear. Colloidal platinum also acts as hydrogenase and many ferredoxins have hydrogenase-like properties.

These ~~organo-molybdenum microstructures~~ OMM were ~~then~~ then tested for the presence of nitrogenase-like activity ~~in them~~ also (3). Nitrogenase enzyme is a Mo-Fe-protein complex and as the ~~environmental~~ parental medium in which ~~the~~ OMM are synthesised contains high concentration of molybdenum and these ~~particles~~ OMM contain about 39% of molybdenum, a search for nitrogenase activity in these was made. It was observed that if an aqueous mixture of ~~the~~ OMM is exposed to ~~light from a~~ Xenon lamp, keeping acetylene in the overhead space, with increasing periods of exposure the concentration of acetylene ~~in the overhead~~ decreases and ethylene increases (4,5).

~~It was further observed by~~ Folsome, Smith et.al (6) observed that if OMM and D_2O mixture is exposed to the radiations from Rayonet UPR 2537 nm lamp keeping acetylene in the overhead space, it is converted into CHD=CHD indicating that the protons needed to convert acetylene to ethylene come from water and that these microstructures are capable of splitting water molecules in light ~~(6)~~.

These ~~microstructures~~ OMM were then tested for ~~their~~ ability of fixing carbon dioxide. ~~For this~~ On exposing an aqueous mixture of OMM and $Na^{14}CO_3$ ~~was exposed~~ to light, ~~and~~ it was observed that ^{14}C appeared in the organic material formed in the mixture (6). The fixation of CO_2 was confirmed by chemical estimation also (7).

It has been observed that when an aqueous mixture of OMM is exposed to sunlight bubbles of gas evolve from the mixture. The evolution of gas stops when sunlight is cut off. The evolution of gas continues for sometime and shaking helps in evolution of gas that day. However, if this mixture is allowed to stand in dark overnight and exposed to sunlight the next day, the mixture shows evolution of gas. This

process can be continued for 7 or 8 days and after that the mixture becomes inactive and no more evolution of gas takes place on subsequent exposure to sunlight.

Warburg's study indicated that on exposure of an aqueous mixture of OMM to sunlight under oxygenic and better under anoxygenic conditions, hydrogen and oxygen are produced. The observation is confirmed by gas chromatography. ~~In presence of OMM~~ The hydrogen produced by OMM combines with the atmospheric nitrogen in the ratio of ~~1 volume of nitrogen with 1 volume of hydrogen~~ 1:1, thus forming ~~indicating the formation of~~ di-imine, NH = NH as an intermediate compound. If the nitrogen fixation is inhibited a mixture of hydrogen and oxygen is obtained.

Under certain conditions when the fixation of nitrogen is very fast, after the fixation of nitrogen is stopped due to the consumption of available hydrogen, loss of nitrogen is observed as indicated by the increase in ~~the~~ pressure of the Warburg's flask caused either by decomposition of diimine yielding hydrogen and nitrogen or by disproportionation of diimine resulting in hydrazine and nitrogen. In these OMM, the fixation of nitrogen is so fast that decrease in the pressure of the Warburg's flask is observed as soon as the aqueous mixture of OMM is exposed to sunlight. The liberation of hydrogen and oxygen by ~~exposing~~ the aqueous mixture of OMM ~~to~~ in sunlight is accompanied by simultaneous decrease in the pH of the mixture during the exposure indicating that protons are set free. After exposing this mixture for 30 min. to sunlight, if the mixture is transferred to shade there is an increase in the pH of the mixture showing that protons are disappearing from the mixture and ~~in~~ in about 45 min. ~~in shade~~ its pH returns to the original, ~~pH.~~

The photochemical electron transfer is of considerable help in splitting water by this system. OMM-doped with titanium are more efficient in splitting water in sunlight. Photochemical fixation of nitrogen on the surface of wet TiO_2 powder has been observed by Schrauzer and Guth (8).

Photochemical splitting of water on titanium surface closely resembles photosynthesis and is being extensively investigated due to its possible use in energy conservation technology (9,10,11).

~~The overall reaction is~~ :

$$H_2O\ (l) + n\ h\nu \xrightarrow{TiO_2(s)} H_2\ (g) + \frac{1}{2}\ O_2(g)$$

$$\Delta G^{298} = 68.35\ \text{K.Cal./Mol.}$$

Schrauzer and Guth observed that if N_2 is present in the overhead space instead of argon, the yield of O_2 remains the same but the quantity of hydrogen produced is not in accordance with the above equation. Instead of H_2, ammonia and traces of hydrazine are found :

$$N_2(g) + 3H_2O(l) + m\ h\nu \xrightarrow{TiO_2(s)} 2NH_3(g) + 1\tfrac{1}{2}\ O_2(g)$$

$$\Delta G^{298} = 183\ \text{K.Cal/Mol.}$$

$$N_2(g) + 2H_2O\ (l) + x\ h\nu \xrightarrow{TiO_2(s)} N_2H_2(l) + O_2(g)$$

$$\Delta G^{298} = 149.7\ \text{K.Cal/Mol.}$$

The photolysis of H_2O on TiO_2 has been described in light with the current concept of electronic of semiconducting solid (9,10,11). On irradiation with ultra-violet light ~~of wave length between~~ (390-420 nm), electrons from valency bands are excited into the lowest conducting bands. The band gap

is of the order of 2.9-3.2 eV corresponding to 70 to 80 K.Cal. providing sufficient energy for splitting water. The positive holes thus formed in the valence band provide site for oxygen production and other oxidation reactions. The electrons in the conductance band can be utilised for the reduction of substrates as H^+, C_2H_2, C_2H_4 and N_2. In this case oxygen is obtained in sunlight and hydrogen in dark from the mixture and it is an observation of considerable significance because this is the ideal way of splitting water by sunlight.

(c) Detailed research ~~plan or~~ programme:

Hypothesis of the realistic work to be tested experimentally

Organo-molybdenum microstructure (OMM) have ferredoxin-like and nitrogenase-like materials and these split water in sunlight and fix CO_2 and N_2. Though OMM is heterogenous with boundary wall and internal structures, on treatment with sodium carbonate solution some reaction sets in leaving insoluble bluish rod-like microstructures ~~in the mixture~~ and a fraction of OMM is dissolved. This soluble fraction can be reprecipitated with hydrochloric acid. This precipitated ~~material~~ in all probability is a single complex containing molybdenum and this fraction also shows some ability of water splitting and fixation of nitrogen in sunlight.

In another specific mixture in which OMM are produced ~~by exposure to sunlight,~~ some blue rod-like structures are formed after some hours of exposure to sunlight. This mixture shows a new phenomenon. In sunlight ~~during exposure~~ the structure of the particles formed is rod-like. On keeping this mixture in dark overnight, next morning the mixture is

full of blue spherical particles of 1 to 2 μ in diameter with distinct boundary wall and internal structures. When this mixture is ~~put out of exposure to~~ kept in sunlight again by the evening (after about six hours) ~~of exposure to sunlight~~ the exposed mixture is again full of blue rod-like microstructures. This mixture on standing in dark overnight, ~~on the next morning~~ on the next morning is again full of only spherical particles. This process can be repeated for ~~about~~ 6 to 7 days ~~when~~ and finally this interconversion stops and only blue rod-shaped structures remain.

The relationship between the blue rod-shaped microstructure with spherical OMM with boundary wall and internal structures has to be investigated with X-ray diffraction and other possible technics.

Microstructures with specific morphology and with ability to utilise the energy of sunlight for not only their formation but even for splitting water ~~in sunlight~~ is of considerable interest because this process will set up an energy flow through the system and this will provide additional stability (12,13). By incorporating semiconductors and transitional elements in OMM, the properties of photochemical splitting of water and fixation of nitrogen can be significantly increased and these particles may become of commercial interest.

The preparation of such efficient OMM will be undertaken and the condition in which the interconversion of blue rod-like forms and spherical particles with boundary wall, determined and water splitting by both of these microstructures studied.

General description of the scope to be tested experimentally

The aqueous mixture of OMM on exposure to sunlight shows splitting of water and fixation of nitrogen. ~~In presence of OMM,~~ The fixation of nitrogen continues even after exposure is stopped. It has further been observed that under the conditions when rapid fixation of nitrogen is observed, it is followed by loss of nitrogen.

The ability of water splitting ~~of~~ by OMM is considerably increased by incorporating titanium or organic materials, as acetic acid in the parental mixture in which OMM are produced. ~~on irradiation with sunlight~~. We wish to prepare efficient OMM by incorporating silicon and germanium in them and determine the conditions optimum for splitting of water and fixation of nitrogen by the modified OMM. The study of their gas exchange in sunlight and in shade, following the reaction by the estimation of different gases present in the overhead space of the reaction mixture, using gas chromatograph will be undertaken.

The condition under which OMM show transformation into blue rod-shaped, crystal-like appearance after exposure and then formation of spherical particles with boundary wall and internal structures in dark, will be created and this transformation of the particles will be studied under electron microscope and with X-ray diffraction to determine the factors which cause this ~~change~~ interconversion.

It has been observed that OMM are made of two distinct type of materials, one is alkaline which does not dissolve in a dilute solution of sodium carbonate while the other is acidic and is soluble in it. From this solution it can be precipitated by hydrochloric acid. The possibility of utilising OMM or some of its modified variety and their

alkali insoluble and soluble constituents for the commercial exploitation of solar energy is also to be explored.

~~General description of the approach to be followed~~ Specific experiments to be done and equipments and chemicals needed:

First different OMM will be prepared incorporating Ti, Si, B, Mn, Co, Ni, Zn or Cd in them and the gas transformation by these doped particles when their aqueous mixture is exposed to sunlight and kept in shade will be investigated using gas chromatograph and Warburg's apparatus. Some scanning has also to be done to see whether the process of photochemical splitting of water can be enhanced at some particular pH using suitable buffer under oxygenic or anoxygenic conditions. The particles which show better splitting of water in sunlight will be then used for separation of their acid and base constituents. An attempt will be made to determine how these constituents are arranged in OMM.

~~Specific experiments to be done and equipments and chemicals needed~~: Phase-wise plan:

1. Different types of OMM will be prepared incorporating semiconductors and transitional elements in them and a few particles which appear good in splitting water in sunlight or in fixation of nitrogen, particularly under oxygenic conditions will be selected. For that gas chromatograph and Warburg's apparatus are required.

2. The OMM is to be fractionated into its acidic and basic constituents. The acid constituent which is a molybdenum complex is sensitive to sunlight and its structure will be determined using chemical methods, elemental analysis and X-ray diffraction.

3. The factors which help in the interconversion of spherical microstructures with boundary wall and internal

structures into rod-shaped structures and vice versa in the medium in which OMM are produced on exposure to sunlight and on standing in shade will be investigated by electron microscope and X-ray diffraction.

4. Efficient OMM in (i) splitting water in sunlight, (ii) fixation of nitrogen and (iii) and showing good loss of nitrogen and hence able to produce oxygen in sunlight and hydrogen in dark, will be prepared. The process will suggest a cheap method of converting solar energy into chemical bonds.

(d) Previous work done:

In 1978, OMM were found to contain ferredoxin-like material (2,3) and in 1981 nitrogenase-like material was detected in these particles (6) and we have discussed these particles in this project. Since then a number of OMM have been prepared in our laboratory showing different efficiency in photochemical splitting of water. We have been continuing this work since last 15 years and have published a number (about 120) of papers.

(e) Research Experience:

Prof. Krishna Bahadur, one of the applicants has been working in Allahabad University since 14th August, 1950 and he retired from the University on 20th January, 1986 when he completed sixty years of age. He was Professor and Head of the Chemistry Department. During this period of 36 years of his service in the University he has published about 200 scientific papers out of which about two-thirds are in standard foreign journals of the world. About 40 research students have been awarded Doctorate working under his guidance. He is a Nuffield Fellow and a Canadian Commonwealth Research Fellow. He has

been working in the field of 'Origin of Life' since last 30 years and has published more than 70 scientific papers on origin of life alone. Our school in this field is pioneer in India.

Dr.(Mrs) S.Ranganayaki has been working in the Chemistry Department of the University of Allahabad since 1962 and is at present Reader in Chemistry. She will be retiring in June 1990. She has published about 80 scientific papers and 20 students have got D.Phil under her.

(f) Institutional facilities:

The facilities necessary for the work are available in the Chemistry Department of the University of Allahabad.

(g) Assistance:

We will need a pay for ourselves as Chief Investigators, (Dr.S.Ranganayaki will draw pay after retirement) and for two research associates, two senior research assistants and three junior research assistants. We will need a contingency grant of Rs.15,000/- each for the purchase of chemicals and glass apparatus and Rs.10,000/- per research associate, Rs.10,000/- per senior research assistant and Rs.5000/- per junior research assistant per year for the same purpose.

(h) Funds requirement

We request that the project be sanctioned for 3 years. The expenses break-up during the first three years will be as follows :-

One solarimeter costing about Rs.30,000/- is required for measuring the intensity of the sunlight during the exposure of the mixture.

(12)

	1st year	2nd year	3rd year	Total
Staff				
Chief Investigators				
(1) Prof. Krishna Bahadur @ Rs. 5000/- p.m.	60000	60000	60000	180,000
(2) Dr. (Mrs.) S. Ranganayaki @ Rs. 5000/- p.m.	60000	60000	60000	180,000
2 Research Associates @ Rs. 2200/- p.m. Rs. 100/- annual increment	26400	27600	28800	82,800
	26400	27600	28800	82,800
2 Senior Research Assistants @ Rs. 2100/-p.m.	25200	25200	25200	75,600
	25200	25200	25200	75,600
3 Junior Research Assistants @ Rs. 1800/-p.m.	21600	21600	21600	64,800
	21600	21600	21600	64,800
	21600	21600	21600	64,800
Total	288,000	290,400	292,800	871,200
Contingencies				
1. Chief Investigators (two)	1. 15,000	15,000	15,000	45,000
	2. 15,000	15,000	15,000	45,000
2. Research Associates (two)	1. 10,000	10,000	10,000	30,000
	2. 10,000	10,000	10,000	30,000
3. Senior Research Assistants (two)	1. 10,000	10,000	10,000	30,000
	2. 10,000	10,000	10,000	30,000
4. Junior Research Assistants (three)	1. 5,000	5,000	5,000	15,000
	2. 5,000	5,000	5,000	15,000
	3. 5,000	5,000	5,000	15,000
	85,000	85,000	85,000	255,000

Staff = Rs. 8,71,200
Contingency = Rs. 2,55,000
Grand total Rs. 11,26,200

Rs. 3,75,400 per year for 3 years

(i) Number of publications in this area during the last 5 years

List attached.

References

1. Bahadur, K. and Ranganayaki, S. (1970), J. Brit. Inter-Planetary Soc., 23, 813-829.

2. Rao, K. K., Adams, M. W. W., Morris, P., Hall, D. O., Ranganayaki, S. and Bahadur, K. (1978), Proc. International Sym., Biol. Appl. Solar Energy, Madurai, India, Eds. A. Gnanam, S. Krishnaswamy and J. S. Khan, The MacMillan Co. (India), Madras, 1980.

3. Rao, K.K., Morris, P. and Hall, D.O. (1978), Presented at workshop meeting in "Hydrogenases - Their Activity, Structure and Function". Held at Gottingen in August.

4. Bahadur, K., Ranganayaki, S., Smith, A. and Folsome, C. (1980), Natl. Acad. Sci., India, Golden Jubilee Commemoration Volume, 181-198.

5. Bahadur, K. and Ranganayaki, S. (1981) Origin of Life- A functional approach, p.404, Ramnarain Lal Beni Prasad, Allahabad, India.

6. Smith, A., Folsome, C. and Bahadur, K. (1981) Experientia, 37, 357.

7. Ranganayaki, S., Bahadur, K. and Sajal, K. (1981). J. Brit. Interplanetary Soc., 34, 251-254.

8. Schrauzer, G.N. and Guth, T.D. (1977) J. Amer. Chem. Soc. 99 (22), 7189-93.

9. Fujishima, A. and Honda, K. (1972) Nature 238, 37.

10. Kawai, T. and Sakata, T. (1979) Nature 282, 2834.

11. Kiwi, J. and Gratzel, M. (1979) Nature 281, 657-58.

12. Briggs M.H. (1965) Spaceflight 1(4), 129-131.

13. Cairns-Smith, A.G., (1982) Genetic Takeover and the Mineral Origin of Life. Cambridge University Press, Cambridge.

D. SINGH:

सत्यमेव जयते

Telegram : RENEWABLE
Telephone :

D. O. No. 8/4/83-Proj.

भारत सरकार
गैर पारम्परिक ऊर्जा स्रोत विभाग
ऊर्जा मंत्रालय
Government of India
DEPTT. OF NON-CONVENTIONAL ENERGY SOURCES
MINISTRY OF ENERGY
BLOCK NO. 14, C.G.O. COMPLEX, LODI ROAD
NEW DELHI-110 003

Dated 18.6.83.....

Dear Dr. Bahadur,

Kindly refer to your project on Production of Hydrogen from Water by Organo molybenum Micro Structures Utilising Solar Energy submitted to this Department for funding. Your project has been examined by the referees. Their comments are enclosed herewith for your kind perusal. Kindly expedite your reply immediately on the points raised by the referees, so that we could process the case further.

With regards,

Yours sincerely,

(D.SINGH 9/6/83

Encl. As above.

Dr. Krishna Bahadur,
Department of Chemistry,
University of Allahabad,
Allahabad. U.P.

No.8/4/83-Proj.

Comments on the Research Proposal entitled "production of hydrogen from water by organo molybdenum microstructures utilising solar energy

.....

EXPERT NO.1

The main objective of the project is to develop a system for commercial splitting of water by sunlight using organo molybdenum complexes. It is an interesting proposal and the objective seems to be achievable. The scope of the work proposed is good. However, like the immobilized enzymes and whole cells of hydrogen-producing microbial systems, the organomolybdenum complex is also unstable and is rendered inactive after short use. How the inactivation of this complex is to be prevented has not been mentioned? Technical details, literature review and methodology available are inadequately described. Time schedule is all right. The author is quite capable of carrying out the proposed research. The budget, in my opinion, is out of proportionate. No justification for equipment, especially for ultracentrifuge, has been given. In my opinion for this work only a high speed refrigerated centrifuge giving 20,000 rpm (approx. 38000xg) should be good enough. Some good Indian Made are available.

Recommendations : The project may be supported with revised BUDGETARY estimates.

I suggest the following budgetary provisions :

A. Salaries and Wages :

Research staff :	1 SRJ	@ Rs.900.00 p.m.	
	2 JFF	@ Rs.600.00 p.m.	
	Total	@ Rs.25,200.00 per year	
	Total	Rs.75,600/-	

B. Permanent Equipment :

As proposed with following changes :

i) Only one pH meter instead of two

ii) Refrigerated high speed centrifuge to give 20,000 r.p.m., (38000xg) instead of an Ultracentrifuge.

Total Rs.1,58,000/-

C. Expendable Equipment and supplies :

		I yr.	II Yr.	III yr.
i)	Repair and working cost	5,000	10,000	10,000
ii)	Glass apparatus	10,000	10,000	10,000
iii)	Chemicals	20,000	20,000	20,000
iv)	Books	10,000	5,000	5,000
v)	Stationery	1,000	1,000	1,000
		46,000	46,000	46,000

Total Rs.1,38,000/-

D. Travel expenses

Ist yr.	IInd yr.	IIIrd yr.
2,000/-	2,000/-	2,000/-

Total - Rs.6,000/-

Total = Rs.3,86,600/-

EXPERT NO. 2

The project is a mixture of mystic and scientific and with the data given I am unable to assess the value. The actual phasing is also not clear. But the objective of obtaining hydrogen by biophotolysis is an attractive proposition, therefore, the authors may be requested to revise the project so to first establish that Hydrogen can be generated in this manner, identify the so called jeevanu, and the gas produced (which has not been done) and then come in for an extended project for large scale production. No quantitative data is given. Often the language is not clear. But the idea is a good one. Minimum assistance of 1 senior and 1 junior fellow can be given for the laboratory demonstration and quantification of the idea. The equipment request seems reasonable. Travel can be cut to about a third, Nitrogen fixation part can be separated and only the hydrogen production part can be funded.

A. 1 Sr. } Research associate
1 Jr. }

1 part time clerk

B. about Rs.1,00,000 only

C. 1, has to be explained.

2 + 3 Rs.1,00,000 only

4 + 5 O.K.

D. Rs.20,000 only

EXPERT NO.3

I regret to state that the project, as proposed, just does not merit any consideration for funding. The status of art regarding the photolytic splitting of water through co-ordination complexes and microstructures has not been covered in depth at all. The objectives proposed and the scope of the work are extremely deficient in scientific content. The extent of development envisaged is totally out of proportion with the objectives proposed. Excellent reviews and work of very recent date are available on the feasibility of splitting water photolytically using transition metal complexes and semiconductor electrochemistry. No where has molybdenum figured in these investigations nor is there any likelihood of its being of major importance in this field. Contrary to what the authors envisaged, just because molybdenum figures in an important enzyme for fixing of nitrogen it does not mean it will be worthwhile in the splitting of water. The investigators in their objective have set-forth on a cook book approach with little or no rationalisation. In the context of these criticisms the project does not merit any consideration for funding.

PROFORMA FOR SUBMITTING THE RESEARCH PROPOSAL
COMMISSION FOR ADDITIONAL SOURCES OF ENERGY
(DEPARTMENT OF SCIENCE AND TECHNOLOGY)
*APPLICATION FOR GRANT OF RESEARCH PROJECT

1.	TITLE OF THE PROJECT	:	Production of hydrogen from water by organo molybdenum microstructures utilising Solar energy
2.	NAME & DESIGNATION OF THE INVESTIGATOR(S) AND COMPOSITION OF THE TEAM	:	1. Dr. Krishna Bahadur, D.Sc., DIC (London), Reader, Chemistry Deptt., University of Allahabad. 2. Dr. S. Ranganayaki, D.Sc., Lecturer, Department of Chemistry, University of Allahabad Team - 2 Senior research assistant and 4 Junior research assistant
3.	POSTAL ADDRESS OF THE PRINCIPAL INVESTIGATOR	:	Chemistry Department, University of Allahabad.
4.	NAME OF THE INSTITUTION AT WHICH THE PROJECT WILL BE CARRIED OUT	:	Chemistry Department, University of Allahabad, Allahabad.
5.	NAME OF OTHER INSTITUTION: IF INVOLVED IN THE PROJECT		-
6.	OBJECTIVES	:	To produce hydrogen by photolytic splitting of water.
7.	(a) DATE OF COMMENCEMENT: OF THE PROJECT		July 1983
	(b) DATE OF COMPLETION OF THE PROJECT	:	June 1986
8.	TECHNICAL PROGRAMME AND THE MANNER OF IMPLEMENTATION	:	1. Study of the condition under which water can be efficiently broken to hydrogen and water mixture by organo molybdenum microstructures. 2. Effort to get one gas-oxygen-in light and another gas-hydrogen - in dark so that separation of hydrogen oxygen mixture can be avoided. 3. Organo molybdenum microstructures incorporating transitional metals as Fe, Co, Ni and semiconductor metals will be prepared with a view to increase the efficiency of water splitting. 4. Experiments will be made to collect the gases produced by photolytic splitting of water in 0.25 square meter and 1 Sq.m. surface area suitable device and apparatus will be designed and developed.

*20 typed copies of the applications are required to be submitted to the Department of Non-conventional energy sources, Block No. 14, C.G.O. Complex, New Delhi - 110 003.

9. TOTAL AMOUNT OF ASSISTANCE (FIRST YEAR) REQUIRED (FOREIGN EXCHANGE INVOLVED, IF ANY TO BE SPECIFIED (SECOND YEAR) SEPARATELY WITH CURRENCY DETAILS)	Rs.	4,28,000
(THIRD YEAR)	Rs.	2,37,000
	Rs.	2,37,000
TOTAL :	Rs.	9,02,000

10. Following documents are enclosed :

i. Appendix I giving biodata and brief background of the Investigator(s) relevant for undertaking the project.

ii. Appendix II giving detailed project proposal which should include objectives, methodology and phasing of the project.

iii. Appendix III indicating facilities available at the institution for carrying out the project.

iv. Appendix IV - project Budget in the attached prescribed format.

I/we have carefully read the terms and conditions of the Commission research grant and agree to abide by them.

Signature of the Investigator (s) K. Bahadur (K. Bahadur)
S Ranganayaki (S. Ranganayaki)

Seal

Dated : 12-4-83

Place : Chemistry Department, Allahabad University, Allahabad

ENDORSEMENT

Certified that basic facilities for undertaking the proposed project are available at our institution and the same will be extended to the Investigator, and such other administrative facilities as per the terms and conditions of of the grant.

BBL Saxena

Signature of the Head of the Institution _____

Name & Designation Dr. B.B.L. Saxena
Prof. & Head

Date : 12-4-83

Place : Chemistry Department, Allahabad University, Allahabad

APPENDIX I :

1. Dr. Krishna Bahadur : Is D.Sc. of Allahabad University Reader and second man in order of seniority in the Chemistry Department of Allahabad University, has published about 200 Scientific papers and 40 students have got their Doctorate under him. Has been working on Origin of life since last 30 years and on the Organo molybdenum microstructures since last 14 years, Date of Birth 20th Jan. 1926. Nuffield fellow 1958, Exchange Scientist 1963, Canadian Commonwealth research fellow 1968.

2. Dr.(Mrs.) S. Ranganayaki : Is D.Sc. of Allahabad University and working as lecturer in the Chemistry Department of Allahabad University since last 20 years. Has published 65 scientific papers and 14 students have got Doctorate under her. She is also working on Origin of life since last 30 years and on the Organo molybdenum microstructures since last 14 years Wife of Dr. Krishna Bahadur. Date of Birth 16th June 1930. Visited England in 1958, worked in Sir George Williams University Montreal, Canada in 1968-69.

APPENDIX II :

PRODUCTION OF HYDROGEN FROM WATER BY ORGANO MOLYBDENUM MICROSTRUCTURES UTILISING SOLAR ENERGY

World in general is facing an acute energy crisis. Several alternate sources of energy are being tried to meet the crisis which, otherwise, will bring the world to total collapse particularly when out petroleum reserve is finished. We will not noly be short of fuel to run our engines, but will also be exhausting our cheap source of hydrogen in the form of naphtha and this will threaten the closure of all our nitrogen fertiliser plants resulting in immediate cut down of our grain production leading to total chaos.

The real solution of this crisis can come by splitting water to hydrogen and oxygen utilising the energy of sunlight. Actually plant photosynthesis does it and the hydrogen thus produced reduces CO_2 to organic carbon which is the most massive reaction of our earth by sheer bulk and is the main supplier of all the energy we need in the form of food, fibre or fuel.

We have been working on origin of life since last ~~25~~ 30 years. Our earlier experiments were confined to the study of abiogenesis of amino acids, peptides and other biochemicals. In 1963 we synthesised microstructures by the action of light on sterilised aqueous mixtures containing simple organic and inorganic substances. These particles grow from within, multiply by budding and have metabolic activity(1). These particles have definite boundary wall, and internal structures (2,3) and can be fixed with biological fixatives and stained with biological dyes. The particles were named jeewanu, a sanskrit word for particles of life (4,5).

It was observed that the material of the particles have a number of enzyme- like activities and it was further observed that Jeewanu have ferredoxin- like material and these can be substituted for ferredoxin in the chloroplast-ferredoxin-hydrogenase system for splitting water molecules by sunlight to hydrogen and oxygen (6,7). This chloroplast-ferredoxin-hydrogen system helps in splitting water to hydrogen and oxygen by certain algae (8).

As the particles showed nitrogenase like activity (8,9) and showed fixation of nitrogen (10) and also fix carbon dioxide (11) they were tested for their ability to split water in sunlight. It was observed that if a mixture of Jeewanu and water is shaken and exposed to sunlight, After about 10 min. gas bubbles start coming out of the mixture (12). The liberation of gas continues for about 60 min. The mixture then becomes dormant and next day after standing

overnight in dark the water splitting activity is again restored (13). Night phase activation of the Jeewanu is interesting and same sample can be used for splitting of water for some days. The factors which activate this water splitting ability by Jeewanu have been investigated.

The manometric observation in Warburg's apparatus indicated that when Jeewanu and water mixture with phosphate buffer of 7.5 is exposed to sunlight under anoxygenic condition more water splitting takes place than in oxygenic atmosphere.

It was further observed that if the mixture of Jeewanu, water and phosphate buffer is exposed to sunlight the increases in pressure continues for about one hour and then the pressure becomes steady. It at this point the apparatus is put in shade rapid decrease in pressure takes place indicating fixation of molecular nitrogen of the over head space of the mixture with the hydrogen produced by water splitting. The fixation of nitrogen takes place even in presence of oxygen in the over head space and is more in oxygenic conditions than in anoxygenic condition. This poses an interesting problem. The reaction which takes place in shade is an ionic reaction and not photochemical i.e. this reaction will take place both in light and dark. Thus when mixture is exposed to light, water is split into hydrogen and oxygen and the hydrogen thus produced reacts with the nitrogen in over head space of the Warburg's flask and so far increase in pressure due to splitting of water is more than the decrease in pressure due to fixation of nitrogen there is increase in pressure observed during the exposure of the mixture. When the mixture is transferred to shade the photolytic splitting of water stops but the nitrogen fixation being ionic, the reaction continues causing decrease in the pressure in the Warburg's flask.

The water splitting ability of Jeewanu was examined by isotopic technique. Jeewanu and D_2O mixture was exposed to light keeping acetylene in the overhead space. It was observed that the acetylene is converted to only CHD=CHD indicating that protons are supplied by D_2O only and not from any other source.

Water is transparent to light above 184nm and for splitting it by sunlight we need suitable catalysts and sensitisers. The process of photochemical splitting of water using inorganic minerals has been recently reported by a number of workers and fixation of nitrogen by modified molybdenum compounds has been reported but in most of these cases there is a compound which after splitting of water is rendered useless and a fresh sample is needed for further splitting. Unlike this the Jeewanu are though rendered inactive after

some hours of exposure can be activated again after keeping the mixture in dark overnight. No activation of Jeewanu is observed when the mixture is kept exposed to the light of a 1000 watt electric bulb kept at a distance of 1 m from the mixture during night.

We are developing the system with a view to use it for commercial splitting of water by sunlight to get hydrogen which can be used as the cleanest fuel and we are also determining the condition which can make nitrogen fixation a commercial proposition.

1. Bahadur, K. and Ranganayaki, S. (1964), Zbl. Bakt. 117(2), 567-574.

2. Bahadur, K. and Ranganayaki, S. (1970), J. Br. Interplanetary Soc., 23, 813-829.

3. Upadhyaya, G. (1977), "Cytological and histochemical studies of self-sustaining coacervates", D. Phil. Thesis, Chemistry Dept., University of Allahabad, India.

4. Bahadur, K. (1964), Zbl. Bakt., 118(2), 671.

5. Bahadur, K. and Gupta, J.L. (1972), Zbl. Bakt. 127(2), 643.

6. Rao, K.K., Adam, M.W.W., Morris, P., Hall, D.O., Ranganayaki, S. and Bahadur, K. (1978), Proceeding of National Symposium on Bio. Appl. of Solar Energy, Madurai, India, December 1978, ed. A. Gnanam, S. Krishna Swamy and J.S. Khan, The macrillan Co. India, Madurai, 1980.

7. K.K. Rao, P. Morris, and Hall, D.O. (1978), Presented at the Workshop Meeting on "Hydrogenase", their catalytic activity, structure and function", held at Gottingen, August.

8. Bahadur, K., Ranganayaki, S., Folsome, C., and Smith, A.(1980), Natl. Acad. Sci., India. Golden Jubilee Commemoration vol. 181-198.

9. Smith, A., Folsome, C. and Bahadur, K. (1981), Experientia, 37, 357, Birkhanser Verlag Basel (Schweiz).

10. Verma, P.K. (1980), "Cytological investigation of photochemically formed self-sustaining molecular association". D.Phil. Thesis, Chemistry Dept., University of Allahabad, India.

11. S. Ranganayaki, K. Bahadur, S. Kumar (1981), J. Brit. Interplanetary Soc., 27, 251-254.

12. Bahadur, K., Ranganayaki, S. and Gupta, V.K. (1981), Proc. Nat. Acad. Sci., India 51(A), II, 232-240.

13. Verma, P. (1982), D.Phil. Thesis, "The study of cytology of photochemically formed microstructures". Chemistry Dept., Allahabad University, India.

DESCRIPTION OF METHODS TO BE USED

1. Closed system containing different types of microstructures and water will be exposed to sunlight and the gaseous products obtained will be analysed by (a) gas chromatograph, (b) gas analysis.

2. The gas exchange under solar radiation will be studied with the help of Warburg's apparatus.

3. Different types of organo molybdenum mircostructures will be prepared photochemically incorporating semiconductor and transitional elements with a view to increase the efficiency of water splitting.

4. Pilot plant experiments will be conducted in containers of 0.25 meter square and one meter square surface area.

PHASING OF THE PROJECT

Ist Year

Preparation of different organo molybdenum microstructures incorporating transitional and semiconductor metals and study of the conditions under which maximum water splitting can be achieved.

IInd Year

Efforts to get one gas-oxygen- in light and another gas, hydrogen, in dark so that separation of hydrogen oxygen mixture can be avoided.

IIIrd Year

Construction of a pilot plant-designing and development of suitable apparatus.

APPENDIX III :

All the necessary facilities for carrying out the work exist in the Chemistry Department of Allahabad University.

APPENDIX IV :

THE APPLICATION GRANT OF RESEARCH PROJECT UNDER PROJECT BUDGET

A. SALARIES & WAGES	I YEAR	II YEAR	III YEAR	TOTAL
1. INVESTIGATOR(S)	Nil Rs.	Nil Rs.	Nil Rs.	Nil Rs.
2. RESEARCH ASSOCIATE 4 JUNIOR AND 2 SENIOR AT 600/-p.m. & 900/- p.m. resp.	50,400	50,400	50,400	1,51,200
3. SUPPORTING TECHNICAL STAFF OR OTHER PERSONNEL, IF ANY. ONE PART TIME CLERK & LAB.SERVANT AT Rs.300/- & AT Rs.250/- p.m.resp.	6,600	6,600	6,600	19,800
GRANT TOTAL ..	57,000	57,000	57,000	1,71,000

Please specify the rate of salary and wages per month for each category.

B. PERMANENT EQUIPMENT	I YEAR	II YEAR	III YEAR	TOTAL
	Rs.			Rs.
1. GAS ANALYSER	15,000	-	-	15,000
2. ELECT.SOMMERSON PHOTOELECTRIC COLORIMETER	20,000	-	-	20,000
3. PHOTO WARBURG'S APPARATUS	25,000	-	-	25,000
4. 2 pH METERS	16,000	-	-	16,000
5. LYPHOLYSER	50,000	-	-	50,000
6. ULTRA CENTRIFUGE LOW TEMP.	50,000	-	-	50,000
7. LIGHT METER	10,000	-	-	10,000
GRAND TOTAL	1,86,000	-	-	1,86,000

C. EXPENDABLE EQUIPMENT AND SUPPLIES	I YEAR Rs.	II YEAR Rs.	III YEAR Rs.	TOTAL Rs.
1. REPAIR AND WORKING COST OF PERKINS ELMER . MODEL 990 GAS CHROMATOGRAPH	50,000	50,000	50,000	1,50,000
2. GLASS APPARATUS	50,000	50,000	50,000	1,50,000
3. CHEMICALS	50,000	50,000	50,000	1,50,000
4. BOOKS	10,000	5,000	5,000	20,000
5. STATIONERY	5,000	5,000	5,000	15,000
GRAND TOTAL	1,65,000	1,60,000	1,60,000	4,85,000

D. TRAVEL EXPENSES

	I YEAR	II YEAR	III YEAR	TOTAL
	Rs.	Rs.	Rs.	Rs.
	20,000	20,000	20,000	60,000
GRAND TOTAL (A+B+C+D)	4,28,000	2,37,000	2,37,000	9,02,000

E. OTHER PROJECT COSTS, IF ANY

	I YEAR	II YEAR	III YEAR	TOTAL
	Rs.	Rs.	Rs.	Rs.
	Nil	Nil	Nil	Nil
GRAND TOTAL OF THE PROJECT	4,28,000	2,37,000	2,37,000	9,02,000

F. WHETHER THE SAME INVESTIGATORS ARE RECEIVING FUNDS FROM ANY OTHER AGENCIES

~~YES~~/NO

If Yes,

Name of the Investigator :

Title of the project :

Agency :

Amount :

) - Not applicable

A copy of the project proposal financed from other sources should also be attached with the application for grant of research project under the Commission for Additional Sources of Energy (CASE).

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