

## PROJECT DESCRIPTION

### RICE HUSK AMORPHOUS SILICA AS GELATION AGENTS FOR VERTICAL CONCRETE STAINS, CEMENT ADDITIVE, FILLERS AND ABSORBANTS

#### A.1. IDENTIFICATION AND SIGNIFICANCE OF THE INNOVATION

Rare Earth® Labs is independently owned and operated company<sup>1</sup> located in El Dorado, Arkansas manufacturing concentrated concrete and masonry acid stains that are uniquely manufactured for customers who want to achieve a natural earth tone appearances in whatever application they might choose whether it be for floors, walls, counter tops, or decorative accessories. I, Marvin Dodson, as the owner and the product developer have patented my application: "Chemically reactive concrete stains, US Patent No: 6,500,249 B1.

We have recently developed a new product using fumed silica with a high viscosity for staining vertical, horizontal, overhead and irregular surfaces. This is a viscous or gelled fluid containing a metallic salt mixture, acids, thickening agents such as colloidal silica (silicon dioxide from fumed silica) and surfactants such as polyhydroxyic **alcohols** and their **polyalkoxylated** derivatives.

This is a phase 1 proposal relating to research efforts and feasibility study to produce sol-gel stains from rice husk amorphous silica an alternative to fumed silica. Rice husk which usually burnt without controlling temperature and disposed off is of no use since amorphous silica has been converted crystalline silica, cristobalite. Rice husk burnt under controlled conditions can be the raw material for our process. The technology of converting rice husk ash to amorphous silica is to dissolve it in acid/base solutions to form precipitate or gels. This can be washed and dried to yield the intended product.

I have already established collaborations with Louisiana Tech University (Dr. Upali Siriwardane) and Grambling State University (Dr. Naidu V. Seetala) and I plan to use their research expertise and facilities to streamline a process for making amorphous silica for my acid stain applications, and as well to sell amorphous silica as a commodity item for cement additive, filler and absorbent applications.

## **A.II. BACKGROUND, TECHNICAL APPROACH, AND ANTICIPATED BENEFITS**

### **A.II.1. BACKGROUND**

Fumed silica made for electronic industry in an exceptionally pure form of silicon dioxide by reacting silicon tetrachloride in an oxy-hydrogen flame. Silicon dioxide is normally generated from sand, which is extracted after a fusion of high temperature. These procedures require energy and is investment intensive driving the cost of fumed silica higher. The process of making gel-stains from fumed silica is not cost effective. To make this process industrially feasible we need an alternative path way to amorphous silica or drastic reduction of the cost of fumed silica.

#### **A.II.1.1. Silica**

Silica has played (Socio - Economic Review of Crystalline Silica Usage, Brian Coope, September 1997) a continuous part in the development of technology and been one of the basic raw materials supporting the industrial revolution. It has been used in refractory (Refectories, **Publisher:** McGraw-Hill; (June 1992), flux, glass making (*Glass Science* (Mar 94) by Robert H. Doremus. A classic reference text on glass.), and today's information technology revolution (The Physics of Information Technology by Neil Gershenfeld (Author)Cambridge ) by providing the raw material for silicon chips). It is also used for precision casting, dental applications and jewelry casting. Industrial silica is also used in construction aggregates; concrete(Design of Concrete Structures by Arthur H. Nilson, David Darwin, Charles W. Dolan, Arthur Nilson, Charles Dolan), dimension stone, masonry mortars, tile glues, floor screeds, cement manufacture, road line markings, asphalt, and decorative bricks. Industrial silica is a structural ingredient of clay bodies and a major constituent of ceramic glazes, ranging from refractory to wall bricks, and in sanitary ware, tableware and tiles. Silica derivatives are used in many areas, such as pesticides, fertilizers and pharmaceuticals preparations. Another derivative from industrial silica is silicon carbide, which is the raw material for abrasives, anti-slip and polishing products. Silica in its finest forms finds important usage as reinforcing filler for use in paint, plastics, rubber, and sealants. In paints, silica is used to render the paint more resistant to chemicals and for enhancing hardness and wear resistance. (Need references through out this paragraph).

#### **A.II.1.2. Silica as thickening agent in concrete stains**

The vast majorities of known decorative stains (Architectural Concrete – Colored and Decorative Concretes and Concrete Staining, Materials World, Vol. no. pp 16-17, April 2001)

available commercially are composed of pigments or stain (colored metal oxides/hydroxides and ions) along with some type of applicable carrier base such as water or solvent. These types of stains are commonly used on masonry, concrete, plaster and similar horizontal surfaces but have problems when applied to vertical, horizontal, overhead and irregular surfaces due to creeping.

Silica can be used to make stain compositions that contain saturated mixture of metallic salts and hydrochloric acid blended with surfactants such as polyhydric alcohols and their polyalkoxylated derivatives. This produces a viscous gel to stain vertical, overhead and irregular surfaces that are chemically reactive or penetrative to the gel such as masonry concrete, plasters, stone, and unglazed decorative ceramic.

#### **A.II.1.3. Silica as cement additive**

In the production of high strength, low permeability concrete, for use in bridges, marine environments, and nuclear power plants, fumed silica has been added to the Portland cement. It boosts the chemical reaction called the "pozzolanic" reaction where hydration (mixing with water) of Portland cement produces many compounds, including calcium silicate hydrates (CSH) and calcium hydroxide (CH). The CSH gel is known to be the source of strength in concrete. When silica fume is added to fresh concrete it chemically reacts with the CH to produce additional CSH. The benefit of this addition is twofold; increased compressive strength and chemical resistance. The bond between the concrete paste and the coarse aggregate, in the crucial interfacial zone, is greatly increased, resulting in compressive strengths that can exceed 15,000 psi. The additional CSH produced by silica fume is more resistant to attack from aggressive chemicals than the weaker CH.

#### **A.II.1.4. Silica as industrial absorbents**

Activated carbon is the commonly used adsorbent in adsorption/separation technology in industry because of the easy operation and low operating cost. However, it has a few problems such as combustion of adsorbents and pore blocking<sup>4,5</sup>. Therefore, there has been a focus on finding alternative adsorbents. Hydrophobic zeolite adsorbents have been proven to be advancement in volatile organic compounds (VOCs) adsorption/separation technology in which the problems associated with activated carbon adsorbents could be overcome.

In a recent study<sup>2</sup> the adsorption of trichloroethylene, tetrachloroethylene, and carbon tetrachloride was studied over our synthesized mesoporous molecular sieves derived from a

rice husk silica source. More than 99% Silica has been extracted from rice husk under acid refluxing and then calcination at controlled temperature to produce rice husk silica based materials with high surface area and uniform pore size. The absorption capacity of these materials is shown to be higher than those for commercial mordenite and activated carbon.

Reference:

1. 4. Zhao, X.S.; Ma, Q.; Lu, (Max) G. Q. *Energy and fuels*. **1998**, 12, 1051-1054.
5. Zhao X.S.; Lu G.Q.; Hu X. A. *Physicochemical and engineering aspects*. **2001**, 179, 261-269.

2 Utilization of Mesoporous Molecular Sieves Synthesized  
from Natural Source Rice Husk Silica to CVOCs Adsorption  
Paper # page. 727 9th APCCChE Congress and CHEMECA 2002 , Siliruk Chiarakorn  
Nurak Grisdanurak  
Jatuporn Wittayakun

The discovery<sup>1</sup> of mesoporous molecular sieves, MCM-41, which possesses a regular hexagonal array of uniform pore openings, aroused a worldwide resurgence in this field. It has opened a new avenue for creating zeolite type materials. MCM-41 have been used as catalysts and absorbents.

In the past decade, MCM-41 and ZMS-5 were synthesized when an aqueous solution containing silica (e.g. fume silica, sodium silicate) was added to a clear aqueous solution of a micelle-forming surfactant (e.g. long-chain quaternary ammonium halides) under constant stirring. Similarly MCM-41 type absorbents could be made from rice husk amorphous silica.

Recently, white rice husk was used as a silica source in the preparation of ZSM-5, a

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highly siliceous zeolite used as a catalyst in the petrochemical industries and in organic synthesis.

Reference: Zainab Ramli and Hasliza Bahruji Synthesis of ZMS-5-Type Zeolite using  
Crystalline Silica of Rice Husk Ash  
*Malaysian Journal of Chemistry, 2003, Vol. 5, No. 1, 048 - 055*

Review: 1 Xiu S. Zhao, G. Q. (Max) Lu, and Graeme J. Millar, Advances in Mesoporous Molecular Sieve MCM-41, 2075 Ind. Eng. Chem. Res. 1996, 35, 2075-2090-2089.

Zainab Ramli and Hasliza Bahruji Synthesis of ZMS-5-Type Zeolite using Crystalline Silica of Rice Husk Ash

6. Zhao, X.S.; Lu, G.Q.; X. Hu. *Microporous Mesoporous Mater.* **2000**, 41, 37-47.

7. Selvam P.; Bhatia K. S.; G. Sonwane G. C. *Ind. Eng. Chem. Res.* **2001**, 40, 3237-3261.

### **A.II.2. TECHNICAL APPROACH**

Crystallite sizes, estimated by transmission electron microscopy (TEM), were found to be a few nanometers in size. Particle size distribution, however, was not reported. This paper reports on silica prepared from acid-treated rice hulls. The work focused on the use of silica in the production of mullite whiskers and cementitious materials, in which the reactivity and particle size of silica are important features. hydrochloric acid solution for 24 h, followed by a 20 vol% sulfuric acid solution for 24 h. Both treatments were done by boiling the solution under atmospheric pressure, followed by washing with distilled water. The hulls were then heated at 550 °C for 2.0 h; C) The rice hulls, acid treated and washed according to process A, were subjected to lignin extraction through refluxing in glacial acetic acid, followed by washing in distilled water at room temperature and then burning at 500 °C for 2.0 h. In each process, the silica was desegregated by ball milling in water with 0.5 cm zirconia balls. The silica was named according to the processing route, *i.e.*, silica A, B, and C. A commercial silica, dubbed D, was also used in this study for purposes of comparison. The powders and powder suspensions were chemically characterized by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP), while the surface area was analyzed by the BET method, particle size distribution determined by the sedimentation technique and crystallographic structure by XRD

#### **A.II.2.1. Impurity Removal from rice husk**

There are several methods have been reported to remove impurities from rice husk. The first method involves treatment of the husk with hot inorganic (Pattaraporn Lohsoontorn and Paisan Kongkachuichay, "Phase Diagram of Zeolites Synthesized from Perlite and Rice Husk Ash," 9th **APCChE** Congress, 29 September-3 October 2002, Christchurch, **NZ**, Paper # 731) and organic acid solutions before burning, the second with boiling water, both using an autoclave at temperatures close to 150°C. The third method turns the husk into a fine powder by treating it at

250°C before calcinations. However this maybe connected to the amorphous to cristobalite transformation and should be avoid. The first two methods result in white amorphous silica that can show 500 m<sup>2</sup>/g of surface area. The third method also does not remove the alkaline elements from the husk and it seems to produce a gray carbon-free powder whose surface area is much lower. A comparison is made(SOUZA, M.F. de, MAGALHAES, W.L.E. y PERSEGIL, M.C., "Silica Derived from Burned Rice Hulls,"*Mat. Res.*, oct./dic. 2002, vol.5, no.4, p.467-474. ISSN 1516-1439) of these processes and the dissolution of silica by sodium hydroxide solutions is discussed.

#### A.II.2.2. Calcination/Controlled burning of rice husk

There are two limitation in the rice husk ash obtained as a by-product from current energy technology used in burning. First, they contain unacceptably high concentrations of residual carbon. Second, a portion of the amorphous silica has been transformed into crystalline silica called cristobalite. The second problems is the more severe because the cristobalite formed is hard to dissolve and does not have the same pozzolanic (cementations) properties, as the amorphous form, and is not in the particle size range at which it could be used in concrete. The transformation to the crystalline state takes place if the ash is exposed to high temperatures over 500°C and becomes even more likely if it is exposed to these high temperatures for extended time periods. Most of the current rice husk energy generation technology does not control temperatures well enough and most allow the ash to remain at high temperatures for a relatively long residence time. With controlled residence time and temperatures an ash can be produced at a moderate temperature, which has zero, or at most minor trace quantities of cristobalite and a lower residual carbon content.

#### Fluidization technique

Rice husk particles are placed in a bed of air/gas mixture and the mixture is passed through a heated chamber. As the flow velocity of the gas mixture is steadily increased, bed particles are found to be in a state of suspension within the stream. As the velocity is increased further the bed becomes highly turbulent leading to the vigorous mixing of the particles. At certain velocity the bed attains the properties of a fluid. This fluidized bed is preheated to the ignition temperature of the fuel. The resulting combustion of this fuel in the bed is known as fluidized combustion. A fluidization technique could be adopted to fit into existing and/or new

facility to combust rice husk for energy production to produce useful ash. The capital investment in a replacement combustor will generate an attractive return on investment based on the benefits of turning a waste disposal cost into a by-product credit.

#### **A.II.2.3. Chemical digestion of rice husk silica**

Porous silica with nm-sized pores, are generally prepared from fine silica powder, by: (1) acid deposition from  $\text{Na}_2\text{SiO}_3$  solution; (2) sol-gel method, from organo-silicone compounds, or (3) vapor deposition from a silica fume. Another precursor, calcium silicate, used for the preparation of porous silica powder, could be obtained from  $\text{Ca}(\text{OH})_2$  and various silica materials, under hydro-thermal conditions. The starting calcium silicates is usually produced from a mixture of  $\text{Ca}(\text{OH})_2$  and amorphous silica, or alternatively rice husk amorphous silica, under hydrothermal conditions. Subsequent treatment of slurry containing calcium silicate precursors: after cooling and adding 1 M HCl in order to leach out calcium. The resultant material could be collected by filtration, and washing.

M. Ono, K. Yoshii, T. Kuroki, N. Yamasaki, S. Tsunematsu and G. Bignall.; High Pressure Research, 2001, Vol. 20, pp. 307 - 310

#### **A.II.2.4. Preparation Absorbent**

In the digestion of amorphous silica to produce absorbents following chemicals would be used: hexadecyltrimethylammonium bromide (CTAB), sodium hydroxide, hydrobromic acid, ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) 29.8 %, ethanol 99.8 % and deionized water will used to prepare MCM-41 type absorbents.

#### **A.II.3. ANTICIPATED BENEFITS**

By the end of Phase I we aim to demonstrate 1) a convenient procedure to pre-clean rice husk; 2) that the rice husk could be burned to obtained amorphous silica; 3) convenient acid/base digestion method to from gel mixtures from rice husk; and 4) that acid stain gels, absorbent materials, and cement additives can be derived from the rice husk silica.

The Phase II program would be directed toward producing a prototype rice husk calcinator for evaluation by Rear Earth Labs or a potential Phase III partner. Also during Phase II we would investigate further commercial uses of acid stain gels, absorbent materials, and cement additives from the rice husk silica.

Limited supply and high demand has pushed the price of silica fume to as much as US\$1,000/tonne. Rice husk has the potential to generate 16.5 to 22 million tones of ash containing over 90% amorphous silica, which could be used as a substitute for silica fume. Assigning a more realistic price of US\$300/tonne would make the potential value of this ash product worldwide US\$5-6.5 billion/year.

Global production of rice, the majority of which is grown in Asia, is approximately 550 million tones/year. Arkansas and Louisiana have substantial rice cultivation and rice a major export item. The milling of rice generates a waste material, which is the husk surrounding the rice grain. This is generated at a rate of about 20% of the weight of the product rice, or about 110. The annual worldwide output of rice hulls is approximately 80 million tons, which corresponds to 3.2 million tons of silica (Natajara, E.; Nordin, A.; Rao, A.N. *Biomass & Energy*, v. 14, n. 5-6, p. 533, 1998.). million tones/year globally. The husk in turn contains between 15 and 20% of mineral matter the majority of which is amorphous silica. The husk has an energy content of about 13.5GJ/tonne, so that the worldwide energy potential would be about 1.5 billion GJ/year, which at US\$5/GJ would have an annual value of US\$7.5 billion. This amount of energy is equivalent to over 1 billion barrels of oil per year.

#### **A.II.4. PHASE I RESEARCH OBJECTIVES**

##### **A.II.4.1 INTRODUCTION**

The objective of the Phase I program is to experimentally verify the feasibility of amorphous silica production from rice husk ash. The Phase I experimental program will be designed to increase our current understanding of amorphous silica production from rice husk. We will also attempt to improve the quality and quantity of amorphous silica obtained from rice husk, which can be used in applications as gelation agents for vertical concrete stains, cement additive, fillers and absorbents with a lower production cost. The program is divided into the three major task areas summarized below.

##### **A.II.4.2. Pretreatment of rice husk**

Objectives: Removing surface contaminants those affect desired properties of the ash

- Removal of unwanted rice husk surface contaminants using acids, boiling water, or using an autoclave at temperatures close to 150°C.



- Measure major contaminants on the rice husk surface prior/after washing using SEM/EDX and analyzing rice husk washed solution using chemical methods.
- Measure properties such as transition temperature, surface area, and particle size of amorphous silica obtained after various decontamination methods.
- Correlate the effects of contaminants on ash properties and optimize method of pretreatment.

Questions to be answered:

- What are the main contaminants on rice husk surface?
- How does the contaminant affect the properties (transition temperature, surface area, and particle size) of rice husk derived amorphous silica?
- What is the best way to remove unwanted rice husk surface contaminants?

#### **A.II.4.3. Calcination of rice husk**

Objectives: Maximize content of amorphous silica in the rice husk ash.

- Measure the transition temperature of rice husk at different heating rates using DTA and DTG.
- Heat rice husk at different temperatures to find the transition temperature at which amorphous silica is converted to cristobalite using XRD.
- Optimize fluidization temperature and flow rates of the rice husk burner to maximize the production of amorphous silica.

Questions to be answered:

- What is the transition temperature of amorphous to cristobalite conversion.
- How much time is required for these transformations?
- What is tolerable high temperature of the fluidization reactor without affecting the quality of amorphous silica and how does it depend on the residence time?

#### **A.II.4.4. Rice husk amorphous silica digestion**

Objectives: Maximize the digestion of rice husk ash in aqueous solutions.

- Measure the solubility and viscosity of rice husk amorphous silica in aqueous solutions.
- Study the influence of temperature and various chemicals on the solubility of silica.
- Study the affect of pH of aqueous silica solutions on viscosity.
- Obtain optimal conditions (pH, temperature, additives etc)

Questions:

- What factors directly effect the solubility and rheological properties of amorphous silica derived from rice husk?

#### **A.II.4.5. Application of rice husk amorphous silica in concrete gel stains**

Objective: Obtain concrete gel stains from rice husk ash

- Measure the solubility and viscosity of rice hush amorphous silica in acid solutions containing stains.
- Study the influence of temperature and various chemicals on the solubility of rice hush amorphous silica in acid solutions containing stains.
- Study the affect of pH of acid stain silica solutions on viscosity.
- Obtain optimal conditions (pH, temperature, additives etc) for acid satins gels.

Questions:

- What factors directly effect rheological properties of acid stain gels amorphous silica derived from rice husk?

#### **A.II.4.6. Application of rice husk amorphous silica as cement additives**

Objective: Obtain concrete products containing rice husk ash

- Measure the degree of reaction between silica and calcium hydroxide, the so-called pozzolanic character of rice husk silica.
- Vary the amount of rice husk silica added and measure the compressive strength cement bodies.

Questions:

- What is the correlation between amount of rice husk silica added and the pozzolanic character and mechanical strength of the cement.

#### **A.II.4.7. Application of rice husk amorphous silica as fillers**

Objective: Obtain paint products containing rice husk ash.

- Measure the viscosity of rice hush amorphous silica added to water based paint solutions.
- Study the influence of temperature and various chemicals on the solubility of rice hush amorphous silica in water based paint solutions.
- Study the affect of pH of water based paint solutions on viscosity.
- Obtain optimal conditions (pH, temperature, additives etc) for water based paint solutions.

Questions:

- What factors directly effect rheological properties of water based paint solutions containing amorphous silica derived from rice husk?

#### **A.II.4.8. Application of rice husk amorphous silica as absorbents**

Objective: Obtain absorbents containing rice husk ash.

- Synthesize MCM-41 and ZMS-5 type absorbent materials starting from rice husk silica.
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#### **A.II.5. SIGNIFICANCE TO FUTURE RESEARCH AND COMMERCIAL APPLICATIONS**

Phase-I will establish a proof of concept, i.e., that rice husk silica can be used to create amorphous silica that could be raw material as thickening agent in concrete gel-stains, cement additive and industrial absorbents. Once this proof of concept is established, we will develop narrow procedures that are economical for the processes. This work will carry on into Phase II with the potential of a pilot plant scale and small-scale productions by the end of Phase II.

### **A. III. PHASE I RESEARCH PLAN**

#### **A.III.1. TASK A: Pretreatment of rice husk**

The first systematic study on acid rice hull treatment before its thermal decomposition was reported by Amick<sup>19</sup>, whose objective was to produce solar grade silicon. By treating silica obtained by thermal decomposition of untreated hulls in an aqueous 1:1 HCl solution, Amick<sup>19</sup> found that it was possible to reduce the level of impurity from 5 wt% to 0.15 wt%. Since the author was interested in silicon rather than in silica, however, silica particle size and specific area were not measured. Acid treatment and leaching are necessary steps to obtain pure, low average particle size and high surface area silica. Alkaline oxides such as K<sub>2</sub>O, the most abundant impurity in rice hulls, are known (M.F. de Souzaa, P.S. Batistaa, I. Regiania, J.B.L.Liboriob, D.P.F. de Souzac, Rice Hull-Derived Silica: Applications in Portland Cement and Mullite Whiskers Materials Research, Vol. 3, No. 2, 25-30, 2000.) ) to react with silica to produce potassium silicate, thus resulting in bridging among the ultimate particles when the hull is burned. James and Rao<sup>20</sup> studied burned untreated rice hulls, followed by hydrochloric acid leaching of silica. They found that acid treatment produces silica with a very low impurity content (0.035 wt%). The maximum specific surface area reported for carbon-free silica was around 150 m<sup>2</sup>/g. Rice husk will be washed to remove water soluble impurities and dried prior

to calcinations step, then refluxed in hydrochloric acid at 80°C for several hours. Afterwards, remaining organic substances will be removed by calcination at 250°C for several hours as described below. Rice husk was cleaned with water and boiled with 1 N HCl for 3 h to remove some impurities.

### **Task 1: Measurement of Contaminants**

The objective of this task is to determine the contaminants. The experimental arrangement will be essentially that shown in Figure x, except that a xxxx will be used.

It should be noted that Figure x illustrates the basic configuration of the pretreatment

To determine removal of contaminants, we will also measure the concentration of the xxx. This will be relatively straightforward. Both measurements will be conducted with conventional technology.

The key result to be obtained is the xxxx vs. xxx. XXXX will be used to achieve an xxx and xx. We anticipate using a xxxx in this work.

### **A.III.2. TASK B: Calcination Experiments**

The ultimate crystallite size was estimated by X-ray diffraction (XRD) pattern to be  $\approx$  5.0 nm, although particle size was not reported. More recently, Real *et al.*<sup>21</sup> reported on silica preparation by thermal decomposition of HCl treated rice hulls. These authors successfully produced high purity silica (99.4%) with high surface area (260 m<sup>2</sup>/g) by thermally decomposing acid treated rice hulls at 600 °C.

The thermal decomposition of untreated rice hulls has been studied (.James, J.; Subba Rao, M. *Thermochimica Acta*, v. 97, p. 329, 1986) and it was found that lignin decomposes at higher temperatures than cellulose does. XRD study (Hamad, M.A.; Kattab, I.A. *Thermochimica Acta*, v. 48, p. 343, 1981.) of silica obtained from untreated hulls by thermal decomposition under three different conditions and found that thermal treatment below 800 °C results in amorphous silica however duration of temperature was not discussed. Then it was burned at 700 °C for 2 h under oxygen atmosphere. The chemical compositions will be determined using the X-ray Fluorescence (EDX). In addition, it could be characterized by the density, specific surface area and average pore size.

### **Task 1: Identification of amorphous to cristobalite transformation temperature**

Bartha and Huppertz<sup>17</sup> found that the microstructure of silica released from rice hulls by hydrochloric acid treatment is similar to that obtained by thermal decomposition of the hull.

The objective of this task is to determine the xx. The basic experimental configuration will be that xxx. These results will provide a good understanding of the xxx can be pushed when used as xxx.

#### A.III.3. **TASK C:** Chemical digestion of rice husk ash

The objective of the work in this task area is to produce digestible rice husk ash. This work would be expanded in any Phase II continuation of this program.

##### **Task 1:** Digestion of amorphous silica into acid stain gels

This work will be conducted in a xx available at xx

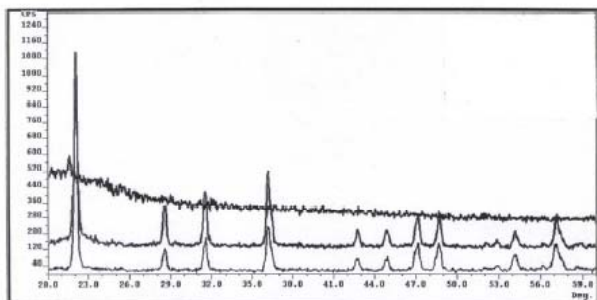
**Task 2:** Silica A was added to Portland cement to study its effects on the compressive strength of cured cement bodies. The degree of reaction between silica and calcium hydroxide, the so-called pozzolanic character of silica, was previously measured by the Chapelle-modified procedure<sup>(23. Chapelle J. *Revue des Matériaux des Construction*, v. 512, p. 136, 1958. 24. Raverdy, M.; Brivot, F.; Paillere, A.M.; Dron, R. *7e Congrès International de la Chimie des Ciments*, Paris, v. 3, IV-36-41, 1980.)</sup>

#### A.III.4. **EXPERIMENTAL TECHNIQUES**

##### A.III.4.1. **X-ray diffraction (XRD)**

Powder XRD patterns will be obtained from a Scintag ZMX diffractometer. The X-ray was generated from a Cu K<sub>a</sub> target with a current of 35 mA and a potential of 45 kV. Amorphous to cristobalite transformation could be clearly identified. We can distinguish and identify three different crystalline forms (polymorphs), quartz, cristobalite, and tridymite. Our preliminary studies on sol-gel derived amorphous silica are in agreement with reported\* data shown in Fig.1, before and after heat treatment.

Peak	(2θ Degrees)	
Substance	Primary	Secondary
Quartz	26.66	20.85
Cristobalite	21.93	36.11
Tridymite	21.62	20.50



**Figure x.** X-ray diffraction pattern, intensity vs. diffraction angle,  $2\theta$ , before and after the heat-treatment for crystallization. Top: sol-gel derived amorphous powder. Bottom: powder heat-treated at 1350°C for 48 hours, Middle: powder heat-treated at 1400°C for 48 hours.

#### A.III.4..2. **Surface area measurement**

Specific surface areas of the rice husk based materials will be calculated using the standard BET method. Pore diameters will be estimated from the peak positions of BJH pore size distribution curves calculated from the adsorption isotherms. The mesoporous volumes will be estimated from the amount adsorbed at the relative pressure used. The surface area and pore structure of alumina granules were analyzed by NOVA 2000 high speed gas sorption analyzer using BET method. The data calculated were based on nitrogen desorption isotherm at liquid nitrogen temperatures and the software provided by NOVA.

#### A.III.4..3. **Scanning electron microscope (SEM)**

Silica sample powder will be sprinkled as a thin layer on a conducting adhesive tape attached to an aluminum stub. The sample will be coated by gold, if needed, in Ametech sputter coater for charge dissipation in SEM in order to get a clear picture. SEM will be used to study the grain size distribution and EDX will be used to obtain the elemental analysis of the grains.

Through a grant from the Office of Naval Research GSU has established a SEM facility consisting of Carl Zeiss DSM 942 SEM along with Kevex LPX1 Super Dry Quantum Detector EDX system. The SEM has 3.5 nm resolutions at 30 kV, magnification range of 4X to 500,000X and produces high quality digitized images with point-to-point image measurement, image storing and processing capabilities. The EDXS is equipped with super quantum dry Si(Li) detector that has elemental analysis capability in the wide range : from Boron through Uranium with better than 145 eV resolution.

#### **A.III.4..4. Fourier transform Infrared spectrometry (FTIR) Absorption Study**

Samples was ground with an agate mortar and pestle until it was approximately the same consistency as the KBr powder. KBr was added with the weight ratio of 1:10 (KBr:sample), mixed thoroughly, and the mixture powder was poured into sample barrel and pressed at 13 tons for 1 minute and put on a V-mount cell. The FTIR spectrum was measured with a resolution of 4 cm<sup>-1</sup> and scan number of 12. It was recorded in the 400-4000 cm<sup>-1</sup> range. The hydroxyl content in the powder was determined by measuring IR absorbance of the powder immersed in a reagent-grade, index matching liquid, CCl<sub>4</sub>. A weighted amount of the powders was placed, together with CCl<sub>4</sub>, in a sample holder made of fused silica and IR absorbance was measured. The cell length of the sample holder was 1 mm and the absorbance of the sample holder was below the detection limit. The effective thickness of the sample was calculated from the mass of the sample powders employed and the density of silica powders. The water content in the silica powders was calculated from the absorbance at 3670 cm<sup>-1</sup>, using the extinction coefficient of 77.5 l/mol-cm [14] and the effective thickness of the sample.

#### **A.III.4..5. TGA Adsorption Behavior Study by Direct Weight Loss**

A certain amount of amorphous silica adsorbent, dried at 383 K for 4 h., was placed into a desiccator in which contained a given VOC. The adsorption will be carried out at room temperature for 4 days until the equilibrium adsorption is reached. Known weight of adsorbent was then quickly transferred to a platinum pan and later placed inside a TGA analysis. The weight loss due to desorption during temperature programmed with heating rate of 2-20 K/min was recorded.

#### **A.III.5. FINAL REPORT PREPARATION**

A final report containing all of the important results, conclusions, and recommendations will be prepared and submitted to NSF. Based on the success of the Phase I program, a Phase II proposal will be submitted for work aimed at small scale production of amorphous silica as raw material to suitable for evaluation by a potential Phase III commercialization partner.

#### **IV. COMPANY INFORMATION**

#### **V. COMMERCIAL POTENTIAL**

Phase-I will establish a proof of concept, i.e., that rice husk silica can be used to create amorphous silica that could be raw material as thickening agent in concrete gel-stains, cement additive and industrial absorbents. Once this proof of concept is established, we will develop narrow procedures that are economical for the processes. This work will carry on into Phase II with the potential of a pilot plant scale and small-scale productions by the end of Phase II.

## **VI. CONSULTANTS SUBAWARDS/SUBCONTRACTS**

## **VII. EQUIVALENT OR OVERLAPPING PROPOSALS TO OTHER AGENCIES**

No equivalent proposals are under consideration or equivalent awards have been received for the proposed work.

## **VIII. LETTER OF SUPPORT OR COMMITMENTS**

## **IX. REFERENCES**

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3. Zhao, X.S.; Ma, Q.; Lu, (Max) G. Q. *Energy and fuels*. **1998**, 12, 1051-1054.
4. Zhao X.S.; Lu G.Q.; Hu X. A: *Physicochemical and engineering aspects*. **2001**, 179, 261-269.
5. Zhao, X.S.; Lu, G.Q.; X. Hu. *Microporous Mesoporous Mater.* **2000**, 41, 37-47.
6. Selvam P.; Bhatia K. S.; G. Sonwane G. C. *Ind. Eng. Chem. Res.* **2001**, 40, 3237-3261.
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## **VIII. KEY PERSONNEL AND BIBLIOGRAPHY**

It is anticipated that Mr. Marvin Dodson will serve as principal investigator for the proposed program, with key contributions being made by Dr. Upali Siriwardane. (Dr. Siriwardane, an associate professor of chemistry at Louisiana Tech University, Ruston, Louisiana, nad Dr. Naidu V. Seetala (Dr. Seetla is a professor of physics at Grambling State University) devote one month each of their time to this project.

Abbreviated resumes for these individuals follow:



