

Chapter I

Introduction



1.1 Background

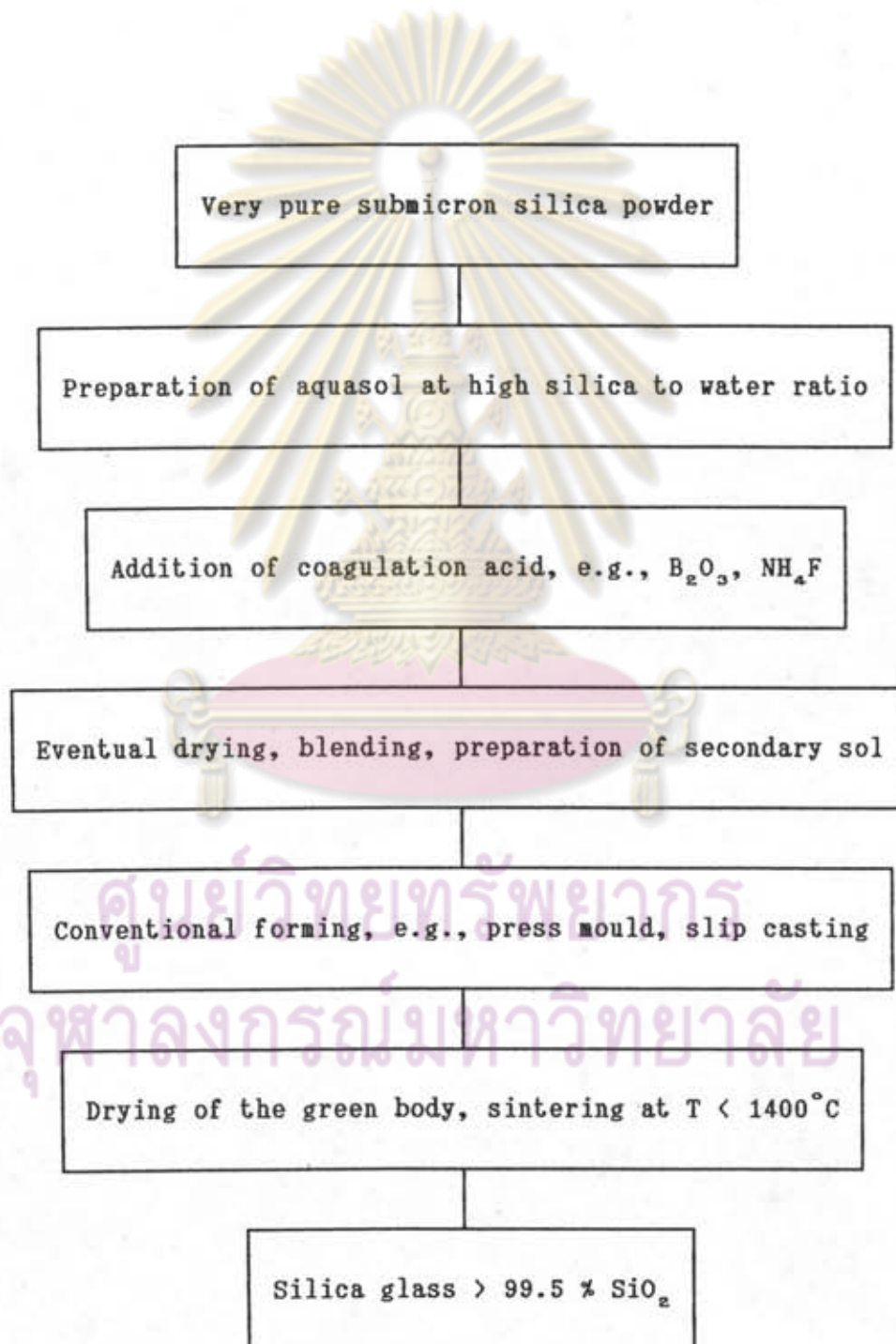
Many interesting materials preparation routes are burdened with high raw materials costs. As an example, the preparation of porous or dense vitreous silica requires the use of commercial products available for retail prices of \$US 2-10 per kg. It is the intent of the present thesis to investigate silica prepared from rice husk as a competitive raw material. Rice husk is an agricultural waste material abundantly available in rice producing countries. The annual world rice production amounts to approximately 400 million tons [Sacher, et al., 1988] of which more than 10% is husk. Dry husk contains 70 to 85 % organic matter (lignin, cellulose, sugars) and the inorganic remainder consists of silica [Sacher, 1988; Ong, et al., 1990; Sharma, et al., 1984]. Thailand, as one of the leading rice producers, has a good chance to make significant contributions to the science and technology of rice husk utilization. Earlier work performed at the Department of Materials Science in this area was reported by (Conradt, et al., 1992). Rice husk is a resource of silica, which is one of the basic raw materials in glass and ceramic industries and in the preparation of as semiconductor grade silicon, silicon carbide whiskers, silicon

nitride, fillers (medicine, cosmetic, paper industries). Utilization of rice husk as a resource of silica is often based on the removal of cations, with impurity levels below 500 ppm., by mineral acid leaching such as HCl, and H_2SO_4 . Subsequently, sample are incinerated.

Conventionally, silica glass is produced by a very expensive high-T melting process. Process temperatures of $2000^\circ C$ are expensive with respect to both energy consumption and furnace wear. Since the viscosity of molten silica is high even at $2000^\circ C$, big quartz lumps of sufficient purity are used as raw material. Alternative production routes have been development, i.e., the preparation of silica glass from condensed gels. Sol-gel processing of ceramics and glass have become an area of intense research interest because of inherent advantages compared to conventional processing. The high surface area of dried gels results in very high reactivity which in turn permits low temperature processing or even the formation of nonequilibrium phases (glass). By starting with well mixed solutions or sols, chemical homogeneity even on the molecular scale can be obtained. High purity can be achieved. Finally, the sol-gel process can provide a means of convenient shaping of articles using low temperature casting methods. Later, production routes have been development, i.e., the preparation of silica glass from condensed gels. Until now, this route is not feasible economically for mass products due to the high price of the starting materials used (high grade silica aerogels). The methods to prepare silica glasses have many ways, which shall be labelled by the names of authors such as Rabinovich, 1983; Clasen 1987, 1988, 1989; Scherer, 1977; Clegg, 1989; Sacks, 1984; Sakka, 1985. For rice husk ash, the method based on

Clasen, Rabinovich or Scherer are especially promising.

Alternatively, the method by Clegg (sol in organic solvent) may have good prospects, too. Previous reports have shown the prospect of the method to make silica glass. This is shown in the diagram below.



The purpose of this thesis is to try to prepare silica glass by the sol-gel method with rice husk ash being used as the starting material. Silica glass is a special kind of one component glass (SiO_2) with a very low level of impurities (mostly water in the form of OH groups). It is useful and important to make silica glass as a key part of instruments (such as dilatometers, spectrometers), as cuvettes, as observation windows in furnaces. Beside this, silica can be employed to produce silica wares such as crucibles, tubes, etc., i.e., labware with high chemical durability and excellent thermoshock resistivity and high-T stability.

1.2 Literature Survey

1.2.1 General Survey of Silica : Aerosils[®]

Aerosils are so widely used in laboratories as a source of pure silicas that the name has almost become generic for fumed silicas. The flame hydrolysis method for making aerosil was discovered in 1942 by Kloepfner of Degussa. Essentially, the method involves burning silicon tetrachloride vapour with hydrogen, oxygen and optionally an inert gas. The reactions are said to be (Wagner, et al., 1960, 1968).



Aerosil[®] is a registered trade mark of Deutsche Gold-und-Silber-Scheideanstalt vormals Roessler (Degussa).



or



The gas mixture is homogeneous and so the formation conditions for each silica particle are the same. As a result, a very narrow particle size distribution is obtained with a diameter of 10.0 - 20.0 nm (Bode, et al., 1968). The surface area can be modified by the reaction conditions (SiCl₄ concentration, flame temperature and residence time in the flame) over the range 50 - 400 m²/g. After leaving the combustion zone, the silica, in the form of an aerosol is coagulated to particles of diameter 1-2 μm, and then centrifuged to separate it almost completely from the HCl-containing combustion gases. The solid is then treated with hot, moist air and this reduces the HCl content to < 0.025 %. Overall, the dried Aerosils have a purity of > 99.8 % SiO₂. Other properties quoted by Bode, et al. are:

Skeletal density : 2.2 g/cm³
Solubility : 150 mg/l at room temperature
Refractive index : 1.452

Additionally, the pH of a 10 % aqueous slurry is 3.6 - 4.3. Surface area of commercial aerosils by nitrogen adsorption take the following values:

Aerosil OX-50 : 50 ± 15 m²/g
Aerosil 200 : 175 ± 25 m²/g
Aerosil 300 : 300 ± 30 m²/g
Aerosil 380 : 380 ± 40 m²/g
Aerosil U : 175 ± 25 m²/g
Aerosil TT 600 : 200 ± 50 m²/g

Aerosils have a pronounced thickening effect upon many liquid systems and render them thixotropic. They also have many other uses including the reinforcement of elastomers, for improving the free

properties of powdery materials, and as carriers for liquids, but it is probably the first of these uses which raises the greatest interest.

1.2.2 General Survey of Rice Husk Ash

Silica in general is an important materials used by many industries such as cosmetic, glass, paper, filter, medicine, pigment industries. The ash from rice husk has a high content of SiO_2 . Chakraverty, et al., 1988 described the effects of various acid treatment of rice husk on removal of its metallic ingredients and different combustion temperatures on production of amorphous silica (white ash). Leaching of husk in dilute HCl (1 N) was proved to be effective in substantially removing most of the metallic ingredients and producing ash completely white in colour. Irrespective of the treatment given, the minimum temperature required for complete combustion within a reasonable period was found to be 500°C (which according to later experiments, is insufficient) to 1.5 h at 700°C . The combustion time varied from 5 h at 500°C . The ash residues obtained from complete combustion of acid-treated husk samples were completely white in colour. On the other hand, under similar conditions, the ash residues obtained from untreated husk remained light brown. The acid treatment of husk did not change the amorphicity of the silica. Patel, et al., 1987 gave details about the effect of thermal and chemical treatment of carbon and silica in rice husk. Thermal treatment of rice husk was conducted up to 1000°C in air, oxygen, argon and non-oxidizing atmospheres. Chemical treatment consisted of HCl, H_2SO_4 , HNO_3 , NaOH and NH_4OH . Purity, particle size distribution and SEM micrographs of chemically treated samples are presented. Carbon and SiO_2 contents in rice husk, coked

at different temperature and time, have been determine to show that a C : SiO₂ ratio of 2 : 1, required for the production of solar grade silicon, can be achieved at low temperature. SiO₂ of 99 % purity can be obtained by acid leaching. The properties of silica in rice husk ash e.g., morphology, particle and crystallite, size, surface area and pore distribution, and crystallographic phase, were investigated by a combination of techniques : XRD, electron microscopy and low temperature adsorption-desorption studies. X-ray amorphous samples have been shown to consist of cristobalite with a crystallite size < 5 nm. (This must be considered a mis-interpretation of experimental results, since densified rice husk ash definitely has the thermal expansion of silica glass and not of cristobalite, as will be shown in this thesis). No noticeable crystal growth takes place below 700°C (Jose; James; and Rao, 1986). A recent paper (Conradt, et al., 1992) reports on nano-structured silica from rice husk. The potential and limits of rice husk to become a competitive source of nano-structured silica were investigated. Husk samples were submitted to a chemical pre-treatment using cellulose enzyme, NaOH, HCl, or H₂SO₄ solution. Subsequently, samples were incinerated at 600°C under static and flowing atmospheres (air, oxygen or steam). The product was characterized in terms of silica content, particle size distributions at different levels of agglomeration, and specific surface area (BET, N₂). A product with properties intermediate to those of fumed silica and xerogel was obtained. The size distribution for secondary particles followed a log-normal distribution with $d_{50} = 26 \text{ nm}$ and $d_{0.4}/d_{15} = 2$. Tertiary agglomerates range from 0.3 to 30 μm . The specific surface area reaches values of 250 m^2/g . Purity is better than 99.8 % silica.

1.2.3 General Survey of Colloidal Sol-Gel Method

Rabinovich, et al., 1983 reported a new method for preparing fused silica and high silica glasses through the sol-gel process. The authors prepared porous bodies by mixing colloidal silica with water, drying, redispersion, molding by coating followed by gelation, drying and sintering at 1450°C to 1500°C. The sintering is facilitated by addition of 3 to 5 wt. % B₂O₃. The process of dispersion-drying-redispersion (called "double process") results in the formation of a two mode pore structure which permits drying of cast tubes and rods. The preparation of very pure silica glass with low OH content exceeds the limits of the conventional melting process. Two alternatives are the well known technologies for the production of optical fibers which meet the highest purity requirement, and the sol-gel process (Clasen, 1987, 1988). With the increasing demands being made on the properties of glass and ceramics, conventional preparation techniques are reaching technical limits. The diffusion lengths are short in submicron particles, green bodies made from these powders can be easily purified. Furthermore, considerably reduced sintering temperatures are possible due to the high sintering activity of powder with large surface areas.

1.2.4 General Survey on Drying

Simpkins, et al., 1989 reported the observations of the drying behavior of thick-wall colloidal silica gel structures. Various techniques are examined to prevent cracking during the drying of these high-strain viscoelastic materials. Experiments are described which illustrate the effect of relative humidity on the drying rate and on the shrinkage of various samples under isothermal conditions. Surface temperature measurements indicate

that evaporation occurs at approximately the wet-bulb temperature of the surrounding atmosphere. Acoustic detection of the internal strain activity during drying leads to the conclusion that control of the sol-gel surface tension in the material preparation is crucial to reducing the interior stresses. Scherer, 1990 examined the stages of drying, with the emphasis on so called the constant rate period (CRP), when the pores are full of liquid. It is during the CRP that most of the shrinkage occurs and the drying stresses rise to a maximum. He examined the forces that produce shrinkage and the mechanisms responsible for transport of liquid. By analyzing the interplay of fluid flow and shrinkage of the solid network, it is possible to calculate the pressure distribution. The pressure in the liquid is found to be greatest near the drying surface, resulting in greater compressive stresses on the network in that region. This causes differential shrinkage of the solid, which is the cause of cracking during drying. The probability of fracture is related to the size of the body, the rate of evaporation, and the strength of the network. A variety of strategies for avoiding fracture during drying are discussed.

1.2.5 General Survey of Sintering

Clasen, 1989 described the sintering process is the final step in the preparation of transparent silica glass via a powder ceramic sol-gel route starting from fumed silica glass powder. As high green densities can be obtained with this method, the shrinkage during drying and sintering is small and compacts like rods and tubes can be easily prepared. The study of the sintering behavior of these compacts made from submicron particles are based on two aspects, namely that of the parameters influencing the sintering

rate of the sample (macroscopic behavior) and that of the interaction between single particles (microscopic behavior).

The sintering rate depends on the furnace temperature and the thermal conductivity of the sample. As the thermal conductivity in the sintered silica glass is about two orders of magnitude higher than in the porous compact, a dominant axial head flux during zone sintering should be expected. This could be experimentally confirmed by measuring the sintering behaviour of rods and tubes and making the isotherms of the samples in the sintering zone visible.

The viscous flow of single particles was measured by the decrease of the surface area of the compact during sintering.



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