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PREPARATION OF INORGANIC BINDER FOR COLD-HARDENING MIXTURES

Aung Htut Thu[1,2] **and A. I. Zakharov**[1]

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A solution of sodium silicate (liquid glass) was prepared and used as an inorganic binder for cold-hardening mixtures of refractory molds for metal casting. Wastes from rice production, i.e., rice hulls, were the source of silicon oxide. Several methods for synthesizing liquid glass were examined and characterized.

Keywords: liquid glass, cold-hardening mixtures, inorganic binder.

INTRODUCTION

Cold-hardening mixtures are widely used to produce molds for metal casting. They are based on a large-grained filler (quartz, olivine sand, nepheline, etc.) bonded by an inorganic binder. Liquid sodium glasses are used to mold most articles despite the development of polymer adhesives (epoxides, polyesters, other resins) [1 – 4]. Aqueous solutions of Na_2SiO_4 with various SiO_2 and Na_2O ratios are called liquid glasses. The various proportions of Si and Na oxides and the concentration of solids produce liquid glasses with various properties that have industrial applications from sealants to refractory components [5, 6].

Liquid (sodium) glass is a thick yellow or gray liquid without mechanical inclusions and impurities. Many applications of liquid glass are related to its ability to harden spontaneously and to form artificial silicate rock. A unique property of liquid glass is its high adhesion to substrates of various chemical natures. Liquid glass is used as a binder to glue various materials and coatings and to produce composites for various purposes [7, 8]. Currently, silica minerals (quartz, quartz sand) that fuse with soda or sodium sulfate and coal are the main feedstock for water-soluble silicates.

The sodium-silicate production process consists in general of the following steps:

1) calcination of a mixture of Na_2CO_3 and natural quartz sand (SiO_2) in appropriate furnaces at 1200 – 1400°C to cause the reaction $Na_2CO_3 + nSiO_2 \rightarrow nSiO_2Na_2O + CO_2$ (where n can be a fraction);

2) dissolution in H_2O in a reactor at high pressure and temperature of solid glass produced in a preceding step;

3) filtration depending on the desired purity to produce sodium silicate solution or liquid glass that is transparent and slightly viscous;

4) evaporation of H_2O from the silicate solution to produce solid sodium silicate if needed;

5) additional step for reaction of silica with aqueous NaOH in solvents at high pressures and temperatures [8, 9].

The key parameter determining the properties of soluble silicate solutions is the liquid glass modulus, i.e., the molar ratio SiO_2/Na_2O. The ratio typically ranges from 1.6 to 3.2.

The synthesis of liquid glass is costly because of the fuel consumed to heat to high calcination temperatures and the air pollution released as dust and N and S oxides. A method based on the reaction of silica with aqueous NaOH solution in an autoclave at high pressure and temperature without calcination is also known [10 – 12]. The synthesis of liquid glass from rice-production wastes, i.e., rice hulls, is one possible version of liquid-glass production. The synthesis of liquid glass using highly disperse silica obtained by reprocessing rice hulls as the source could be easier and cheaper than the aforementioned methods.

The goals of the work were to produce a sodium silicate (liquid glass) solution from rice hulls by several methods, to compare the characteristics of the obtained products, and to select the optimal synthesis method.

The rice plant absorbs silica as soluble silicic acid $Si(OH)_4$, which enters the root from the surrounding soil.

[1] Dmitry Mendeleev University of Chemical Technology of Russia, Moscow, Russia.
[2] aunghtutthu1991@gmail.com

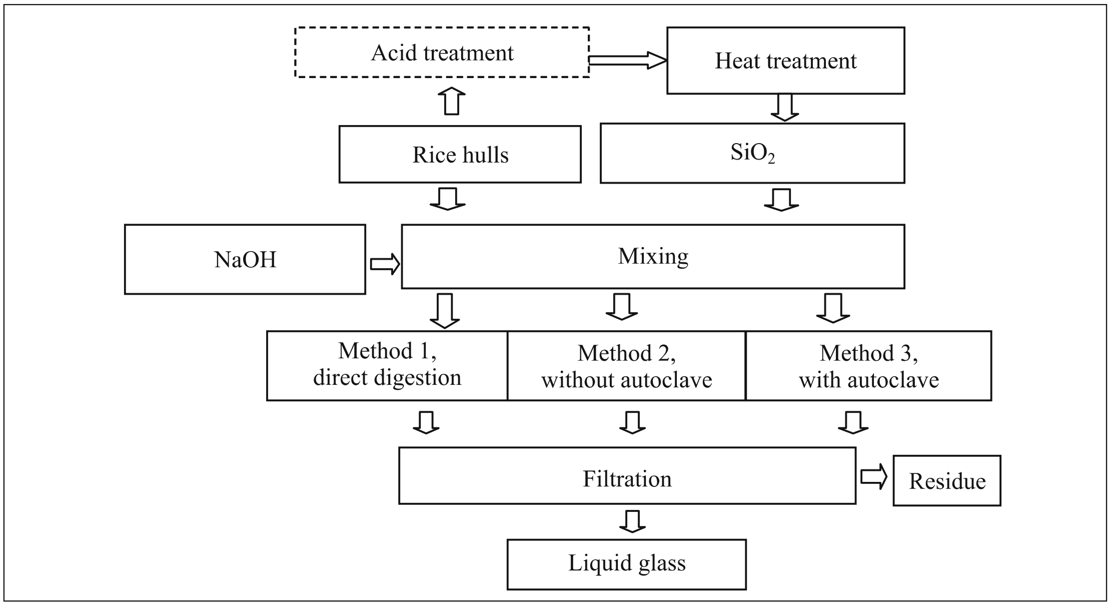

Fig. 1. Diagram for production of liquid glass from rice hulls (the dashed line shows an optional step).

The absorption mechanism and silicon transfer in the plant that results in the formation of a cellulose – silica composite membrane is little studied [13 – 16]. The silica content in rice hulls depends on the climate, soil conditions, and rice variety. The constituent composition of rice hull includes cellulose (~50%), lignin (25 – 30%), and silica (15 – 20%). Rice hulls are most suitable of all plant feedstocks for extracting silica because of its high content in the ash (92 – 97%). White amorphous silica is produced by combustion of this feedstock at low temperature. The main impurities of silica prepared from rice-hull ash that contain Na, K, Ca, and other ions can be removed by acid treatment [18, 19].

Methods are known for preparing water-soluble silicates from rice hulls in which hulls or their ash are soaked with KOH or NaOH solution (10 – 12% or 1 N) and heated in air at 90 – 150°C and greater for 60 – 120 min. Then, the rice hull residue is pressed and rinsed with H_2O [20, 21]. Rice hulls are briefly immersed in a tank with NaOH solution of various concentrations in some methods for preparing sodium silicate solution. After heating at 100 – 200°C for 1 – 8 h, residual carbon is removed using filter paper to produce a solution corresponding to liquid glass with normalized parameters. The precipitate is pressed and rinsed with H_2O [22]. A method in which rice hulls or their ashes are treated with NaOH solution (1 N) to extract silica was reported [23]. The silica content in the feedstock after treatment was determined gravimetrically.

A common drawback of the method for preparing water-soluble silicates directly from rice hulls is the formation of colored solutions because many applications require colorless ones [24, 25].

EXPERIMENTAL

Rice hulls were rinsed with copious amounts of tap water and then distilled H_2O and dried. The amounts of impurities were reduced to insignificant levels by treatment with HCl. This increased the silica yield in the rice-hull ash and its purity. The amount of residual carbon in the ash decreased to %. Figure 1 shows a general diagram for the production of liquid glass from rice hulls including from SiO_2 produced by heat treatment of rice hulls.

The starting feedstock was rice hulls from Vietnam. A part of the material for impurity removal was treated with acid. Rice hulls were combusted in an electrical resistance furnace with metal-alloy heaters at 600 – 800°C to produce SiO_2. The maximum temperature was held for 4 – 6 h. Ash formed by the combustion made up 17 – 20% of the initial mass.

The temperature of complete combustion of rice hulls was determined using differential thermal analysis (DTA) and differential scanning calorimetry (DSC) on a QD-1500 system (Paulik-Paulik-Erdey) in the temperature range 25 – 1000°C at heating rate 10°C/min and on a QD-1500 DSC (Netzsch) in the temperature range 25 – 1000°C at heating rate 10°C/min, respectively (Table 1). DTA was performed in an open crucible; DSC, in a closed crucible in an Ar atmosphere. Temperature ranges of exotherms and mass losses differed significantly, indicating the need to supply air to the sample to produce silica without residual carbon.

The resulting rice-hull ash was studied using scanning electron microscopy combined with elemental analysis on a JEOL JSM 6510LV microscope (Fig. 2).

Table 2 presents elemental analyses of rice-hull ash prepared by heat treatment at 600°C for 4 h at the maximum temperature.

Next, starting hulls and ashes prepared from them were used to produce liquid glass by several methods (Fig. 1), i.e., with and without an autoclave and direct digestion in NaOH solution.

Production of liquid glass from rice-hull silica with an autoclave

The reaction between silica and NaOH to produce liquid glass was carried out in two types of systems, i.e. open and closed. Feedstock in the closed system (with an autoclave) was placed within a stainless-steel Teflon-lined autoclave at 8 bar and 100 – 200°C. Rice-hull ash that was not treated with acid was used. According to the literature [22, 24], residual carbon in the ash of 2 – 8% by this method acts as a reductant for multivalent ions and provides silicate solutions.

Sodium silicate was synthesized from a mixture of ash and aqueous NaOH in various proportions to give a silica modulus from 2 to 3.5. The synthesis was performed in an autoclave at 170 – 200°C and 7.5 – 8.0 bar for 4 – 8 h. The following reaction occurred:

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O.$$

The solution obtained after the autoclave cooled was filtered.

Preparation of liquid glass from rice-hull silica without an autoclave

The reaction was carried out in an open system (without an autoclave) at atmospheric pressure. High-quality amorphous SiO_2 was produced from rice hulls by preliminary heat treatment at 600°C. Next, NaOH powder was dissolved in distilled H_2O and added slowly to the ash. A solution of sodium silicate with modulus 3.0 was prepared using 30 parts silica ash, 20 parts dry NaOH, and 50 parts distilled H_2O. The mixture was refluxed for 30 – 60 min with continuous stirring, cooled, and filtered.

TABLE 1. Mass Losses of Rice Hulls Treated Under Various Conditions

Conditions	Temperature range, °C	Mass losses, %
DTA-TG, open crucible	50 – 150	5
	150 – 250	—
	250 – 400	60
	400 – 750	18 (17)
DSC-TG, crucible with lid, Ar	50 – 150	5
	150 – 230	—
	230 – 350	43
	350 – 1000	30 (22)

* Residual mass (%) given in parentheses.

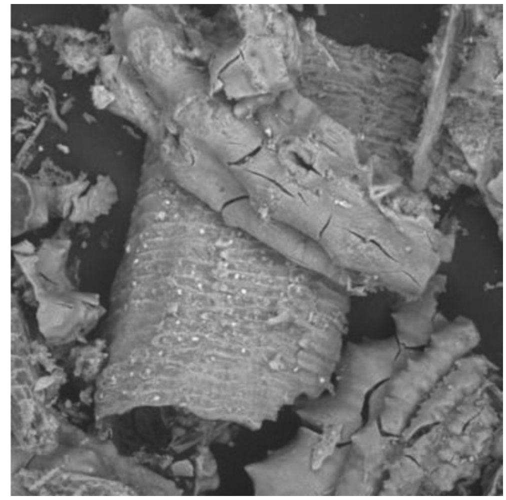

Fig. 2. Particles of rice hull ash, ×550.

Preparation of liquid glass by direct digestion of rice hulls

Sodium silicate was synthesized by direct digestion of rice hulls by rinsing rice hulls with distilled H_2O, drying at 150°C for 30 min, treating with HCl solution (1 N) at 100°C for 60 min, rinsing with hot distilled H_2O, and drying. Dried samples were loaded into a flask with NaOH solution (12%), stirred at 90 – 100°C for 60 – 90 min, cooled, and filtered.

RESULTS AND DISCUSSION

Conditions were created for producing liquid glass from rice hulls (or their ash) with or without an autoclave by the corresponding industrial methods. Table 3 presents several characteristics of the glasses obtained by the various methods.

Direct digestion did not produce high-modulus glass and gave solutions of low densities. Evaporation of the solution to increase the characteristics of the obtained product was

TABLE 2. Chemical Composition of Rice Hull Ash

Element	Content, %	
	atom	mass
C	11.32	8.31
O	63.18	56.03
Mg	0.12	0.07
Mn	0.04	0.02
Fe	0.05	0.03
Al	0.17	0.11
Si	23.65	34.33
S	0.05	0.04
K	1.19	0.88
Ca	0.23	0.16
Total	100.00	99.98

TABLE 3. Characteristics of Liquid Glass Samples Produced by Various Methods and Their Compliance to Regulatory Requirements [26]

Parameter	Liquid glass characteristic by GOST 13078–81	Synthesis results		
		method with autoclave	method without autoclave	direct digestion of rice hull
Appearance	Yellow or grayish-yellow thick transparent liquid	Gray transparent	Transparent	Reddish-gray
Mass fraction of Na_2O, %	13.5 – 9.5	13 – 9.8	13 – 10	12 – 10
Mass fraction of SiO_2, %	29.5 – 33.6	28 – 33.5	26 – 35	24 – 30
Density, g/cm^3	1.26 – 1.45	1.25 – 1.45	1.27 – 1.46	1.07 – 1.25
Silicate modulus	2.0 – 3.5	2.0 – 3.5	2.0 – 3.5	>1.5

TABLE 4. Synthesis Parameters and Characteristics of Liquid Glasses Prepared from Rice Hull Ash

Synthesis method	Content, %, recalculated as			Synthesis parameters			Liquid glass yield, %	Insoluble residue, %
	SiO_2	Na_2O	H_2O	temperature, °C	pressure, bar	time, h		
With autoclave	30	10 – 15	60 – 70	170 – 200	7.0 – 8.5	5 – 8	80 – 97	3.1 – 12.6
Without autoclave	30	10 – 16	62 – 72	90 – 100	—	1.0 – 1.5	78 – 94	5.5 – 13.1

considered unfeasible. Moreover, this method could not produce colorless silicate solutions. Therefore, additional experiments are needed to refine its applications.

Table 4 presents the synthesis parameters and compares characteristics of liquid glasses produced using ash with and without an autoclave. These methods typically gave high yields of product that consistently complied with regulatory requirements. The amount of insoluble precipitate varied significantly depending on the synthesis parameters.

A comparison of the various methods for synthesizing liquid glass from rice hulls showed that synthesis without an autoclave was the most rational choice because a product that could be used to prepare cold-hardening mixtures could be produced in a short time.

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