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DRYING PROCESS AND RESOLUTION OF ALKALI SILICATE POWDERS

M. HASZNOS-NEZDEI and E. PALLAI-VARSÁNYI

(University of Kaposvár, Research Institute of Chemical and Process Engineering,
Veszprém, Egyetem u. 2., P.O.Box 125, Veszprém H-8201 (HUNGARY)

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Methods and conditions of dehydration of sodium silicate solutions were investigated in mechanically circulated spouted bed dryer with inert packing. The used commercial silicate solutions were set to a definite mole ratio. The qualification of the powderlike dried products was done using different analytical methods and also the resolution properties were determined.

Keywords: Inert particles, MSB-dryer, Silicate ratio, Thermal treatment, Water-glass.

Introduction

Alkali silicate solutions are used for many purposes, as basic materials or auxiliary products. Taking into account the volume of their industrial applications, sodium silicates are more important as potassium silicate solutions. For special use other soluble silicates (e.g. lithium silicate, etc.) are also produced. The use of sodium silicate solutions (water-glass) is important in the manufacture of detergents and cleaning agents utilizing their favourable colloidal and dirt binding properties as well as their corrosion reducing effect. Sodium water-glass solutions are processed also in the rubber and dye industries, that is in the production of ingredients and extenders (precipitated silicic acids and silicates), furthermore in manufacturing of synthetic zeolites having catalytic and ion-exchange characteristics. Moreover, sodium silicate solutions are used in the formation process of foundry moulds and of acid- and heat resistant putties, in the flotation process, as well as to accelerate the setting process of cements [1-3].

Potassium water-glass solutions are mostly used for the coating of welding electrodes, in the production of video tubes as binders, furthermore in silicate base paints employed for handling of external plasters. In certain special cases water-glass powders are used instead of water-glass solutions. The powderlike products are made by different drying processes from the appropriate solutions [4-7]. The moisture content of the obtained dried product is generally of 15-25% depending on the SiO_2/alkali oxide ratio and on the applied drying conditions. On effect of heating the dried powderlike product dissolves in water, and the obtained solution keeping likewise its colloidal properties can be used advantageously.

The composition of alkali silicate solutions, that is these special colloidal systems are in general not strictly stoichiometric [1-3]. The characteristic SiO_2/alkali oxide mole or mass ratio, the amount of the dissolved material vary between definite limits depending on the composition of the solid water-glass basic material and on the method of the dissolution process as well.

The water-glass solutions are produced from commercial solid water-glasses by hydrothermal method. The characteristics of the commercial (Henkel) solid water-glasses are shown in *Table 1*.

Table 1. Characteristics of solid commercial water-glasses [2]

Type	SiO_2/alkali oxide mole ratio	SiO_2/alkali oxide mass ratio
Sodium water-glass	SiO_2/Na_2O	
high silicic acid content	3,9-4,1	4,0-4,2
neutral	3,3-3,5	3,4-3,6
alkaline	2,0-2,2	2,1-2,3
Potassium water-glass	SiO_2/K_2O	
	3,3-3,5	2,1-2,2
	4,1-4,3	2,6-2,7

Experimental

In our experimental work both commercial and silicate solutions were applied where the module was set to a definite value by industrial processes. Our aim was to investigate the possible methods and conditions of dehydration of alkali silicate solutions in mechanically circulated spouted bed dryer with inert packing and to qualify the obtained hydrated powderlike dried products. For this reason different analytical methods were used and also the resolution properties were determined.

The most important characteristics of the used sodium silicate solutions are summarized in *Table 2.*

In *Fig. 1.* the Na_2O-SiO_2-H_2O ternary diagram is represented with the phase areas of the water-glass solution and of the hydrated powderlike dried water-glass product at temperatures under 100°C. The compositions related to a and b solid (anhydrous) water-glasses, furthermore the composition of the crystalline anhydrous sodium- metasilicate Na_2SiO_2 ($Na_2O.SiO_2$) are given too. Detailed presentation of further phase areas can be found in the monograph of Vail [3].

By the areas indicated in the ternary diagram it is demonstrated that the phase areas of sodium silicate solutions are localised by the SiO_2/Na_2O ratio. The water content of the solutions is different (45-70%) depending on the conditions of their production. The hydrated water-glass powders of given moisture content are produced by different drying processes. The dried products are dissolved in water to different degrees depending on the final moisture content and on the SiO_2/ Na_2O module value. The less is the moisture content, the less is the resolution ability. The compositions a and b correspond to the state of total dehydration.

Experiments to investigate dehydration conditions of water-glass solutions were performed in a mechanically circulated spouted bed dryer (MSB-dryer) with inert packing of big laboratory scale (*Fig. 2.*).

Intensive, well controlled heat and mass transfer can be carried out in the MSB-dryer which is developed to improve the operation conditions of the traditional spouted beds. The characteristic particle circulation is provided in this new-type dryer by a houseless screw conveyor that works in the vertical axis of the bed. The hot air entering the bottom of the dryer through slots at high velocity in tangential direction causes intensive gas-solid contact. The spouted bed of circulating inert particles consists of three zones which are separate and differ significantly in their flow characteristics, that is:

- the zone characterised by turbulent particle and gas flow, enables intensive gas-solid contact in the vicinity of the gas inlet;
- the zone of particles transported vertically upward by the screw-conveyor is concurrent to the drying air flow;
- the dense annular part sliding downward is countercurrent to the air flow.

For drying materials of high moisture content inert particles can be applied advantageously.

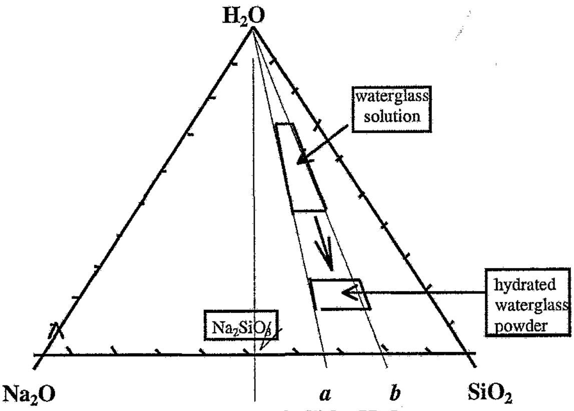

Fig. 1. Ternary system Na_2O-SiO_2-H_2O
a - alkaline character,
b -solid water-glass of high silicic acid content

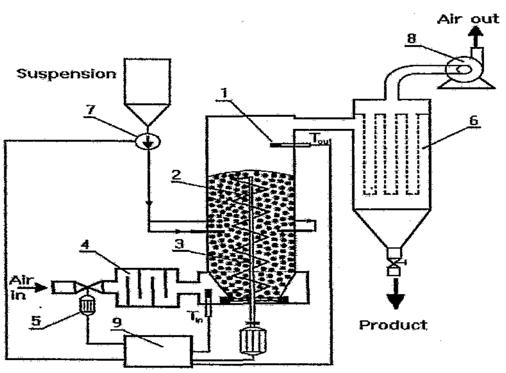

Fig. 2. MSB-dryer with inert particles
1 - drying column; 2 - inert particles;
3 - housless srew; 4 - air heater; 5 - electric valve;
6 - bag filter; 7 - pump;
8 - fan; 9 - A/D converter and PC

Table 2. Characteristics of the sodium silicate solutions applied in the drying experiments

Mark of samples	Concentration of solution, w% Na_2O	SiO_2	Σsolid	SiO_2/Na_2O Mass ratio	Density** g/cm^3	Viscosity** mPa.s
SWG-1*	14,18	28,94	43,12	2,04	1,542	351,0
SWG-3*	11,22	26,35	37,57	2,35	1,456	104,9
SWG-2*	8,34	25,57	33,91	3,06	1,370	87,8

* - water-glass solutions of different types.
** - The values of density and of viscosity are related to 25°C.

The principle of drying on inert particles is that pastes, pulps or suspensions of high moisture content are fed into the bed of inert particles (plastic, ceramic, glass, etc. spheres) circulated by the inner conveyor screw. In this way, an almost uniform, film-like coating is formed on the surface of the particles. The thickness is in optimum case 2...4 times higher (d = 20...40mm) than that of the primary particle size of the material to be dried. Since the inert particles have a large specific surface, the wet solid dries in a short time even at relatively low bulb temperature. Due to the intensive friction inside the screw conveyor, the dried coating wears off the particles and the fine dried product is carried out by the air stream leaving the dryer.

From the point of view of drying, the following partial processes are of basic importance:

- formation of coating (in the annular part of sliding down inert particles);
- drying of coating (in the inlet air area, that is in the conical bottom part of the dryer, in a bed height of a few (6...8) centimetres;
- wearing of coating (in the rotation area of the conveyor screw transporting the inert particles upward in the dryer).

There is no significant particle mixing between the zone of the sliding down annular layer and that of the vertical particle transport. Due to the „mechanical particle circulation", the characteristic spouted bed movement is independent of the air flow rate thus, the latter can be set to an optimum from the point of view of drying.

Taking into account the advantages of this well controllable drying system, the water-glass solutions were dehydrated in MSB-dryer with inert packing. The drying parameters are summarized in *Table 3*.

Results and Discussion

According to the results of X-ray diffraction measurements the dried water-glass powders are of amorphous structure. This could be attributed first of all to the fact that the ratio of the solid components (SiO_2 and Na_2O) of water-glass solutions are not stoichiometric.

Dehydration of water-glass solutions

Dehydration of water-glass solutions is a rather complex process deriving from its colloidal nature. The solid material content corresponding to the composition of the water-glass colloidal system is present in sol-form in the very alkaline dispersion medium. The sol particles consist of polysilicate anions which are built of SiO4-4 tetrahedrons. The polysilicate anions are connected to one another by H-bridge bonds. One part of the Na-ions is inside the sol particles, another part is outside the associated polysilicate anions which are in the solutions. The water-glass solution itself is a colloidal system of metastable state. The kinetic changes that happen in this colloidal system point to the direction of gelation. The dimension (molar mass) of the polysilicate anions depends considerably on the module of the water-glass solution and on the type of cations being in the solution. The molar mass values of polysilicate particles being in water-glass solutions of different modulus were published by Nauman and Debye [8]. They were determined by light diffraction measurements and vary between 90-500 in sodium water-glass solutions and between 1150-1538 in potassium silicate solutions. The mole mass values measured in potassium water-glass solutions are considerably larger than of those measured in sodium water-glass solution.

At drying in spouted bed dryer with inert packing the water-glass solution fed into the dryer forms a filmlike layer (coating) on the surface of inert particles (ceramic spheres). The dehydration process proceeds in this coating in several steps. At first the water content leaves from the disperse phase and as a consequence of the moisture content decrease, the coating becomes gelatinous. As a result of the intensive heat transfer existing in the drying zone, further dehydration occurs, the continuous gel-structure breaks up and in the thin water-glass coating small dehydrated gel-fragments appear.

On effect of the hot air flowing through the circulating inert bed the dehydration process continues until the moisture content achieves the required value necessary to wear off the inert particle surface, or until attainment of a final moisture content required from other technological point of view. The final moisture content can be adjusted by the temperature and velocity of the drying air, furthermore by setting the appropriate particle circulation velocity and by the feeding rate that determines the residence time of the water-glass coating.

Table 3. Drying of water-glass solutions. Process parameters.

Samples	Volumetric flow rate of drying air (20°C) m^3/h	Temperature of inlet air °C	Temperature of outlet air °C	Water-glass feeding rate g/min
SWG-1	65,0	155	120	10,5
SWG-3	70,0	145	105	21,7
SWG-2	70,0	150	110	19,4

Inert packing - ceramic particles with diameter of 7mm.

Table 4. Characteristics of hydrated water-glass powders dried in MSB-dryer with inert packing

Sample code	N m. r.**	ρ kg/dm³	Particle fractions by screening <100µm	100-250µm	>250µm	Thermal dehydration % ΣH_2O	<200°C	200-400°C	600-700°C
SWG-1D*	1,98	0,874	74,2	19,5	6,3	24,3	23,7		0,6
SWG-3D*	2,28	0,880	59,1	30,7	10,2	27,3	26,4		0,9
SWG-2D*	2,96	0,898	63,5	29,0	7,5	18,8	11,0	5,5	2,3

* - dried water-glass products,
** - m.r. mole ratio.

Fig. 3. shows the scanning electron microscopic picture of a dried water-glass sample. It can be seen that the particle size distribution is unequal, the product consists of fragmentary, broken particles of irregular shape. The particle size distribution was determined by vibration screening in a dry state. 60-70% of the particles are smaller than 100mm, the bulk density is rather high (0.87-0.90kg/dm3) and do not depend on the SiO_2/Na_2O module of the initial solution. The final moisture content of the dried hydrated product (18.8%-27.3%) changes with the composition of the water-glass solution and with the drying conditions (see *Table 4.*).

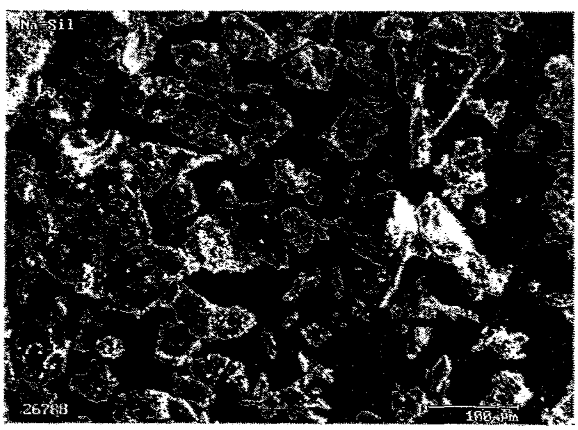

Fig. 3. SEM picture of the hydrated water-glass powder dried in MSB-dryer with inert packing

The powderlike dried water-glass samples were tested by thermoanalytical method to examine the bonding characteristics of the water molecules remaining in the dried products. Experimental data were obtained on the basis of dehydration processes carried out after the spouted bed drying process are summarized in *Table 4*. It can be seen that the final moisture content of the dried, alkaline products (sample code: SWG-1 and SWG-3) is rather high (24.3% and 27.3%). On effect of further heat -treatment the greatest part of the moisture content is removed at temperatures below 400°C. The water part that could be removed during the thermal dehydration at temperatures below 200°C does not appear in the thermal-analytical pictures. The small water content that remains still at 400°C in the water-glass powders could be removed between 600-700°C indicating its stronger bonding in the water-glass structure.

The SWG-2D samples is less alkaline water-glass product. At the thermo-analytical measurements it can be proved that the moisture removal proceeds in three phases. Below 200°C about 60% of the final moisture content departs, 30% between 200-400°C, and the rest water content - similarly to the alkaline samples (SWG-1D and SWG-3D) - is removed between 600-700°C.

On the basis of differential thermal analytical measurements the dehydration process of hydrated water-glass powders proceeds similarly to that of insoluble silicates, such as e.g. precipitated silicic acid [9]. This similarity is getting more end more expressed with the increase of the silicate module.

During the differential thermal analytical measurements the water-glass samples of low module values show a characteristic increase in their volume. Namely, the diffusion of the water content remaining after drying is hindered by the dried gelatinous structure. On effect of the heating process vapor is originated that tightening (increasing) the structure leaves the water-glass product. This effect appears at the SWG-1 sample to the greatest extent, while the increase in volume at sample SWG-3 is already less, and it is scarcely observable at the SWG-2 samples. Products of a structure being increased on effect of heat treatment can be used as isolators. Application of such sodium water-glass powders is patented [10].

Resolution of amorphous sodium water-glass powders

Hydrated water-glass powders of amorphous structure are produced by different drying processes. The obtained powderlike products dissolve in different degree depending on the water content and on its module value. By this special property it becomes possible to utilise the favourable characteristics of water-glass solutions by employing a drying method even in such cases when the direct use of water-glass solutions meets with difficulties. Before the use of powderlike water-glass products it is necessary to investigate both the conditions and the degree of resolution. By setting the best drying parameters it is possible to control the final moisture content of the dried product. It can be seen in *Table 5.* that by the increase of the final moisture content increases the degree of resolution. The solubility of the hydrated amorphous products dried in MSB-dryer with inert packing was investigated in distilled water depending on the temperature and on the duration of the dissolution process. At resolution solutions of 20-25% solid content were prepared, that is from the investigated samples 40-50g amounts were dissolved in 150-160g hot water by mixing under constant temperature and the degree of the solubility was determined.

Table 5. Resolution of the hydrated amorphous water-glass powders

Samples	Degree of resol.** %	Concentration of the solution Na_2O	SiO_2	Σsolid	SiO_2/Na_2O mass %	Density g/cm^3	Viscosity mPa.s
SWG-1R*	98,6	7,65	14,69	22,34	1,92	1,215	3,3
SWG-3R*	89,3	5,15	11,78	16,93	2,29	1,158	2,1
SWG-2R*	83,4	3,93	12,30	16,23	3,13	1,146	2,0

* - solution obtained by resolution of the dried water-glass powders
** - time of dissolution in hot water was one hour.

At the end of the measurements the obtained solutions were filtered by a filter-paper of type MN 640W and the amount of the dissolved material, as well as the density and dynamical viscosity were determined from the filtered solution. The sample SWG-1D dissolved in hot water quickly and the degree of resolution decreases by the increase of the silicate module.

The considerable resolution ability of the hydrated amorphous water-glass powders indicates that during the drying process of water-glass solutions of low module values (2.0-2.5) does not occur, or only in a small measure irreversible changes in the course of the sol-gel transformation. The decrease of the resolution degree of the hydrated powderlike amorphous sample SWG-2R relates to the fact that during the drying process of the water-glass solution - on effect of the high drying temperature and the not very much alkaline surrounding - partial dehydration of polysilicate anions and also its association take place. That means that a part of the sol particles is transformed into insoluble polysilicate anions of silicic acid. These latter anions already do not redissolve. Increasing the drying temperature, the final moisture content of the powderlike product obtained by drying of the water-glass solution of sample code SWG-2R decreases quickly, while the proportion of the fraction that can not be resoluted increases in parallel.

The results of experiments carried out in order to dry water-glass solutions proved that the hydrated amorphous water-glass powders produced under suitable chosen drying conditions, are of considerable resolution ability. This is due to their successful use in more special fields, e.g. as additives (water softener, dirt binding component) in solid detergent compositions.

Conclusions

Water-glass solutions of different modulus values were dried in a so-called „Mechanically Spouted Bed"-dryer (MSB-dryer) with inert particles. In this way, hydrated amorphous powderlike products were obtained with a final moisture content depending on the composition of the solutions and on the drying conditions.

To examine the dehydrated powderlike products thermoanalysis were applied. It was found that the dehydration process of alkaline water-glass powders differs from that of water-glass powders of less alkaline character.

The investigated hydrated water-glass powders dissolve well in hot water. The degree of resolution depends on the silicate-modulus.

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