

Sodium and potassium water glasses – present and new challenges

Longin OGŁAZA – Zakłady Chemiczne „Rudniki” S.A., Rudniki k/Częstochowy

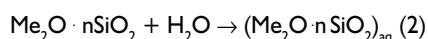
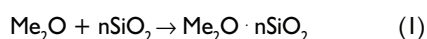
Please cited as: CHEMIK 2010, 64, 3, 133-136

Introduction

A water glass one is called water solutions of alkaline silicates (lithium, sodium, potassium). Often the same name have also alloys of sodium and potassium silicates, and these in turn is at times called a sodium silicate glass and a silicate potassium glass. These simple in its own chemical composition silicates do not appear in nature. They are soluble in water. There appear instead in nature various forms of composite silicates (about 800 minerals), they are a main component of Earth's crust rocks and are not soluble in water. Sodium and potassium water glasses have universal applications, although the knowledge regarding their structure is small. They are also not examined constantly and research works concerning silicates (in aqueous solutions and in the solid state) are lead by little scientific centres. In Poland such research were lead by Institute of Chemistry (Department of the Building, the Mechanics and the Petrochemistry) of Varsovian Technical University in Plock [1], Institute of Inorganic Chemistry in Gliwice [2] and Institute of Technology and Chemical Engineering of Technical University in Poznań [3]. One ought to underline that research concerning silicates (also the lithium silicate) are made by research squads of producers of these products, especially in the area of future uses. Certain information can also be obtained from patent-descriptions [4]. Currently used definition of water glass as the alloy of the silicate of alkali metal or its aqueous solution with molar relation of silicon dioxide to the oxide of alkali metal most often within 2 to 4 [5] should be changed because now days general are also stable water glasses with different ranges of molar relations or mixed glasses (for example natrium and potassium water glasses). Lack of possibility of estimating exact date of discovery for sodium or potassium silicate has no meaning as research of the use for silicates using its specific properties for example: strong buffer-properties was the main reason to its later industrial production. Finding following uses for silicates modifications of the chemical composition of resultant products has been made across the change of the proportion of the silica to the alkaline. The relation of SiO_2 to for example Na_2O (as the weight percentage) is called **weight ratio** and multiplied by the quotient of molar masses of these oxides ($\text{SiO}_2/\text{Na}_2\text{O} = 1,032$) is called **molar ratio**. Besides the ratio for every solution of water glass there are stated density of solution in definite temperature, the content of insoluble parts and sometimes viscosity or content of Fe_2O_3 , Al_2O_3 .

Methods of production of water glasses

1. *Method of melting*: calculated quantity of sand together with calculated quantity of soda ash or potash is melted in the furnace. We receive the alloy with properties of the typical glass product, which is dissolve in water (often using melting process in autoclave). As the result we receive silicate solution which is water glass. There exist detailed formulas for production of different kinds of glasses taking into account chemical analyses of raw materials (sand and the soda). Technological processes described above can be generally presented ad chemical reactions:



- (1) the reaction takes place in about 1400°C (it is made in furnace)
- (2) dissolving process (depending on kind of Me) is made in autoclave under enlarged pressure (boiling temperature of water is higher than 100°C in this case).

In the reaction of dissolving there can uses the addition of the hydroxide (MeOH), what causes the decrease of the ratio of the resultant glass.

2. *Method of mixing*: it is based on intensive mixing in the reactor of two different kinds of water glasses (in calculated quantities), for sodium glasses with short lead to boiling temperature of mixed solutions of these silicate. Mixing time depends on the kind of glass (its density and viscosity). Potassium water glasses has to be mixed for substantially longer period of time and avoiding heating to boiling temperature. It has also to be marked that mixing process helps to correct physicochemical parameters of these glasses and should be made by experienced operators. Mixing of glasses means also interference into internal structures which has not been specified until now. As the result of very few research works it has been found that molecular composition of glasses depends on among the others: concentration, ratio and method of preparation used by manufacturer [6]. In order to produce another glass it is not applicable to mix glasses from different manufacturers. However, it is practiced to use as a raw material, water glass originating from different manufacturers if they have a similar composition (maintenance two or more suppliers).

3. *Method of hydrothermal dissolving of sand*: is carried out in autoclaves or pressure reactors (under much greater pressure than dissolving of the silicate glass and therefore also in the higher temperature). Raw materials are sand (with appropriate purity) with a high content of SiO_2 , soda lye or potash lye and water, partly derived from steam, which is used to achieve the proper temperature and pressure in the autoclave. This reaction is exothermic similarly to reaction of dissolving silicate glass. The relationship between achieved ratio of formed water glass from pressure is known (the higher module you want to achieve the higher pressure and temperature must be used). This method is used primarily for the production of sodium water glasses with molar modules of 2,0 – 2,5 and also sodium metasilicate (molar module amounts 1,0) as it is competitive in cost comparing to method of dissolving previously melted silicate glass. It was observed that water glasses obtained by this method are different in some of its properties from the same glasses obtained by dissolving of silicate glass, which is assigned by a different degree of agglomeration of silicate ions present in these solutions of silicate.

Due to the high cost of melting silicate glass and necessity to reduce silicate solutions production costs (of water glass) some of the manufacturers apply all these mentioned above technologies of water glass production to dependence of requirements of customers. Water glass with lower modules is produced then using method of hydrothermal dissolving, high modules water glasses (above 3,0) are produced by dissolving of silicate glass and other glasses by mixing different water glasses. Descriptions of technologies and applied technical solutions are rarely presented to the public due to the competition and the parameters of the offered products (excluding general mentioned in catalogues) are individually negotiated between trading partners.

Technology-generated modifications of aqueous solutions of silicates

Production of silicates requires the use of significant quantities of energy supplied in the form of steam, electricity, gas and sometimes compressed air. Handling large masses of the raw materials and control of manufacturing processes is also associated with high energy consumption. Making melt of water glass (in the form of silicate glass) causes large emissions of carbon dioxide into the atmosphere, derived from the decomposition of soda ash and combustion of fuel (usually natural gas) will be in the future an additional cost due to the need to purchase the quantities of emissions (melt silicate glass is placed in a group: production of glass products with a capacity exceeding 20 tons/day). Thus, it dictates the need for further exploration of other technological solutions in order to lead the process with the installation of a minimal impact on the environment, among other things, where the early melting of silicate glass is eliminated. One of such possible solutions may be:

Production of water glass with high modules (above 2,5) from cristobalite

Silica exists in three polymorphic varieties: quartz and tridymite (in crystallographic hexagonal system) and cristobalite (in the regular system) [7]. Each of these polymorphic varieties has a variety of low temperature (α) and high temperature (β). Tridymite and cristobalite may exist as metastable varieties at low temperatures. Quartz and tridymite are constructed of tetrahedrons SiO_4 in such a way that each oxygen atom is common for two tetrahedrons, which form a spiral arrangement. In cristobalite silicon atoms are arranged so that, there are oxygen atoms in the middle of the distances between them and the whole system is layered. Cristobalite can be a good resource for certain types of water glasses obtained by hydrothermal method because some manufacturers of sand have mastered the low-temperature production technology of cristobalite from sand. Although the price of cristobalite is much higher than the sand it seems that this is a good direction, because it was observed that the dissolving of cristobalite requires a lower pressure reaction than used for dissolving of typical sand and that it is possible to obtain a water glass with a higher ratio. Naturally, it is also possible to carry out hydrothermal reaction for receiving of water glass with a ratio over 2,5 from the sand, but required reaction pressure exceeds 20 bars. Construction of apparatus for such high pressure is expensive and to obtain the steam pressure of 20 bars is possible in steam boilers where the cost of construction and operation are higher than conventional steam generators.

Methods used to study the structure of water glasses

Measurements viscosity of solutions of sodium silicates as a function of the molar ratio and concentrations described by Maina [8] are also carried out. The basis for the identification of these products is formed by identified and measured in the laboratories of process control parameters of water glasses, based on published standards. There are also used traditional analytical techniques (titration, flame photometry, analysis of potentiometric), other test methods presented by W. Koźlak [9] and methods for atomic spectrometry of absorption and emission (ICP-AES, CV-AES), X-ray and mass spectroscopy. There is lack of complete determination of water glasses structure though obtaining much information about the structure of water glasses closer to the knowledge of their specific properties. Strong influence on the properties of solutions of water glass is made by the technology of their manufacture and purity of used raw materials as well. Currently, there are identified about 20 cations and some anions in solutions of silicates. They naturally have an impact on some properties of resulting water glasses (for example for viscosity, storage stability, ease of filtering) which is particularly observed for some of the solutions of potassium glasses. Therefore, new applications for water glasses are

forcing manufacturers of these glasses to find stabilizing additives. And so: potassium water glass used for the production of plaster facade must remain stable in viscosity (within certain limits) of this plaster for about a year. Selected organic compounds that are soluble in water are mainly used stabilizers.

Summary

Sodium and potassium water glasses are used in many industries (as components of laundry detergents and other cleaning agents, they are part of bleaches, they are components of adhesives for paper, they are the ingredients: of moulding masses, ceramic pigments and anticorrosive paint, silicate plasters, they are used to impregnation of wood and manufacture of building insulations, they are used to production of silicazols, pure silica and fillers, they are used for drinking water treatment and sewage treatment, production of ceramic materials and the sealing of land during construction works). They are harmless to the environment from an ecological point of view and therefore some research should be undertaken to examine their properties in order to identify new uses, and their environmentally friendly manufacturing technologies.

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English translation by Author.

Mc Sc Longin OGŁAZA is graduated from Chemical Department of Jagiellonian University (1973). He has been working in Chemical Plant „Rudniki” since 1979 where he oversees the production of silicate and implementation of new products. He is expert of Chemical Engineering Association in the area of technology of silicates.

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