Sodium Silicate Glass as an Inorganic Binder in Foundry Industry

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ABSTRACT

Mixtures of sand, sodium silicate, some additives such as iron oxide, pitch or sugar and an ester can form a temporary mould. Sodium silicate is used in foundries to bind sand grains by means of an appropriate acid, either directly such as CO_2, or indirectly with an organic ester, which hydrolyzes and subsequently gels the silicate sand mass. A gel network is prepared by acidifying concentrated sodium silicate (3.3 ratio of $SiO_2:Na_2O$) solution. Sodium silicate solution, under acidic conditions is polymerized to silica and acts as an inorganic binder. In other word, lowering the pH of an alkali silicate solution below about 10.9 causes the polymerization to occur, thus leading to high molecular weight aggregates of hydrated silica. The produced hydrated silica namely silica gel is responsible for giving the necessary strength to the mould. Concentration of the sodium silicate solution is adjusted to 65%(w/w) in water. The viscosity of this solution is adjusted on 500 cp by addition of sugar in an amount of 1.0–2.0% based on weight of sodium silicate. The sugar or pitch is used as a thickening agent, to concentrate the binder solution at a desirable limit. Sodium silicate solution as an inorganic binder is of particular importance mainly because, the necessary time for curing the silicate is low, and it is environmentally extremely beneficial.

Key Words: sodium silicate, inorganic binder, adhesive, foundry, water glass

INTRODUCTION

Casting is the formation of a solid body of predetermined size and shape from a melt by a process of solidification in a mould. Foundry technology is the art and science of the processes and materials used in manufacturing castings from metals and alloys. It deals with the manufacture of moulds and pattern, melting practice, metal treatment, pouring methods and processes for finishing castings and the equipment used.

Moulding practice deals with the production of moulds and there are two types as follows:

– Permanent moulds
– Temporary moulds

Permanent moulds are reusable, and are usually made of metal, more rarely of graphite or refractory ceramic. These moulds are mainly used for non-

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ferrous metals and iron. Important advantages of these moulds are the high rates of cooling and the clean casting surfaces. Temporary moulds consist of the basic materials, a binder system and some additives.

The basic materials are granular substances of washed, classified and dried different silica sands. These basic materials (moulding sands) may be classified into four different types as follows:

– Natural moulding sand
– High silica sand
– Special sand such as zircon, olivine, chamotte, chromite, chrome-magnesite, corundum, magnesite, sillimanite and mullite.
– Bonding clays (bentonite)

Binder systems may be organic or inorganic, natural or synthetic (as in Table 1).

Special sand moulding processes have been developed to enable moulding with less effort and skill, saving time and expenses, produce better quality moulds and cores and effectively help in improving productivity [1].

Generally, these processes eliminate the need for drying or baking of moulds and cores and rapid hardening action takes place due to chemical reactions. Also, the casting can be produced to a higher degree of accuracy and finish than that possible by conventional dry sand moulding. Special sand moulding processes, which are used for making temporary mould, may be classified under three heads:

– Processes based on sodium silicate binder
– Processes based on organic binders
– Other special moulding processes

Processes Based on Sodium Silicate Binder

The use of sodium silicate as a binder has considerably increased in recent years. It enables the preparation of mould and cores without any need for drying and baking in certain cases even without ramming the sand. The various processes based on sodium silicate are classified into four categories as follows:

– Cement moulding process
– Dicalcium silicate process

Table 1. Sand binders.

Source	Natural	Synthetic
Inorganic	Clays Bentonites	Sodium silicate Cement Plaster Phosphate binders Sulphite lye
Organic	Oil binders Core oils Sugar	Aminoplast resins(UF) Phenoplast resins(PF) Furan resins Epoxy resins Polyester resins Polyurethane resins

– Ferro-silicon process
– Carbon dioxide process

Differences between these various processes lie in the quality of hardener used, the type of catalysts or other additives, and in the nature of the chemical reactions that cause the hardening. These processes are being used for production of cast iron, steel as well as non-ferrous castings required in small, medium and heavy sizes. Patterns used with these moulding processes may be made of wood, metal or plastic.

Cement Moulding Process

Portland cement may be used as an inorganic binding material to bind sand grains together. Efficiency, however is further increased and a good combination of strength, permeability and flowability achieved by using cement along with sodium silicate. The sand mixture may consist of about 2% cement, 4-5% sodium silicate and 1% pitch or molasses. The large sized moulds can be produced for ferrous castings by the sand mixture, By using foaming chemicals in the sand mixture, flowable cement slurry can also be produced.
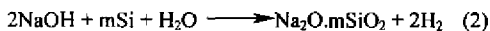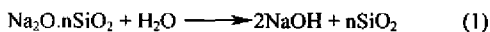
Dicalcium Silicate Process

Dicalcium silicate has been found to be a very effective hardening agent when used with sodium silicate as a binder. Unlike the ferro-silicon process

where hardening is due to exothermic reaction, the chemical reactions taking place in this process do not cause any evolution of heat. The rate of hardening depends on the grain fineness of the silicate and the temperature of the sand. The fineness of the silicate grains should not be less than 200 mesh. To prepare the mixture, about 2–3% of dicalcium silicate and 5% sodium silicate are mixed with sand, along with suitable foaming chemicals. The mixture can flow easily in the mould. Mixing time is from 3–5 min. The sodium silicate used in this process should have a high mass ratio 1:2.3 to 1:2.8 and specific gravity between 1.48 and 1.50. This process finds its main application in medium and heavy castings, both in grey iron and steel.

Ferro-silicon Process
In this process, silica sand is hardened and bonded with the reaction product obtained by exothermic reaction between sodium silicate and ferro-silicon powder. The method is based on the principle that if sodium silicate and powdered ferro-silicon are mixed in a weight ratio of 2.25:1, foaming action takes place and the temperature is rises simultaneously, reaching a boiling condition at about 90 °C. During the chemical reaction, steam and hydrogen are liberated.

The reactions taking place are:

$$Na_2O.nSiO_2 + H_2O \longrightarrow 2NaOH + nSiO_2 \qquad (1)$$

$$2NaOH + mSi + H_2O \longrightarrow Na_2O.mSiO_2 + 2H_2 \quad (2)$$

The reaction continues as long as silicon and water are present and finally the products of reaction form a hard spongy mass. The sand used in the mixture should be dry and should have a grain size to suit the requirements of the metal to be cast. Normally, for ferrous castings, silica sand of 65 mesh and for non-ferrous work, 100 mesh would be suitable. The sand is first mixed with about 2% of its weight of ferro-silicon, containing 75–80% silicon, which should be powdered to 3–3.5 microns size. Sodium silicate of the correct grade, specific gravity and mass ratio is then added (about 5% of the weight of the sand) and the mixing continued. The specific

gravity and mass ratio suitable under moderate climatic conditions are 1.3–1.35 and 1:2.0–1:2.3, respectively, precise control of the mixing cycle and basic additives is necessary to obtain the desired mould characteristics. When using ferro-silicon, the same process may be modified by adjusting the basic additives and mixing it by a foaming agent to enable the use of the mixture as flowable slurry in the mould.

The slurry is poured over the pattern and it occupies all the areas uniformly.

Carbon Dioxide Process
The principle of working the CO_2 process is based on the fact that if CO_2 gas is passed through a sand mixture containing sodium silicate as the binder, immediate hardening of sand takes place as a result of the chemical reaction between sodium silicate and carbon dioxide. The bonding strength obtained by the hardening action is sufficient to eliminate the need for any drying or baking of the mould and the metal can be immediately poured. The main chemical reaction can be represented in simplified form as:

$$Na_2O.mSiO_2.xH_2O + CO_2 \longrightarrow Na_2CO_3 +$$
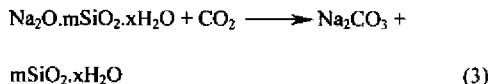
$$mSiO_2.xH_2O \qquad (3)$$

The sodium silicate used is based on $Na_2O.mSiO_2.xH_2O$ system where the ratio of total soda to total soluble silica, called mass ratio is a variable factor affecting the characteristics of the process. The common sodium silicate used for the CO_2 process in foundries should have a mass ratio varying from 1:2.1 to 1:2.5. Adding a suitable quantity of sodium hydroxide can raise this ratio.

The specific gravity of the liquid depends on the mass ratio and its water content, which for foundry use may vary from 1.55 to 1.71. The sand used for the process must be dry and free of clay. This sand is usually mixed in a sand mixer with about 3–5% of sodium silicate.

But since sodium silicate systems with hardeners such as ferro-silicon, portland cement and dicalcium silicate are less widely used, we pay our attention to detailed discussion of sodium silicate

systems with an appropriate acid such as CO_2 or an organic ester [2, 3], where sand mixture is hardened by gasification with carbon dioxide or by heating with flame for a few seconds respectively. In both two cases of acidification, either directly or indirectly, the produced SiO_2 from the reaction contains a certain number of water molecules and is represented as $SiO_2.xH_2O$, which is called silica gel. This silica gel is responsible for giving the necessary strength to the mould.

Suitable additives may be introduced to obtain specific properties. Additives to the moulding materials improve their properties; such as: flow-ability, compactability, bond improvement, prevention of sand expansion defects and breakdown properties. Common additives are sawdust, iron oxide, sugar, invert sugar, dextrin, glycol, coal powder, wood flour, sea coal and kaolin clay among many others. Dextrin, as also coal powder, wood flour and sea coal, improves collapsibility. Iron oxide prevents hot deformation of cores and produces a smooth interface between the mould and the metal, thus helping prevention of metal penetration and achieving good surface finish. Kaolin clay is added to promote mould stability and is often used in steel casting work. Invert sugar is often mixed in these compounds, as it is an effective breakdown agent and an aid in improving collapsibility.

Some moulding sand additives produce lustrous carbon, e.g. coal dust and hydrocarbons. These are vaporized at high temperatures and are simultaneously decomposed and therefore, the sand particles become coated with lustrous carbon and then are not easily wetted by molten metal. The aims of using these kinds of additives are to reduce metal penetration into the sand, to improve the casting surface finish and facile separation of the casting from the temporary mould [4].

Finally the temporary mould is then filled with molten metal. The production of molten metal involves selection of the alloy composition, raw materials and alloying elements. The refractory materials that come into contact with the molten metals are of vital importance. Breaking down the bond of the moulding material with heavy hammers, vibrating grates, and tumbling mills or water jets causes the separation of the casting from the mould. The casting surfaces are then cleaned and descaled by shot or sand blasting and ground smooth.

EXPERIMENTAL

Materials
The sodium silicate of technical grade and pitch or sugar was obtained from a local supplier in Iran and was used as received.

Apparatus
The viscosity of prepared solutions was measured using a Brookfield-viscometer model LV1 at 25 °C.
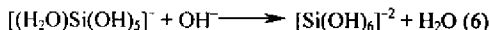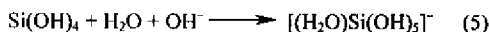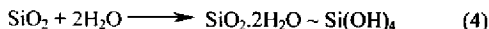
Preparation of Sodium Silicate Solution
Sodium silicate (65 g) was added to 35 mL water. The mixture was then heated to 70 °C, while stirring. The solution was kept under these conditions for 60 min until the dissolution was completed. The concentration of this solution was adjusted to 65% (w/w) in water. The mixture was stirred during the whole time. Adequate granular sugar was added to this solution in an amount of 1.0–2.0% weight percent with respect to sodium silicate used to achieve a concentrated silicate solution. The viscosity of this solution was controlled to 500 centipose by addition of sugar. The solution was cooled to room temperature and its apparent viscosity was measured at 25 °C. This solution was then ready for use as an adhesive.
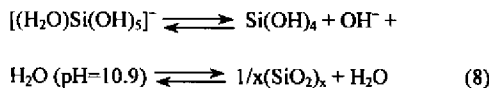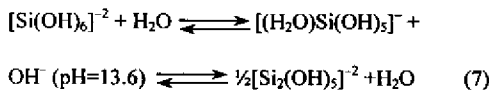
RESULTS AND DISCUSSION

The soluble silicate glasses are prepared by fusion of glass sand with sodium or potassium carbonate. Glasses over a wide range of mass ratios may be obtained, but only those glasses containing less SiO_2 than the proportion of about $1Na_2O: 4SiO_2$ can be dissolved in water. The soluble sodium silicates of commercial value include orthosilicate (Na_4SiO_4), metasilicate (Na_2SiO_3), disilicate ($Na_2Si_2O_5$) and more

highly siliceous products ($Na_2Si_4O_9$) [5]. One of the most common types of sodium silicate, or water glass, contains the oxides in the proportion $1Na_2O$: $3.3SiO_2$. This material as a viscous solution containing around 28% SiO_2, is used as an adhesive, in water purification and for making silica gel. Silica is slightly soluble in water and the dissolved silica reacts with hydroxyl ion to form silicate ions. Silica dissolves in alkali when the pH exceeds about 10.5. This reaction involves depolymerization of silica through hydration and dissolution to $Si(OH)_4$, followed by addition of hydroxide ion to form silicate ion. The conversion of silica to silicate ion in terms of coordination number of 6, for silicon; may be represented as follows:

$$SiO_2 + 2H_2O \longrightarrow SiO_2.2H_2O \sim Si(OH)_4 \qquad (4)$$

$$Si(OH)_4 + H_2O + OH^- \longrightarrow [(H_2O)Si(OH)_5]^- \qquad (5)$$

$$[(H_2O)Si(OH)_5]^- + OH^- \longrightarrow [Si(OH)_6]^{-2} + H_2O \quad (6)$$
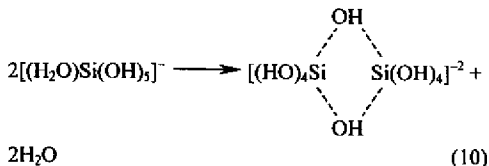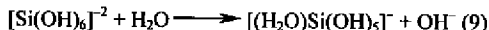
On the other hand, when a solution of a soluble silicate, which is always highly alkaline, is neutralized by acid to a pH below 10.5, the silicate ions decompose to silicic acid, which then polymerizes to silica. The neutralization of a solution of soluble metasilicate may be represented as follows:

$$[Si(OH)_6]^{-2} + H_2O \rightleftharpoons [(H_2O)Si(OH)_5]^- +$$

$$OH^- \text{ (pH=13.6)} \rightleftharpoons \tfrac{1}{2}[Si_2(OH)_5]^{-2} + H_2O \qquad (7)$$

$$[(H_2O)Si(OH)_5]^- \rightleftharpoons Si(OH)_4 + OH^- +$$

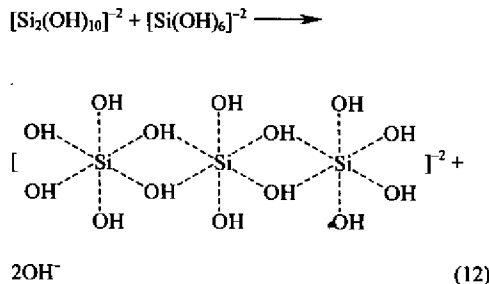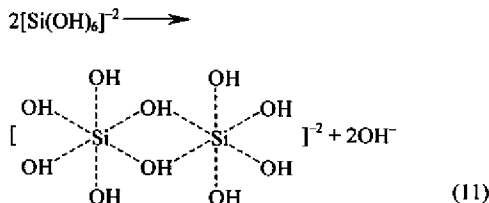$$H_2O \text{ (pH=10.9)} \rightleftharpoons 1/x(SiO_2)_x + H_2O \qquad (8)$$

In the above and next formulations, for the explanation of polymerization phenomena in the silica-water system, the coordination number of silicon is proposed to be 6.

Further studies [6], show that above pH 13.6 the metasilicate ion, corresponding to monomer, is stable; and between pH 13.6 and 10.9, the disilicate ion, corresponding to dimmer is the principal anion present in solution. The dimerization of the silicate ion can be expressed by the following way:

$$[Si(OH)_6]^{-2} + H_2O \longrightarrow [(H_2O)Si(OH)_5]^- + OH^- \quad (9)$$

$$2[(H_2O)Si(OH)_5]^- \longrightarrow [(HO)_4Si \overset{OH}{\underset{OH}{<>}} Si(OH)_4]^{-2} +$$

$$2H_2O \qquad (10)$$

High molecular weight aggregates [7] of silica are formed when the pH of an alkali silicate solution is lowered below about 10.9. This corresponds to SiO_2/Na_2O ratio of 4.0, namely highly siliceous sodium silicate ($Na_2O:4SiO_2$). These higher polysilicate ions may be in equilibrium with metasilicate and disilicate anions, and this polymerization process can be express by the following way:

$$2[Si(OH)_6]^{-2} \longrightarrow$$

$$(11)$$

$$[Si_2(OH)_{10}]^{-2} + [Si(OH)_6]^{-2} \longrightarrow$$

$$2OH^- \qquad (12)$$

So higher molecular weight polymer can be formed according to the following reaction:

$$[Si(OH)_5.[Si(OH)_4]_n.Si(OH)_5]^{-2} + [Si(OH)_6]^{-2} \longrightarrow$$

$$[Si(OH)_5.[Si(OH)_4]_{n+1}.Si(OH)_5]^{-2} + 2OH^- \qquad (13)$$

It is seen that each $Si(OH)_4$ unit is coordinated with the former polymer in a linear chain and a high molecular weight polymer is produced.

According to these chemical reactions, the polymerization of produced $Si(OH)_4$ begins in first stage, its concentration in solution is quickly reduced, and high molecular weight aggregates are formed at low pH in aqueous solution. These correspond to polysilicate ions.

These polysilicate ions are responsible for binding the sand particles.

In other word, when the alkali is added to soluble silicate, the polysilicic acid is depolymerized and by addition of acid to soluble silicate, the polymerization is occurred. Therefore, breaking inter-particle forces holding the polymeric silicate anions in solution by adding a mineral acid, to lower the pH of the solution, silica can be produced. The equilibrium shifts from the monomeric to the disilicate ion when the pH drops below 13.6, while transformation of disilicate to higher polysilicates occurs only as the pH falls considerably lower, namely below about 10.9.

In studying the rheology of polymer solution, the appropriate concentration variable for the particles is their volume fraction $(\emptyset)$, which is the ratio of the volume of the particles to that of the entire dispersion. In prepared solutions the concentration is selected at a constant level, so volume fraction is constant and equal to $\emptyset = 0.65$. According to experimental results, the suitable concentration and viscosity of the silicate solution is 65%(w/w) and 500 cp, respectively. Since viscosity is directly proportional to volume fraction of silicate solution, viscosity increases with increasing the concentration of solution. Viscosity studies on these silicate solutions indicate that the high viscosity of such concentrated solution which may even become syrupy, is not due to aggregation or polymerization, but due to the fact that the molecules are close to one another [8].

Sodium silicate solution in presence of an ester acts as a binder in a two stage reaction; hydrolysis of the ester followed by gelling of the silicate at the lower pH. The bond strength and reaction velocity is dependent on the SiO_2/Na_2O ratio of the sodium silicate and the type and the amount of ester used. Heating the mixture of moulding sand, sodium silicate, hardener (an organic ester), and together with suitable additives for about 1.0 min, produce the temporary mould. The flame causes the ester to decompose to produce acid and alcohol. The produced acid lowers the pH, thereby causing the silicate to gel and binds the sand particles.

In case of using CO_2 as a hardener, the bond strength of the sand mixture depends on the Na_2O/SiO_2 ratio of the sodium silicate, length of time spent and pressure of gasification rate step by carbon dioxide. The hardening process involving gassing of the sand mixture with carbon dioxide first established the importance of sodium silicate as binder. This process became of particular importance for core making on account of its rapid turn-around time (10–25 s), and environmentally it is extremely beneficial [4].

CONCLUSION

The concentrated 3.3 ratio $(SiO_2:Na_2O)$ sodium silicate solution, the moulding sands, and pitches or sugar with suitable additive and cross-link agent are composed to make a temporary mould. The 3.3 ratio sodium silicate solution with a suitable viscosity, as an inorganic binder is responsible for binding the different sand particles, in presence of an organic ester (by using flame) or carbon dioxide. A viscosity study indicates that the high concentrated silicate solution is used to wet the sand grains. Since a suitable viscosity is necessary for improving wettability of sand particles and consequently for increasing the temporary mould stability, the sugar is used as a thickening agent, to concentrate the binder solution at a desirable limit. The suitable limit of viscosity for sand moulding is about 500 centipoise. The produced concentrated silicate solution forms a thin film around the sand particles. The so-called sand particles, when come into contact with each other can form a rigid network rapidly due to gellation in presence of a suitable curing agent.

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