Sodium Silicate a Binder for the 21st Century

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ABSTRACT

EVOLUTION OF SILICATE BASED BINDERS

The 90’s have seen an increased demand in the performance requirements of material being agglomerated. Today it is no longer good enough to have a binder that adheres at a low cost. There is now a demand for binders to be environmentally friendly and allow for better process efficiencies while still being reasonably priced. In recognition of these increased performance requirements, sodium silicate based formulations have been broadened to offer increased performance. This paper discusses silicate chemistry, considerations when using silicate and some generic silicate binder formulations.

1.0 INTRODUCTION

Binders have been described by Englenteitner¹ as “an additive to the material being agglomerated that produces bonding strength in the final product. A binder can be a liquid or solid that forms a bridge, film or matrix filler or that causes a chemical reaction.” This definition is very applicable to sodium silicate since silicates can be either liquids or solids. The diverse chemistry of silicate means that it can bond by forming a film, reacting to form a matrix or chemically binding with the material being agglomerated. An understanding of the diversity of silicate will assist in formulation.

2.0 SILICATE CHEMISTRY

2.1 WHAT ARE SODIUM SILICATES?

Soluble silicates are one of the oldest and most benign industrial chemicals. The industrial beginnings of sodium silicate start in 1818 but references to making sodium silicate like products can be traced back as far as the ancient Phoenicians². One reason for the early development of soluble silicate was the relatively simple process for manufacturing it. Sodium (or potassium) silicates are manufactured by fusing sand (SiO₂) with sodium or potassium carbonate (Na₂CO₃ or K₂CO₃) at 1100-1200°C. The resulting glass can be dissolved with high pressure steam to form a clear, slightly viscous liquid known as “waterglass.” The liquids can also be spray-dried to form quick-dissolving, hydrous powders. Dissolved or liquid silicates are the most popular commercial form of sodium silicate for agglomeration applications, although there are occasions when hydrous powders or ground glass are better suited.

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2.2 SILICATE RATIO

The most important property of sodium silicate is the weight ratio of SiO₂: Na₂O. Silicates are commercially produced in the ratio range of 1.5 to 3.2. The ratio represents an average of various molecular weight silicate species. Figure #1 in the appendix shows a small sample of the various silicate species that can be found in a silicate solution. Figure #2 shows how the ratio of silicate dictates which silicate species is dominant in solution. It is at this molecular level that such things as rate of gelation, precipitation, dehydration, water resistance, etc. are determined.

As will be discussed throughout the paper, there is not one ideal silicate ratio for use in agglomeration applications. Having said that, high “3.2” ratio silicates tend to be the most commonly used. The selection of silicate ratio will be based on such things as:

- type of binding mechanism
- set-up time needed
- material being agglomerated

3.0 CHEMICAL REACTIONS OF SILICATE

Sodium silicate is unique in that it can undergo four very distinct chemical reactions⁴. These reactions have been defined as:

- hydration/dehydration
- gelation
- precipitation
- surface charge modification

These reactions allow silicate to act as a:

- film binder
- matrix binder
- chemical binder

Silicate can adhere an agglomerated material by one or more of its chemical reactions. Sometimes silicate-based formulations achieve their best performance by taking advantage of more than one of these adhesion mechanisms.

3.1 HYDRATION/DEHYDRATION

As water is removed from liquid silicate, the silicate progressively becomes tackier and more viscous. The removal of a relatively small amount of water will render the liquid silicate a glassy film. Liquid silicates with a high 3.2 ratio are best suited for acting as a film binder. The lower alkali content of a 3.2 ratio silicate has less affinity for water and can therefore dry quicker. Upon drying the bond is less susceptible to moisture pick-up, but to achieve more complete water resistance, some degree of either heat or chemical setting needs to occur.

The most commonly sited problem with using silicate as a film forming binder is achieving sufficient green bond strength. A number of things can be done on the processing side to ensure faster and more predictable green strength:
• temperature control of the agglomerated material
• moisture control of the agglomerated material
• lay-up time to correspond with tack development
• proper mixing

The development of green bond strength can also be improved by the incorporation of relatively small amounts of other quicker setting film forming adhesives such as starch, dextrin, molasses or glycerin.

Table 1 in the appendix shows a laboratory study conducted by PQ that looked at improving the green bond strength of silicate by incorporating starch and glycerin as secondary film formers. The material being agglomerated was steel mill ferrous waste. The study showed that green bond strength improved with the addition of either starch or glycerin. A secondary benefit of including a material such as starch or glycerin is that a higher degree of flexibility is imparted to the silicate film. It should be noted that the development of green bond strength can also be improved by the addition of a calcium source such as hydrated lime\(^4\). The reaction of silicate with calcium will be discussed in section 3.3.

When using sodium silicate as a film forming binder, it is sometimes beneficial to include a small amount of silicate-compatible surfactant (e.g., anionic or non-ionic surfactant). Laboratory studies at PQ show that the inclusion of a small amount of surfactant can reduce the surface tension of a 3.2 ratio silicate from 77 dynes to 40 dynes. Benefits of a reduced surface tension are easier application of binder and the ability to apply the binder thinner which will aid in decreasing the drying time.

### 3.2 GELATION/POLYMERIZATION

Gelation/polymerization reactions occur rapidly when the pH of liquid silicate falls below 10.7. Silicate species begin crosslinking to form polymers. Although the bond formed by the polymerized silicate is not as strong as the bond formed by dehydration, it has a higher degree of water resistance. This reaction can play a role in agglomeration where the surface of the material being agglomerated is acidic or the material being agglomerated is exposed to an environment high in CO\(_2\). Setting aids can be added to the silicate to induce gelation/polymerization. Examples of some setting aids are acidic salts, organic acids, esters or carbonates. The inclusion of a polymerizing aid with silicate is quite common in grouting and foundry industries.

Once again a “3.2” ratio silicate would be best suited for promoting the gelation/polymerization reaction. The low alkali content of the “3.2” ratio silicate allows for quicker neutralization.

### 3.3 PRECIPITATION REACTION OF SODIUM SILICATE

Soluble silicates react almost instantaneously with multivalent metal cations to form the corresponding insoluble metal silicate. Examples of common metal ions that are reactive with silicate include: Ca\(^{+2}\), Mg\(^{+2}\), Zn\(^{+2}\), Cu\(^{+2}\), Fe\(^{+3}\), etc. If the material being agglomerated contains a significantly high amount of positive cations on its surface then the silicate can act as a chemical binder. Fly ash is an example of a material that can bond chemically with
silicate. In general, high ratio “3.2” silicates are most suitable for chemical bonding since it is the siliceous portion of the silicate that is reacting with the cations.

### 3.3.1 Portland Cement Acceleration

It is the very quick reaction with Ca\(^{+2}\) that allows silicate to be used as a cement accelerator. A problem commonly encountered with using Portland cement (PC) as a matrix binder is the achievement of sufficient green bond strength. The incorporation of silicate into a cement-based formulation will accelerate the set of the cement.

### 3.3.2 Pozzolanic Cement Activation and Acceleration

Pozzolan is defined as “finely divided siliceous or siliceous and aluminous material that reacts chemically with slaked lime at ordinary temperature and in the presence of moisture to form a strong slow-hardening cement”\(^5\). Examples of pozzolans are cement kiln dust, fly ash, granulated ground blast furnace slag and other metallic slags. The benefits of using pozzolans as a matrix binder for agglomeration is that they tend to be economical, environmentally friendly, more absorbent of liquids and produce a highly durable product. Compared to PC, pozzolans have two disadvantages; they are slower to set and are less tolerant of impurities (e.g., clays, silts, metal ions, sulfides, phosphates, etc.).

In order to achieve the necessary green strength, pozzolans must be “activated” either by heat or chemically by alkali. Silicates are widely accepted as the best material to activate pozzolans\(^6\). The reason for silicate’s effectiveness is that both the cation and anion are useful in making pozzolan cements. The alkali serves to activate (i.e., to release into solution for reaction) the siliceous material present in pozzolans, and the silica, or anion, portion contributes to the formation of calcium silicate hydrate, a cementious phase that is the matrix binder. Due to the importance of alkali, it is recommended that low ‘2.0’ ratio silicates be used for pozzolan cement activation. Figures #3 & #4 in the appendix shows the performance advantage of using silicate with cement kiln dust to solidify a variety of waste materials\(^7\).

### 4.0 CONCLUSIONS

The diverse chemistry of sodium silicate along with the many commercial varieties of silicates presents a complex choice for those who wish to agglomerate with sodium silicate. It is hoped that this paper will have helped clarify the different formulation possibilities.

### REFERENCES:

1. Engelleiter, Glossary of Agglomeration Terms, 1990
4. W. Pietsch, U.S. patent 4, 105, 457 (Midrex Corp.), 1978
5. Webster’s Ninth New Collegiate Dictionary, Merriam-Webster Inc 1990
APPENDIX

SILICATES: CHEMICAL STRUCTURES

**Figure 1:** Sample of Silicate Species

- **Monomer**
- **Trimer**
- **Cyclic Tetramer**
- **Cubic Octamer**
- **Cyclic Trimer**

**Figure 2:** Silicate Ratio vs. Molecular Weight Distribution for 1M Solutions

**Qualitative Interpretation of Silicate Anion Structure**

- EQUILIBRIA - 1 MOLAR SOLUTION
  - Monosilicate
  - Chains & Cyc Trimers
  - Larger Rings
  - Complex Structures

**Graph**

- Apparent Relative Concentration
- Ratio

- Monosilicate
- Larger Rings
- Complex Structures, Polymers
- Chains & Cyclic Trimers
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### TABLE 1: IMPROVED GREEN BOND STRENGTH FOR FERROUS STEEL WASTE

<table>
<thead>
<tr>
<th>Formulation</th>
<th>% total binder</th>
<th>3' drop test</th>
<th>7' drop test</th>
<th>% lost on shaking</th>
</tr>
</thead>
<tbody>
<tr>
<td>80% N® silicate (diluted)*: 20% starch</td>
<td>1%</td>
<td>Breaks</td>
<td>Disintegrates</td>
<td>100%</td>
</tr>
<tr>
<td>&quot;</td>
<td>3%</td>
<td>No breakage</td>
<td>2 halves</td>
<td>62%</td>
</tr>
<tr>
<td>&quot;</td>
<td>5%</td>
<td>No breakage</td>
<td>No breakage</td>
<td>33%</td>
</tr>
<tr>
<td>80% N® silicate (diluted)*: 20% glycerin</td>
<td>1%</td>
<td>Breaks</td>
<td>Disintegrates</td>
<td>100%</td>
</tr>
<tr>
<td>&quot;</td>
<td>3%</td>
<td>No breakage</td>
<td>2 halves</td>
<td>75%</td>
</tr>
<tr>
<td>&quot;</td>
<td>5%</td>
<td>No breakage</td>
<td>No breakage</td>
<td>39%</td>
</tr>
</tbody>
</table>

*N® silicate was diluted to 1 part silicate: 2 parts water

**PROCEDURE:**
- Ferrous steel waste was weighed into a mixer bowl
- Appropriate amount of binder was added to the bowl and mixed
- 20gm were added to a die and pressed for 5s at 6000 psi
- Testing was done immediately out of the press

**FIGURE 3: Efficiency of cement kiln dust with and without silicate**

**FIGURE 4: Strength of Cement Kiln Dust with and without Silicate**