Patented Process to Extract High Purity Silica from Rice Hulls

Sustainably produced amorphous biogenic silica

August 11, 2016
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**Introduction**

Silica (silicon dioxide) is the most abundant compound on Earth. Virtually all of this silica is in the crystalline form, meaning that the silica molecules are aligned in a symmetrical shape. This form of silica, while useful in some applications such as construction, is low value material. In fact, sand is one of the most common forms of crystalline silica. For silica to be more useful in various applications it must be in the amorphous, or non-crystalline, form. The traditional (and current) processes for making amorphous silica are energy intensive, chemical intensive and costly methods which break down the crystalline structure of silica in sand and transform it to the amorphous form. Needless to say these methods have a very large carbon footprint and are not Earth friendly.

IST has taken a different and novel approach. We partner with Nature to produce very high purity amorphous silica, named StratoSil®. Rice plants naturally dissolve and extract silica from the soil and water and deposit amorphous silica into the outer covering of rice seeds, known as rice hulls. There, the silica provides protection for the rice embryo within. In the rice milling process hulls are removed and represent a waste disposal problem. IST’s patented technology pre-treats rice hulls with a very mild process to remove some trace minerals and to condition the carbon based polymers in the hulls to burn away completely in a controlled fashion, thereby leaving behind high purity silica. Nature places the amorphous silica in rice hulls, IST’s technology allows us to harvest it. IST’s low intensity process emits only a small fraction of the CO₂ that is emitted by current methods of making synthetic amorphous silica. In addition to being Earth friendly, IST’s process is also very cost effective.

**Conventional Amorphous Silica Manufacturing**

As previously indicated, current methods for producing synthetic amorphous silica are very energy and chemical intensive. There are two primary methods for making this product. The first process results in a product known as precipitated silica, with about 92 % silica purity. The second process results in a product known as fumed silica, with about 99.95 % purity. Each product is utilized in a number of applications with fumed silica being used in those that require a very high level of purity.

*Approximate volume of amorphous silica usage by application segment:*

<table>
<thead>
<tr>
<th>Application</th>
<th>% of Silica Tonnage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastomers</td>
<td>50.1</td>
</tr>
<tr>
<td>Food and Personal Care</td>
<td>7.2</td>
</tr>
<tr>
<td>Agricultural Products</td>
<td>5.5</td>
</tr>
<tr>
<td>Coatings</td>
<td>5.0</td>
</tr>
<tr>
<td>Adsorbents/Dessicants</td>
<td>4.9</td>
</tr>
<tr>
<td>Batteries</td>
<td>3.5</td>
</tr>
<tr>
<td>Plastics</td>
<td>3.2</td>
</tr>
<tr>
<td>Sealants</td>
<td>2.5</td>
</tr>
<tr>
<td>Anti-foams</td>
<td>1.9</td>
</tr>
<tr>
<td>Catalysts</td>
<td>1.8</td>
</tr>
<tr>
<td>Resins</td>
<td>1.8</td>
</tr>
<tr>
<td>Other Miscellaneous</td>
<td>12.6</td>
</tr>
</tbody>
</table>
As discussed previously, the key to high priced silica is to have a 100% amorphous or non-crystalline form. While IST lets Nature do the work of depositing amorphous silica into rice hulls the chemical industry uses brute force to break down the crystalline structure of sand. In the case of precipitated silica, sand is first reacted with soda ash (caustic) in high temperature furnaces to make sodium silicate. Sodium silicate is then dissolved in water and then sulfuric acid is added until amorphous silica precipitates out of solution. The silica is then washed and dried, followed by milling and packaging. The process uses a great deal of heat which is generated from fossil fuels. The chemicals involved, soda ash and sulfuric acid, are high intensity and dangerous materials that carry a large carbon footprint of their own. The intense nature of the inputs results in a high cost process. The end product is an amorphous silica with a purity of about 92%. In addition, precipitated silica contains about 2-3% salt which is a remainder from the acid/base reaction inherent to the process. A variant of precipitated silica, known as silica gel, is made in a similar manner but in the case of silica gel sulfuric acid is reacted all at once with the sodium silicate. Silica gels range in moisture from very dry to as much as 60% water.

In addition to a high output of greenhouse gases from fossil fuel consumption and chemical inputs, this process also emits a considerable amount of wastewater which must be further treated.

Precipitated silica manufacture by conventional means from sand:

If making precipitated silica is intense the process of making fumed silica is extraordinarily intense. To obtain high silica purity (which we obtain naturally with StratoSil®), producers of fumed silica first combine sand (sometimes gravel) and coke and react the mixture in a very high temperature electric arc furnace. This process results in the breakdown of silica and the formation of elemental silicon. The silicon is then reacted with hydrochloric acid to form silicon tetrachloride, a very dangerous chemical intermediate. Silicon tetrachloride is then reacted in yet another high temperature furnace, fueled by hydrogen, to allow the formation of high purity particles of silica and re-formation of hydrochloric acid. This “fumed” silica (also known as pyrogenic silica) must then be separated from acid vapors and de-acidified. The end result is amorphous silica with a purity of 99.95%. All this high intensity, high input processing results in a very high cost structure for fumed silica.

Given the very large amounts of electricity and hydrogen consumed, which are derived from fossil fuels, the fumed silica process emits a large amount of greenhouse gases. In addition the chemicals and raw materials consumed carry their own carbon footprint.

Wastes from the fumed silica process are the slag from the initial smelting process to produce elemental silicon and some acid neutralization wastes from the scrubbing of acid gases.
In summary, current conventional methods for producing amorphous silica are resource intense, costly, emit a considerable amount of greenhouse gas and produce significant waste streams that must be treated or disposed of.

**The Innovative Silica Technologies Advantage**

As previously discussed, rice plants naturally deposit amorphous silica in hulls, the outer protective coat of rice seeds. Hulls contain about 20% silica with the balance of the hull material in the form of carbon based plant polymers such as cellulose, hemi-cellulose and lignin. The silica is interwoven within these plant polymers in the hull and provides a solid protective barrier for the seed embryo within.

*Why not just burn the hulls to obtain silica without the IST patented pretreatment?*

Fair question. In fact many tons of rice hulls are burned every year, especially in less developed parts of the World, as a low cost fuel for cooking. What we’ve learned is that untreated hulls do not burn cleanly or in a controlled manner which results in overheating of the silica and conversion to the undesirable crystalline form. In addition, in direct combustion some carbon fuses with the remaining silica, resulting in what is known as black or gray rice hull ash – a relatively useless material that often requires land filling or some other means of safe disposal.

*IST’s process provides a high purity white silica, direct combustion results in useless black ash:*
So, what is it about rice hulls that keeps them from burning cleanly and fully?

As they say, the devil is always in the details. In addition to containing a large amount of amorphous silica, rice hulls also contain a tiny amount of metallic oxides (also known as alkali oxides) that act as a flux, meaning that when you burn untreated hulls these oxides create microscopic “hot spots” which crystallize the silica. The other problem is that complex long chain plant polymers such as lignin are difficult to burn away completely, leaving amounts of carbon behind. The combination of hot spots and free carbon also result in the fusing of carbon to silica.

How the IST process gets the job done in a low-intensity manner.

IST founder and inventor Larry Shipley came up with a simple approach to solving the problem. First, rice hulls are washed with a very dilute solution of citric acid in distilled water. Citric acid is a mild food grade acid (it naturally occurs in citrus fruits). Citric acid is excellent at binding with metallic oxides and allows them to be removed from the hulls very efficiently. An added benefit is that citric acid removes trace metals from the hulls, so StratoSil® has a very low metal content, something that helps with many silica applications. After the citric acid wash a second wash with hydrogen peroxide, again in distilled water, is done. As we all know, hydrogen peroxide ($\text{H}_2\text{O}_2$) is found in most medicine cabinets to treat cuts and scrapes. It works by breaking down into water and free oxygen upon contact with organic material. In the case of rice hulls the free oxygen reacts with the lignin polymers to in essence chop them up into smaller fragments at the molecular level. This allows the lignin to burn cleanly and completely during final combustion.

To make the pretreatment process efficient we will employ a counter current washing system. Envision a long conveyor trough with a number of tank sections built into it. Distilled water is added at one end and flows in one direction. Hulls are added at the other end and are mechanically conveyed in the opposite direction, being carried into one tank section after another. Citric acid and hydrogen peroxide are added at appropriate points along the way. All very simple, efficient and uses very little water.

Once the treated hulls emerge they contain about 60 % water and must be dried. This is done in a conventional biomass drier fueled by heat from the next step which is combustion of the treated and dried hulls. So, rice hulls are not only our raw material for amorphous silica but also provide a renewable fuel for our process.

Treated and dried hulls are combusted in a conventional biomass burner such as would be used to burn wood chips or sawdust. Given the pretreatment we can easily control the temperature of the burn and also obtain complete combustion. The silica of course does not burn and exits the burner as a snow white, high purity product. The silica is then ready for grinding into smaller particle sizes according to customer requirements and packaged in 50 lb. bags or larger tote sacks.

The IST process:
StratoSil® and Sustainability

As described above, Nature does the heavy lifting by depositing amorphous silica into rice hulls. Unlike the chemical industry, which relies on large energy and chemical inputs, IST’s process is low intensity. In addition, rice hulls represent not only a source of silica but also a renewable fuel which provides heat for drying wet, treated hulls and also for production of the distilled water we utilize in our process. IST’s only fossil fuel input is the small amount of electricity we use in the process. The burning of rice hulls is carbon neutral – the CO₂ emitted is offset by the amount of CO₂ absorbed from the atmosphere by the next rice crop.

The water utilized in our hull pretreatment process picks up a small amount of organic material and metal oxides from the hulls (parts per million levels). We will utilize a reverse osmosis system to purify this water for re-use in the system. The small waste stream will be land applied where the trace metals and organic materials will be absorbed back into plants where they are needed for growth.

Solid waste? Not in the IST process. We produce none.

At IST we are committed to good stewardship of the World’s resources. By making StratoSil® in a sustainable manner we will make our small contribution toward a bright environmental future for generations to come.

![Net CO2 Emissions - StratoSil® vs. Synthetic Fumed and Precipitated Silica (per ton produced)](chart)

Intellectual Property

IST holds 8 issued patents in the U.S., E.U., China, India and Japan related to the production of high purity amorphous silica from plant sources. We are working on a number of additional patents regarding the use of StratoSil® in several applications.

StratoSil®

Sustainably produced, high purity silica made in partnership with Nature