BGR Industrieworkshop zur Gewinnung und Verarbeitung von Quarzrohstoffen in Deutschland

Hochreiner Quarz – der feine Unterschied

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A leading European supplier of industrial minerals

- Mining and refinement of industrial minerals for the...
  - paper
  - glass
  - ceramic
  - paint
  - plastic
  - construction industries
- ...with 300 products and more than 2000 customers in 40 countries.

Dorner ANZAPLAN
The Service Company in Strategic Minerals and Metals

- Founded in 1985 to become the most independent venture within the Dorner Group.
- A full service specialist in high-purity industrial and strategic minerals and metals.
ANZAPLAN Services
Leading in the Development of Quartz Projects

- Process Development
  - Exploration and Basic Analysis (Resources)
  - Process Design and Technology (Reserves)
  - Mineral Concentration
  - Extraction and Purification
- Pilot Scale Processing
  - Sample production and application tests
  - Customer approval
- Project Valuation and Engineering

Customer Base

- Mining Co.: 33%
- Financial Sector: 20%
- Production Co.: 22%
- Engineering: 3%
- Research Institutes: 3%
- Traders: 6%
- Others: 10%
- Consultants: 3%
- Financial Sector: 20%

DORFNER Analysenzentrum und Anlagenplanungsgesellschaft mbH
Distribution of recent ANZAPLAN Projects

For more information download our Whitepapers on www.anzaplan.com
Why getting interested in Quartz?

Quartz is used in many applications
Different Quartz Deposits serve Different Applications

<table>
<thead>
<tr>
<th>Quartz Type</th>
<th>Properties</th>
<th>Preferred Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>High grade pegmatite and hydrothermal quartz</td>
<td>Chemical purity (&gt;99.9%), pure quartz lumps, white and milky or transparent</td>
<td>High Purity Quartz, optics, lamp tubing, semiconductor (crucibles), UMg-/SoG-silicon, piezo-quartz and microelectronics (EMC filler)</td>
</tr>
<tr>
<td>Quartzite, low grade pegmatite and hydrothermal quartz</td>
<td>Chemical purity (&gt;95%), lumpy hard rock</td>
<td>Refractory materials (SiC), MG-silicon, Silicon Alloys (e.g. FeSi); Engineered Stone</td>
</tr>
<tr>
<td>Quartzitic Sandstone</td>
<td>Chemical purity (&gt;90%)</td>
<td>Construction industries, dimensioning stones, glass sand, aggregates</td>
</tr>
<tr>
<td>Silica (quartz) Sand</td>
<td>Chemical purity (&gt;90%), granulometric properties</td>
<td>Glass sand and foundry industry (molds and cores), filtration, ground silica (filler), ceramics (glazes) and proppants (hydraulic fracking)</td>
</tr>
</tbody>
</table>
... and high purity is of high value

1 ton of quartz can cost as much as one ton of an automobile

- High temperature lamp tubing (e.g. Xenon bulbs)
- Telecommunication and Optics
- Semiconductor Applications incl. Crucibles Production
- Microelectronics (EMC Fillers)
- (Solar) Silicon, UMG or SolSilc Processes
... with only limited amount of suppliers and deposits

- US-based Unimin Corp./Sibelco still dominates the global high purity quartz market with its Iota® Brand.
- Since its restart by Hustadkalk AS in 1996 Norwegian Crystallites (NC) became a reliable second source. Nowadays NC joined Imerys to form the Quartz Co. However, both companies are mining the same deposit located in the US (North Carolina).
- ... with Jiangsu Pacific Quartz (China) claiming a production capacity of 9,000 tpa but limited resources calling for selective mining and small output.

... and most stringent specifications

General Specifications strongly related to final application

- **HT Lamp Tubing, Telecommunication and Optics**
  Al less than 20 ppm, metals less than 1 ppm.
  Particle size: 0.1-0.3 mm (sand),
  Total impurities less than 25 ppm.

- **Semiconductor Base Materials / Crucibles**
  Al less than 10 ppm, metals less than 0.1 ppm.
  Particle size: 0.1-0.3 mm (sand),
  Total impurities less than 10 ppm

- **Microelectronics** (EMC Fillers)
  U and Th less than 1 ppb,
  Particle size: < 0.1 mm (powder)

- **Silicon (SoG-/UMG-Silicon)**
  Low Boron and Phosphorous concentration < 1ppm
  Particle Size: 20-80 (120) mm
Quartz Processing for High End Markets

Stringent specifications call for detailed raw material analyses

Various impurities are responsible for elevated element concentrations in quartz:

- **Structural impurities**, e.g. Boron, Titanium and Aluminum
- **Mineral impurities**, e.g. Phosphate, Iron, Calcium and Aluminum
- **Fluid inclusions**, e.g. Sodium, Chloride and Potassium

**Structural Impurities in Quartz**

Impact on chemical specification of end product

- The electron paramagnetic resonance (EPR or ESR) is a spectroscopic method that detects [AlO$_4$]$^0$ centres produced by the substitution of Si$^{4+}$ by Al$^{3+}$ in the quartz crystal lattice.
- The technique based upon the interaction between the magnetic moment of the unpaired electrons and microwaves in an external magnetic field.
Mineral Inclusions
Impact on chemical specification of end product

Tremolite and Apatite
Calcite
Feldspar

Fluid Inclusions
Impact on melting behaviour in quartz glass

Raman Spectroscopy

Impact on chemical specification of end product

Impact on melting behaviour in quartz glass
Quartz Processing for High End Markets

Stringent specifications call for advanced purification processes and tailor made process design

Conversion of raw quartz into refined high purity and high value quartz products needs advanced processing technology considering all mineralogical details to meet final quality requirements.

The main stages of the process may be summarised as:

- Physical Processing
- Chemical Processing
- (Vacuum-)Drying
- Thermal Processing
- Crushing
- Sensor Based Sorting (SBS)
- Comminution and Liberation of Impurities
- Classification

Surface Coatings

Sensor based sorting to separate surface coatings

MG-/UMG-Silicon Upgrade

- Separation of quartz lumps with surface contaminations and discolorations by sensor based sorting
- Mass distribution:
  - White (good) 76 wt.-%
  - Discolored 24 wt.-%
Sensor Based Sorting (SBS)

Process scheme - Sensor based sorting

Use of Quartz in the Silicon Industry

Quartzite and low grade hydrothermal/pegmatitic quartz

<table>
<thead>
<tr>
<th>Silicon Grade</th>
<th>Fe$_2$O$_3$ [wt-%]</th>
<th>Al$_2$O$_3$ [wt-%]</th>
<th>CaO [wt-%]</th>
<th>Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Grade</td>
<td>0.20</td>
<td>0.20</td>
<td>0.02</td>
<td>2202</td>
</tr>
<tr>
<td>Polysilicon Grade</td>
<td>0.30</td>
<td>0.30</td>
<td>0.03</td>
<td>3303</td>
</tr>
<tr>
<td>Primary Aluminum Grade</td>
<td>0.40</td>
<td>0.40</td>
<td>0.10</td>
<td>441</td>
</tr>
<tr>
<td>Secondary Aluminum Grade</td>
<td>0.50</td>
<td>0.50</td>
<td>0.30</td>
<td>553</td>
</tr>
</tbody>
</table>

Other combinations are also possible: i.e. 3302, 4405, etc

- Due to furnace restrictions in silicon production only lump quartz 20 mm to 80 (120) mm can be used
- This limits the possibility of purification steps and liberation of impurities
Solar Quartz Upgrade

Chemical results of high grade hydrothermal/pegmatitic quartz

<table>
<thead>
<tr>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1-2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crushing and Screening</td>
<td>78</td>
<td>17</td>
<td>26</td>
<td>24</td>
<td>4,2</td>
<td>&lt;0,1</td>
<td>36</td>
<td>6,0</td>
<td>6,5</td>
<td>0,3</td>
</tr>
<tr>
<td>Washing and Scrubbing</td>
<td>56</td>
<td>12</td>
<td>23</td>
<td>18</td>
<td>2,7</td>
<td>&lt;0,1</td>
<td>34</td>
<td>4,8</td>
<td>3,5</td>
<td>0,2</td>
</tr>
<tr>
<td>Sensor based sorting</td>
<td>28</td>
<td>3</td>
<td>20</td>
<td>14</td>
<td>1,8</td>
<td>&lt;0,1</td>
<td>19</td>
<td>4,4</td>
<td>0,8</td>
<td>0,1</td>
</tr>
</tbody>
</table>

- In SoG-Silicon (solar grade) production lump quartz is being used.
- Besides higher overall purity, Boron and Phosphorous are main critical elements.
- For solar quartz upgrade high grade hydrothermal/pegmatitic quartz deposits are to be considered.
- Al and K bearing minerals (e.g. clays, mica) being separated during washing and scrubbing.
- Additional reduction of Fe and significant improvement of P by sensor based sorting offering best qualities to be used for SoG-Silicon feedstock.

High Purity Quartz Processing

Mineral Liberation - Electrodynamic Fragmentation

- Quartz sample in a dielectric liquid is exposed to high voltage pulses (ns/kV).
- The electrical discharge flows through the material and generates tensile stress by creating internal shockwaves.
- Consequently, composite materials are fragmented along grain boundaries and mineral impurities with a high degree of selectivity.
- Liberated minerals can be selectively separated by post treatment processes.
High Purity Quartz Processing
Physical Processing 0,1-0,3 mm

- In order to clean the surface of the quartz particles **attrition** is applied. Thereby fine particles attached to the surface of the quartz e.g. clay minerals or iron oxide coatings are abraded and dispersed in the added liquid.

- In quartz processing **magnetic separation** is used to separate minerals with paramagnetic or even ferromagnetic properties, such as e.g. iron oxides or heavy minerals. Therefore a magnetic force acts on these minerals in the direction of increasing magnetic field strength. Quartz itself has diamagnetic properties. Therefore quartz particles are repelled from magnetic fields. Magnetic Separation can be applied in dry (HGMS) or wet state (WHIMS).

- **High tension separation** is used to separate particles based on their surface charge. The activated feed material is fed between two electrode plates where it is either attracted or repelled by one of the electrodes, depending of the particles surface charge. High tension separation is a dry method.

High Purity Quartz Processing
Chemical Processing 0,1-0,3 mm

- **Flotation** is a mineral separation process, which separates trace minerals from quartz by taking advantage of differences in their hydrophobicity. Flotation process designs vary in complexity depending primarily on the type of mineral, degree of liberation and the desired purity of the product.

- **Acid Leaching** of quartz is one of the most effective processes to reduce impurities. Such chemical refining is carried out in a medium of strong mineral acids at elevated temperatures. Usually hydrofluoric acid is applied, but a combination of certain acids can be used (HF, HCl, HNO3) to further improve the results of chemical refining. Trace minerals (e.g. feldspars, micas) which are intergrown with the quartz crystals are dissolved in the course of leaching. Also impurities can be removed which are enriched in micro fissures and along dislocations, owing to an enhanced dissolution rate of quartz in regions where impurities are concentrated.
High Purity Quartz Processing
Thermal Processing 0.1-0.3 mm

• During **hot chlorination process** quartz is heated to temperatures up to 1,200°C in a chlorine or hydrogen chloride gas atmosphere. Chlorination causes structural impurities to be forced from the crystal lattice into the gas phase. Chlorination is particularly efficient for the reduction of alkali, alkali earth, and transition metals which are highly restricted in semiconductor applications.

• **Calcination** is a technique to reduce fluid inclusions and improve the melting behavior of high purity quartz. Depending on the type, amount and filling rate of the fluid inclusions, significant improvements in melting behavior can be achieved together with the reduction in alkali concentration which may be present in the fluid inclusions.

### High Purity Quartz – Rock to Sand Processing
**An example**

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Fe</th>
<th>Na</th>
<th>K</th>
<th>Li</th>
<th>Ti</th>
<th>Zr</th>
<th>Ca</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Original</td>
<td>41.3</td>
<td>12.9</td>
<td>12</td>
<td>15</td>
<td>0.5</td>
<td>1.3</td>
<td>&lt;0.10</td>
<td>3.2</td>
<td>1.3</td>
</tr>
<tr>
<td>Preprocessing</td>
<td>23.5</td>
<td>10.3</td>
<td>8.8</td>
<td>8.2</td>
<td>1.2</td>
<td>0.9</td>
<td>0.1</td>
<td>2.9</td>
<td>1.1</td>
</tr>
<tr>
<td>Magnetic separation</td>
<td>21.3</td>
<td><strong>4.9</strong></td>
<td>6.4</td>
<td>7.6</td>
<td>0.4</td>
<td><strong>0.5</strong></td>
<td>&lt;0.10</td>
<td>2.5</td>
<td>0.2</td>
</tr>
<tr>
<td>Flotation</td>
<td>12.3</td>
<td>3.8</td>
<td>6.9</td>
<td>3.3</td>
<td>0.4</td>
<td>0.4</td>
<td>&lt;0.10</td>
<td>1.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Leaching</td>
<td>10.4</td>
<td><strong>0.18</strong></td>
<td><strong>1.21</strong></td>
<td><strong>0.45</strong></td>
<td>0.25</td>
<td>0.38</td>
<td>&lt;0.01</td>
<td><strong>0.65</strong></td>
<td>0.12</td>
</tr>
<tr>
<td>Iota Standard</td>
<td>14.7</td>
<td>0.22</td>
<td>0.87</td>
<td>0.62</td>
<td>0.87</td>
<td>1.32</td>
<td>1.30</td>
<td>0.53</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Hot chlorination</td>
<td>9.2</td>
<td><strong>0.07</strong></td>
<td><strong>0.06</strong></td>
<td><strong>0.12</strong></td>
<td>0.20</td>
<td>0.36</td>
<td>&lt;0.01</td>
<td>0.62</td>
<td>0.11</td>
</tr>
<tr>
<td>Iota 6 Data sheet</td>
<td>8.0</td>
<td>0.15</td>
<td>0.08</td>
<td>0.07</td>
<td>0.15</td>
<td><strong>1.40</strong></td>
<td>&lt;0.01</td>
<td><strong>0.60</strong></td>
<td>&lt;0.05</td>
</tr>
</tbody>
</table>
Demand Drivers for High Purity Quartz

Semiconductor

- Demand for high purity quartz products in the semiconductor industries is closely related to new wafer fabs to be built, consuming most of the semiconductor base materials and crucibles.
- SEMI, the global industry association, indicates that total fab spending for equipment needed to ramp fabs, upgrade technology nodes, and expand or change wafer size will be US$ 36.7 billion in 2016.
- Transition from 300 mm to 450 mm wafer manufacturing technology expected to be a major demand driver in coming years.
- In April 2015, Governor Andrew M. Cuomo announced installation of the world’s first ever 450 mm immersion scanner at the SUNY Polytechnic Institute’s Albany NanoTech Complex.

Microelectronics and Lighting

- Microelectronics packaging market shows double digit growth rates boosting the filler market (semi.org)
- Quartz glass crucibles used in Si crystal growth indispensable in Semiconductor industry
- State of the art: Metal halide lamps (Xenon, halogene) lead the high intensity discharge (HID) product segment
- LED market skyrocketing with CAGR of 27 % between 2014 and 2018 (source: Navigant) and Si as alternative substrate taking advantage of low cost semiconductor manufacturing infrastructure
Demand Drivers for High Purity Quartz
Photovoltaics

- 2015, Market research group IHS forecasts a period of strong growth in the global PV module industry due to a new wave of capacity expansions, a relatively stable pricing environment and increasing demand from several established regional markets.
- According to IS global 2016 PV module revenue would hit $41.9 billion, exceeding the previous record set in 2010 by 4%.

Using Sand for (SoG-) Silicon under Development
Limited options for purification of lump quartz push sand into the picture
Sand for (SoG-) Silicon under Development
Limited options for purification of lump quartz push sand into the picture

The use of fine grain quartz materials such as high purity quartz sand is generally not seen as viable for the industrial production of Silicon in standard furnaces for various reasons:

- Fines of any type (quartz or carbon) can reduce the porosity of the furnace and prevent the recovery of SiO.
- High levels of quartz fines may interfere with the cavity formation around the electrodes which plays an important role in the process.
- Sand can sinter and interfere with the process dynamics.

JPM Silicon has developed a unique and patented microwave heating process for the production of silicon from quartzes studied with impurity levels between 20 and 400 ppm and particle sizes ranging from 0.1 to 3 mm. Evonik is scaling up the innovative Solsilc route which uses micronized quartz agglomerated to cm-sized pellets in order to be charged into the electric arc furnace. This offers the advantage to further refine the quartz even below 0.1 ppm in Boron and Phosphorous prior to the furnace process. A pilot plant for production of solar grade silicon has been established in Trondheim 2012.

Viridis IQ follows three different routes: quartz fines are either melted to the glassy stage to form lump pieces, or briquetted with coal or charcoal fines and wood or used in a modified furnace design such that higher pressures are allowed to directly transform the quartz into slag.
Summary
Advanced Quartz Qualities

- High purity quartz resources are of limited availability, but of strategic interest to many fast growing high tech industries with robust forecast.
- The detailed specification of advanced quartz qualities very much depend on the final application.
- Due to most stringent specifications there is no standard technology route that applies to process quartz into high purity or advanced qualities.
- Quartz is a main feedstock for silicon, ferrosilicon and photovoltaics production. However, restrictions in content call for high grade quartz resources and advanced processing technologies with sand still in the conceptual stage.

More Details Needed?
For more information download our Whitepapers on www.anzaplan.com
Thank you!