HELISOL®
- ein Siliconöl basierter Wärmeträger für CSP Kraftwerke

19. Kölner Sonnenkolloquium, 2016 07 06

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Content

- General introduction Wacker Chemie AG
- HELISOL® 5A
  - Requirements, testing methods, properties
  - Safety aspects
  - Economic assessment & Proof of Concept
Over 100 Years of Success

Wacker Chemie AG
- Founded in 1914 by Dr. Alexander Wacker
- Headquartered in Munich

WACKER Group (2015)
- Sales: €5.30 billion
- EBITDA: €1.05 billion
- R&D: €175 million
- Investments: €834 million
- Employees: 16,972
A Well-Balanced Portfolio

Sales 2015

<table>
<thead>
<tr>
<th>Division</th>
<th>Sales 2015 (in million*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Siltronic</td>
<td>€931</td>
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<tr>
<td>WACKER SILICONES</td>
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<tr>
<td>WACKER POLYMERS</td>
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<tr>
<td>WACKER POLYSILICON</td>
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<tr>
<td>WACKER BIOSOLUTIONS</td>
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</tr>
</tbody>
</table>

Group Sales

Total Divisional Sales (incl. internal sales)

- Group Sales: €5,296 million
- Total Divisional Sales: €5,321 million**

* Including internal sales
** Balance of other / consolidation € -25 million
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HELISOL® 5A: a new silicone based HTF developed for Concentrated Solar Power (CSP)

Benchmark HTF: Biphenyl / Diphenyl oxide (BP/DPO)
Maximum process temperature: 400°C

Higher process temperature
→ higher efficiency
→ lower LCOE (Levelized Cost of Electricity)

HTF requirements for CSP:
- High thermal stability
- Low temperature pumpability
- Good heat transfer
- Low volume expansion
- Low vapor pressure
- Low viscosity
- No critical degradation products
- Low toxicity
- Low fire risk
- Low cost
Si-HTF: A public funded project in order to develop and characterize a silicone based HTF

### TOPIC
- Silicone based salts
- HTF development
- Evaluation of physical & chemical properties
- Performance simulation
- Profile of requirements
- Assessment of the results

### TASKS
- Development, synthesis & characterization of Si-Salts
- Project management
- Si-HTF development & production
- Basic evaluation of heat stability
- EHS analysis (critical reactions, safety evaluation (TÜV-Nord))
- Evaluation of physical data @400°C (vapor pressure, density, viscosity, Cp….)
- Thermal stability & durability
- Evaluation of critical reactions
- Characterization of gas formation (H₂, CH₄)
- Process simulation → economic evaluation
- Assessment
  - technical
  - economic

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**Supported by:**

[Image of logos and text: Federal Ministry for Economic Affairs and Energy, on the basis of a decision by the German Bundestag]
Differences between HELISOL® 5A and BP/DPO

BP/DPO eutectic mixture

- 25-28% BP, 72-75% DPO
  (Diphyl, Dowtherm A, Therminol VP1)

- Working temp.: 60 to 400 °C
  Freeze Point: 12 °C → freeze protection

HELISOL® 5A

- HELISOL® 5A is a low viscosity polydimethylsiloxane, a multi-component mixture of molecules with various molecular weights

- Working temp.: -40 to 425 °C
  Freeze Point: -65°C

BP/DPO eutectic mixture diagram:

- DPO
- BP

HELISOL® 5A diagram:

- large molecules
- small molecules

Differences between HELISOL® 5A and BP/DPO
HELISOL® 5A offers an outstanding working temperature

Longterm stability

![Graph showing viscosity over time at 400°C and 425°C for HELISOL® 5A and BP/DPO.]

Degradation after 1000 h

- **BP/DPO (400°C, 1000 h)** → 0.85 wt.%
- **HELISOL® 5A (425°C, 1000 h)** → 0.12 wt.%
Estimation of the degradation rate of HELISOL® 5A and reworking concept

Degradation rate

- Substitution rate to be evaluated: 1-2% HTF/a @ 430°C
- Exchange rate depends on the maximal tolerable viscosity

Reworking Concept

- Effect based on equilibration and dilution
- Viscosity is kept constant
- No Ullage system needed for viscosity control
Comparison of density and vapor pressure

**Density @ 25°C**

- HELISOL® 5A : 0.92 g/mL @ 25°C
- BP/DPO : 1.06 g/mL @ 25°C
- Water : 1.00 g/mL @ 25°C

- Oil separator can be used for HELISOL® 5A only

**Vapor Pressure**

- HELISOL® 5A shows a higher pressure level which has to be considered
Comparison of heat capacity and hydrogen formation

Heat capacity

- The heat capacity of HELISOL® 5A is around 10% lower compared to BP/DPO
- Advantages in the heat transfer at lower temperatures

Hydrogen formation

- Equal amounts of H₂ at 1300 h
- Lower hydrogen formation expected with HELISOL® 5A for long term
Corrosion test DIN EN ISO 2160 showed no significant impact. HELISOL® 5A does not show any fouling effects.

- Corrosion of the copper stripe (3 h/100 °C): grade 1a
- Corrosion of the copper stripe (6 h/100 °C): grade 1a
- Corrosion of the copper stripe (24 h/100 °C): grade 1b

- Test specimen showed almost no change of the surface after testing

No fouling / carbonization effects have been seen with HELISOL® 5A.
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Safety assessment – fire tests at DMT and TÜV-Nord

**Flammability in contact with hot surfaces**
ISO 20823

**HELISOL® 5A:**
self ignition at 475°C
($T_z \sim 367°C$…. DIN EN 14522)

CSP-Loop $\ll 475°C$

**Fire test in a heating furnace**

**HELISOL® 5A:**
no self ignition @ 250-430°C

**rock wool + HELISOL® 5A:**
no self ignition

**rock wool + BP/DPO:**
no self ignition

**Wickflame persistence**
ISO 14935

**HELISOL® 5A:**
combustion products (SiO₂) form protective barrier
$\Rightarrow$ fire stops burning automatically

**BP/DPO:**
a lot more reactive
$\Rightarrow$ fire does not stop burning automatically
**Spray ignition test**
ISO 15029

- **Distance**: 4m
- **Afterflame time**: 3-4 sec.
- **Ignition in the area of the nozzle**
- **Fire area:** HELISOL® 5A: ~1m
- **Fire area** BP/DPO: ~2-3m, ➔ more reactive

**Simulating of leakages in pipes at 430°C**

- **HELISOL® 5A**: no self ignition - neither direct in air nor in insulation

**Simulating of leakages at 430°C with ignition source**

- **HELISOL® 5A**: pyrotechnics have been burned in a distance of 5m, 2m, 1m from the exposure point
  ➔ no self ignition
HELISOL® 5A – reaction with solar salt

**Measurement:** DSC (N\textsubscript{2}) of mixtures of HTF and solar salt (60/40 wt.-% Na/K-nitrate)

**Summary:**

- Onset temperature of the HELISOL® 5A is more than 100°C above the operation temperature (100 K rule)
- Heat of combustion (\(\triangleq\) total oxidation \(\triangleq\) max. exothermicity) of Si-HTF is approx. 20% lower than that of BP/DPO

**HELISOL® 5A is less critical than BP/DPO in combination with solar salt**
HELISOL® 5A – combustion products are not classified as hazardous

Summary:

- Primary particles (10–30 nm) form aggregates (>100 nm), which combine to form agglomerates (some µm in diameter).
- X-Ray (XRD) does not show crystalline structures
- The combustion products have a high similarity to synthetic amorphous silica (SAS)
- SAS are not classified as hazardous
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HELISOL® 5A enables lower LCOE

- Reduced costs TES
- No Ullage system needed for viscosity control
- No freeze protection
- Higher vapor pressure

- No recirculation for freeze protection
- Easier maintenance
- Less pump energy (low viscosity)
- Shorter start up period
- Lower degradation/exchange rate @ same temp.
- Lower H2 generation
- No fouling

\[
LCOE = \frac{\text{CRF} \times \sum \text{CAPEX} + \sum \text{OPEX}_\text{annual}}{\text{Electricity}_\text{annual}}
\]

Working temp.: \(-40°C \text{ to } 430°C\)
EHTF: \(60°C \text{ to } < 400°C\)

*CRF*: Capital recovery factor (Annuitätenfaktor)
HELISOL® 5A enables a reduction of the LCOE of ~ 5%

Restrictions:
- Calculation is based on LCOE calculation in Guadix (E).
- Solarfield- and storage size are based on minimal LCOE.
- Specific solarfield costs are higher...
- Specific costs of the TES are lower...

Conclusion:
- HELISOL® 5A offers advantages over commonly used HTF`s
- in terms of applicability for HELISOL® 5A in CSP plants no hindering issues were found
SITEF: A public funded project (SOLAR-ERA.NET) at the PSA (2016-2017)

Proof of Concept / Qualification of HELISOL® 5A at 425°C and beyond

“PROMETEO“ LOOP

by courtesy of CIEMAT

<table>
<thead>
<tr>
<th>EPC, CSP-Developer</th>
<th>Component Suppliers</th>
<th>Ownership, operation</th>
<th>Certifier</th>
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<tr>
<td>Engineering /Upgrade:</td>
<td>REPAS: Senior Flexonics SF</td>
<td>CIEMAT CI</td>
<td>Lab analysis: DLR</td>
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<td>technoeconomic evaluation: DLR, FS</td>
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<td>Risk evaluation: TN, DLR, FS, WA</td>
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<tr>
<td>TÜV-Nord TN,</td>
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<td>external evaluation: RWE</td>
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<tr>
<td>DLR</td>
<td></td>
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</tbody>
</table>

Early Operation @ 400°C: no limiting issues identified so far

SITEF project is funded by the governments of Spain and Germany
Protarget AG is used to work with HELISOL® 5A already

Micro CSP Plant in Bad Aibling
- Operating since end of 2012
- 570 m² parabolic trough
  250 kW nominal, 320 kW peak
  operating temperature: 300°C

„EDITOR“ Project in Cyprus
- Funded by: EU/BMWi
- Operating temperature: 430°C
- Time frame:
  01.2016 → plant commissioning 01.2017
- Goal: supply of process steam to an orange juice company, proof of dispatchability
Royal Tech (CN) is currently testing HELISOL® 5A beyond 400°C

key findings / issues:

- 600m loop with 4 SCAs located in Inner Mongolia
- Typical configuration similar to Spain’s PTC power plants
- Operating temperature up to 430°C
- Similar operating behavior to organic oil
- Low viscosity under high temperature need to be considered to avoid leakage

(by courtesy of Royal Tech)
With HELISOL® 5A it is possible to realize a parabolic trough plant with a working temperature above 400°C

The authors would like to thank the German Federal Ministry of Economic Affairs and Energy for the funding of the projects Si-HTF and SITEF and their cooperation partners.