

## Thermochem Experience with Silica Control and pH-mod Systems

The Thermochem team has over 30 years' experience with silica scale control in dual-flash plant and bottoming cycles. Currently pH-modification is the only proven and reliable means of amorphous silica scale control in dual-flash and binary plants where the silica saturation index (SSI) is above about 1.2. More than 1000 MW of geothermal power generation in the USA, New Zealand, and soon, Indonesia (Sarulla) relies on pH-modification for silica scale control. This includes units built 20 years ago, and over 500 MW which recently came on-line or will be commissioned soon. Most of the power plants treated by pH-modification are multi-flash plants. Thermochem was involved in the design and operation of all of these systems. The Senior Process Chemist for Thermochem, Darrell Gallup, invented the pH-modification process for Unocal at the Salton Sea in 1985.

### Principle Experts in pH-modification System Design, Operation and Optimization

Darrell Gallup, Senior Process Chemist Thermochem, Inc.

Paul von Hirtz, President Thermochem, Inc.

Date: 1979 - 1987

Project Site: Brawley California

Employer: Unocal

Employee: Darrell Gallup

Darrell developed the pH-mod concept in 1979 and pilot tested the process starting in 1980 at the 10 MW Brawley demonstration plant in the Salton Sea area. Successful pilot testing led to commercial operation starting in 1983. This was the first commercial pH-mod plant in the world. Darrell managed the laboratory and pilot testing, monitored the process and optimized it throughout commercial operation. The pH-mod process was successful in mitigating silica and iron-silicate scale, but the Brawley project was ultimately terminated in 1987 due to contractual issues.

Date: 1979 - 1993  
Project Site: Salton Sea California  
Employer: Unocal  
Employee: Darrell Gallup

#### Scope of Work

Darrell refined the pH-mod concept and pilot tested the process at the Unocal Salton Sea plants. He ran a demonstration test at the Salton Sea in order to supply brine to the crystallizer-clarifier pilot unit. Successful pilot and demonstration testing led to commercial operation starting in 1992 at Salton Sea Unit 2. Again Darrell managed the laboratory and pilot testing, monitored the commercial process and optimized it up to the sale of the Salton Sea assets by Unocal in 1993.

Date: 1992 - 2000  
Project Site: Mak-Ban Philippines  
Employer: Unocal  
Employee: Darrell Gallup

#### Scope of Work

The Philippine National Power Corporation entered into an agreement with Ormat to supply binary bottoming cycle plants. Unocal recognized that running the bottoming cycle would result in scaling of the binary heat exchangers, injection brine piping and wells. Darrell designed the pH-mod process for the binary unit, trained operations personnel, and instituted a monitoring program based on silica polymerization kinetics and TSS. Mak-Ban Unit I ran continuously for 10 years. Units 2 and 3 were operated only intermittently due to difficulties in supplying brine to the Ormat units at rates required for optimum output and proper operation.

Date: 1985 - 1989  
Project Site: Coso, California  
Customer: CalEnergy Company  
Employee: Paul von Hirtz

#### Scope of Work

Paul designed, built and operated a pilot plant test facility to simulate dual-flash plants with pH-mod and NCG injection at the Coso Units, 7, 8 and 9 areas. The tests were run concurrently with plant construction (3 Fuji Dual-Flash 30 MW units). It was determined that dual-flash cycles for Units 7 and 8 were acceptable in terms of scaling rates using NCG injection or pH-mod, but it was concluded that a dual-flash process for the Unit 9 plant was not feasible even with pH-mod due to very high silica and fluid enthalpy (extreme scaling). Unit 9 was modified to provide LP steam to the turbine by pressure let-down of HP steam and only a single flash of the brine. Units 7 and 8 operated without scaling issues with NCG injection to reduce the brine pH and inhibit silica scaling. NCG injection was the initial abatement method for H<sub>2</sub>S at Coso and effectively served as pH-modification for several units as well.

Date: 1999 - 2004  
Project Site: Coso, California  
Customer: CalEnergy Company  
Employee: Paul von Hirtz

#### Scope of Work

Through reinjection management and corresponding reduction in fluid enthalpy in the Unit 9 area, a dual-flash cycle became feasible. Also NCG injection was no longer an option for silica scale mitigation as the H<sub>2</sub>S abatement strategy was changed to surface treatment systems. Pilot-testing was conducted on a pair of full-size HP and LP separators to evaluate pH-modification using sulfuric acid for scale control at Unit 9. The testing was successful and Unit 9 was modified back to a conventional dual-flash plant with pH-mod based on the Thermochem pH-mod design. Other units throughout the 270 MW Coso field, all dual-flash, adopted the pH-mod for silica scale control as enthalpies increased in these areas and scaling became a problem. Ultimately 12 pH-mod systems based on the original Thermochem design were installed to protect 44 injection wells field-wide. The process was considered a huge success and greatly reduced the number of injection well work-overs and re-drills saving \$5MM/year.

Date: 2000 - 2007  
Project Site: Blundell Utah Unit II  
Customer: PacifiCorp  
Employee: Paul von Hirtz

#### Scope of Work

Paul designed, built and operated pilot plant test facilities to evaluate a binary bottoming cycle for Blundell Unit II. The testing demonstrated that pH-mod could effectively control silica scale in a bottoming plant and PacifiCorp proceeded with construction of a 12 MW Ormat unit. Thermochem designed the pH-mod system at Blundell and managed the start-up and routine operation for PacifiCorp. Thermochem is still involved in routine monitoring of the Unit II pH-mod system which has been operating since start-up without scaling or corrosion problems.

Date: 2009 - 2011  
Project Site: Blundell Utah Unit III  
Customer: PacifiCorp  
Employee: Paul von Hirtz

#### Scope of Work

Paul designed, built and operated a pilot plant test facility to evaluate a dual-flash plant for a proposed Blundell Unit III. The testing demonstrated that pH-mod could effectively control silica scale in a new dual-flash plant at Blundell, but PacifiCorp has yet to proceed with the expansion project.

Date: 2003 - 2011  
Project Site: Puna Hawaii  
Customer: Ormat  
Employee: Paul von Hirtz

#### Scope of Work

Paul designed, built and operated pilot plant test facilities to evaluate a binary bottoming cycle for the 30 W single-flash Puna plant, including a Pilot Test process dedicated to cool and treat all fluid to one injection well. The testing demonstrated that pH-mod could effectively control silica scale in the proposed bottoming plant, so Ormat proceeded with construction of the 12 MW expansion plant. Thermochem designed, built and started-up the pH-mod system at Puna. Thermochem is still involved in routine monitoring and maintenance of the bottoming unit pH-mod system, which is operating without scaling or corrosion problems and processing the highest SSI fluids in the world.

Date: 2006 - 2009  
Project Site: Kawerau New Zealand  
Customer: Mighty River Power  
Employee: Paul von Hirtz

#### Scope of Work

Paul supervised the design and operation of a pilot plant test facility to evaluate binary bottoming cycle and dual-flash options for the 110 W Kawerau power plant. The testing demonstrated that pH-mod could effectively control silica scale in both binary and dual-flash cycles. MRP awarded the contract to Fuji for a dual-flash plant and Thermochem was designated the Owner's Engineer for the silica scale control system. Thermochem provided the pH-mod system design and specifications in the Employer's Requirements documents to Fuji. Unfortunately the EPC contractor did not follow the Employer's Requirements and severe scaling and corrosion problems were experienced after start-up.

Date: 2008 - 2009  
Project Site: Nga Awa Purua (NAP) New Zealand  
Customer: Mighty River Power  
Employee: Paul von Hirtz

#### Scope of Work

Thermochem was designated the Owner's Engineer for the silica scale control system for the 138MW triple-flash Nga Awa Purua plant. Thermochem provided the pH-mod system design and specifications in the Employer's Requirements documents to Fuji. Unfortunately the EPC contractor did not follow the Employer's Requirements and some scaling and corrosion problems were experienced after start-up.

Date: 2010 - 2011  
Project Site: Ngatamariki (NTM) New Zealand  
Customer: Mighty River Power  
Employee: Paul von Hirtz

#### Scope of Work

Paul supervised the design and operation of a pilot plant test facility to evaluate binary bottoming cycle options for the proposed 100 MW Ngatamariki power plant. The testing demonstrated that pH-mod was probably not required to control silica scale in the binary cycle given brine mixing with gas-rich condensate. MRP awarded the contract to Ormat for a Hybrid flash-binary plant and Thermochem was designated the Owner's Engineer for a pH-mod system as a contingency, but it was ultimately not required nor installed.

Date: 2010 - 2011  
Project Site: Kawerau and Nga Awa Purua New Zealand  
Customer: Mighty River Power  
Employees: Paul von Hirtz  
Darrell Gallup

#### Scope of Work

Paul and Darrell lead the investigation into the scaling and corrosion problems experienced at the Kawerau and Nga Awa Purua plants after start-up. It was determined after extensive testing that the root cause was non-adherence to the original design and Employer's Requirements specifications for the pH-mod systems, in addition to brine flow instability issues at Kawerau. Thermochem provided a detailed retro-fit design to correct the problems, included a "Trim" acid dosing system for Kawerau reinjection brine to fine-tune the pH-control. Most of the retrofits have been installed and both plants are no longer experiencing corrosion and silica scaling problems.

Date: 2012 - 2015  
Project Site: Salak, Java Indonesia  
Customer: Chevron Indonesia  
Employees: Paul von Hirtz  
Darrell Gallup

#### Scope of Work

Paul and Darrell provided consulting on silica scale control for a proposed bottoming binary cycle plant at Salak as was assigned the lead consultant on the project after some initial work by SKM. Process simulations for the proposed power cycle were made with emphasis on aluminum-rich silica scale. Predictions of scaling rates and recommended minimum brine outlet temperatures were recommended. A pH-modification system was designed with acid dosing rates and costs estimated. A detailed design for a pilot plant facility and test program was developed for Chevron, which was required by management.

Date: 2013  
Project Site: Ulubelu, Sumatra Indonesia  
Customer: Mitsubishi Heavy Industries (MHI)  
Employee: Paul von Hirtz

#### Scope of Work

Paul provided consulting on silica scale control for a dual-flash plant at Ulubelu (Units 3 and 4) proposed by MHI in a formal tender process for Pertamina Geothermal. Process simulations for the proposed power cycle and a comprehensive mass balance were produced. A pH-modification system was designed with acid dosing rates and costs estimated. Predictions of scaling rates and recommended minimum first and second flash pressures were recommended.

Date: 2015  
Project Site: Rantau Dedap, Sumatra Indonesia  
Customer: Ormat, for Supreme Energy  
Employee: Paul von Hirtz

#### Scope of Work

Paul provided consulting on silica scale control for a proposed Ormat binary cycle plant at Rantau Dedap. Process simulations for the proposed power cycle and a comprehensive mass balance were produced. A preliminary pH-modification system was designed with acid dosing rates and costs estimated. Predictions of scaling rates and recommended minimum brine outlet temperatures were recommended.

Date: 2014 - 2016  
Project Site: Ulubelu, Sumatra Indonesia  
Customer: Pertamina Geothermal Energy (PGE)  
Employee: Paul von Hirtz

#### Scope of Work

A Thermochem team developed a comprehensive multi-disciplinary reservoir model (geology, geophysics and geochemistry) and numerical model for the Ulubelu resource and conducted detailed numerical simulations to evaluate options to add binary bottoming cycles to the single-flash plants, Units 1 – 4. The project included consulting on silica scale control for binary bottoming plants at Ulubelu. Process simulations for the proposed power cycle and a comprehensive mass balance were produced. A pH-modification system was designed with acid dosing rates and costs estimated. Predictions of scaling rates and recommended minimum brine outlet temperatures were recommended.

Date: 2006 - present  
Project Site: Sarulla, Sumatra Indonesia  
Customer: Sarulla Operations, Ltd. (SOL)  
Employee: Paul von Hirtz

### Scope of Work

Thermochem provided consulting on silica scale control methods for the original proposed Ormat combined-cycle plants at Silangkitang and Namora Langit (Sarulla). Process simulations for the proposed power cycles and a comprehensive mass balance were produced. Noncondensable gas injection as an alternative to conventional pH-modification was evaluated by detailed chemical process modeling. Predictions of scaling rates, recommended gas injection rates and minimum brine outlet temperatures were recommended. In 2014 SOL requested that Thermochem design, build and operate a pilot test facility to prove the concept of NCG injection for silica scale control, and to compare pH-control performance to conventional pH-modification using sulfuric acid. This work was completed in 2016.

Immediately after commissioning, the Silangkitang plant suffered extreme corrosion and scaling problems related to the pH-modification system designed and installed by the EPC contractor, HDEC. Thermochem was hired by HDEC to perform a complete retrofit of the pH-modification hardware and instrumentation for all 3 power plants (330 MW), including acid dilution systems, main alloy mixers and automatic pH-monitors. The SIL 1 and NIL Units 2 and 3 plants are now operating successfully with pH-modification.

## Thermochem Team Primary Experts and Relevant Experience

### Senior Process Chemist

**Dr. Darrell Gallup**, Ph.D., Senior Process Chemist employed by Thermochem, has a Ph.D. from Utah State University and previously worked for Unocal and Chevron. Darrell has 35 years' experience in production optimization for the petroleum industry, beginning with Texaco, Unocal and then Chevron, finally with Thermochem, Inc. in 2010. He is an internationally recognized authority on oil and gas production, chemistry, flow assurance, geothermal energy production, water treatment and environmental processes. His "hands-on" problem solving and process development philosophy (Laboratory / Pilot / Demonstration / Commercialization) has delivered an impressive track record of success in solving complex process chemistry and engineering problems. Dr. Gallup is the Inventor of the pH-modification process that was originally patented by Unocal and used at the Salton Sea. He is also very familiar with Crystallizer – Clarifier (CRC) technology and the steam purity and corrosion issues at the Salton Sea. Dr. Gallup is the author of over 80 technical papers and several book chapters, numerous presentations to technical and industry forums, inventor of over 50 US patents and foreign counterparts, with several patents pending.

### Senior Chemical Process Engineer

**Paul von Hirtz** is the President of Thermochem, Inc. and Commissioner of PT. Thermochem, Indonesia. Paul has a BS degree in chemistry and minor in Physics from Sonoma State University. He is the chairman of ASTM committee E44.15 which develops and standardizes testing procedures for the geothermal energy industry. Mr. von Hirtz is an editorial board member for the Geoscience journal *Geothermics*, and a board member of the International Geothermal Association. For 32 years, Mr. von Hirtz has specialized in geothermal well testing operations and the design of testing equipment for two-phase flow streams. His expertise is in single- and two-phase flow, steam purity and quality measurement, steam scrubbing and separation techniques. He has extensive experience in pilot-plant and full-scale testing for the evaluation and development of chemical processes. Mr. von Hirtz has developed instrumentation and chemical processes for geothermal energy production such as H<sub>2</sub>S abatement, silica scale control, continuous non-condensable gas monitors, two-phase high-temperature wellbore samplers, removal of HCl from superheated steam, on-line steam quality and purity monitors and is the inventor of the TFT<sup>®</sup> process for two-phase flow measurement. As a chemical engineer with a background in analytical chemistry, Mr. von Hirtz understands the limitations inherent in physical and chemical measurements and how to improve data quality when necessary. He is very experienced in chemical process modeling, propagated error analysis and sensitivity studies, and understanding of complex chemical process systems involving multiple data sources.

## pH-mod related patents

J.W. Jost and D.L. Gallup, 1985. Inhibiting scale precipitation from high temperature brine. US 4,500,434.

D.L. Gallup and J.W. Jost, 1985. Control of metal-containing scale deposition from high temperature brine. US 4,537,684.

D.L. Gallup and J.L. Featherstone, 1986. Acidification of steam condensate for incompatibility control during mixing with geothermal brine. US 4,615,808.

D.L. Gallup and M. E. Obando, 1992. Process for controlling the pH of a brine. US 5,085,782.

D.L. Gallup, M.L. Barnes, D. Cope, Q.S. Kolimlim, and J.K. Leong, 1993. Brine heat exchanger treatment method. US 5,190,664.

K. Kitz and D.L. Gallup, 1997) pH modification of geothermal brine with sulfur-containing acids. US 5,656,172.

K. Kitz and D.L. Gallup, 1999. pH modification of geothermal brine with sulfur-containing acids. US 5,965,031.

D.L. Gallup, 2002. Method for simultaneously abating H<sub>2</sub>S and producing acid for brine treatment. US 6,375,907.