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Nitrate and Nitrite/Nitrate Salt Heat Transport Fluids

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Topics

- Concept
- Comparison with Therminol
- Salt components and systems
- Demonstration program
- Development program

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Salt Heat Transport Fluid



Steam Generator



Isometric View (Source: FlagSol)



- Binary nitrate: 60% NaNO₃; 40% KNO₃; 190 °C (eutectic) → 600 °C
- Hitec : 7% NaNO₃; 53% KNO₃; 40% NaNO₂; 142 °C → 460 °C
- HitecXL : 15% NaNO₃; 43% KNO₃; 42% Ca(NO₃)₂
 140 °C → 500 °C
- Sandia molten salt: xx% NaNO₃; yy% ?NO₃; zz% ?NO₃; 100 °C → 500 °C

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Advanced heat transport fluid

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Comparison with Therminol

- Collector field outlet temperatures
 - ≻ 460 to 600 °C
 - Thermal stability limits on 3 of 4 salts as high as temperature limits on receiver selective surfaces
 - Improves Rankine cycle efficiency at expense of collector field efficiency; likely limit is perhaps 540 °C with current concentration ratios
 - Pipe, tank, and heat exchanger materials available for all combinations of salt temperatures and impurities

Rankine cycle and annual field efficiencies

	Gross	Annual field efficiency	
	<u>cycle efficiency</u>	Current	Prototype
Therminol	0.377	0.483	0.540
Salt			
- 450 C	0.396	0.449	0.517
- 500 C	0.407	0.414	0.492
- 510 C	0.410	0.406	0.487
- 540 C	0.424	0.382	0.470

Emissivity of 0.07 at 400 °C is essentially mandatory

- Thermal storage
 - > Heat transport fluid is thermal storage media
 - Avoid capital cost, and Rankine cycle performance penalty, of oil-to-salt heat exchangers
 - Larger temperature rise across collector field; reduces storage medium volume
 - > Avoids parasitic energy demand of storage salt pumps
 - \$35 to \$40/kWht for indirect Therminol storage
 - \$24/kWht for direct Hitec storage at 450 °C, decreasing to \$13/kWht for binary salt storage at 540 °C

- Overnight freeze protection increases auxiliary demand for thermal energy
 - > 10 hours per year for Therminol
 - ➢ 600 hours per year for Sandia salt (130 °C)
 - > 2,300 hours per year for Hitec and HitecXL (175 °C)
 - > 4,200 hours per year for binary salt (250 °C)
- Capital investment in Joule and resistance heating systems

- Higher temperatures and salt impurities require low alloy ferritic and stainless steel materials
- Ball joint seals are not yet available
- More complex maintenance procedures for draining and filling a collector loop
- Thawing a frozen loop, particularly with lost glass envelopes, will be a time consuming process

Nitrate Salt

Design Parameters and Constraints

- Industrial grades, with total chloride contents up to ~0.6 percent, can be accommodated
- > For 30 year project life:
 - Temperatures below 400 °C → Carbon steel
 - 400 to 480 °C \rightarrow 9 Cr 1 Mo low alloy steel
 - Above 480 °C → Stabilized stainless steels
- Optimum combination of salt impurities and equipment materials probably not yet identified
- > MgNO₃ → MgO_↓ + NO₂ reaction may need to be promoted in some grades of industrial salt

Intergranular Stress Corrosion Cracking

- Susceptible materials: 'H' grades (C > 0.04%) of 304 and 316 stainless steel; chromium carbide formation at temperatures between 530 and 590 °C; chromium depletion at grain boundaries
- Residual tensile stresses: Welding
- Chlorides: 0.6 weight percent in industrial grade salt
- Water: Disassembly for maintenance
- Possible alternate materials: Stainless steels stabilized with titanium (Grade 321) or niobium (Grade 347)

Intergranular Stress Corrosion Cracking

Heat affected zone of welds in stabilized stainless steels

- Weld temperatures dissolve titanium (niobium) carbides into titanium (niobium) and carbon
- As weld cools, carbon combines with chromium, forming chromium carbide; material then susceptible to stress corrosion cracking at grain boundaries
- Post weld heat treatment to 850 to 900 °C
- Chromium carbide dissolves to chromium and carbon
- Carbon preferentially recombines with titanium (niobium) to re-form stable carbides

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- Plant dispatch
- Levelized cost of energy

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Salt Components

- Joule heating
- Resistance cable heat tracing
- Pumps
- Tanks
- Steam generator
- Valves
- Instruments
- Needed, but not yet available
 - Ball joints
 - Selective surface for temperatures above 450 °C

Joule Heating



- > P = I² R
- Uniform circumferential flux
- No vacuum or salt boundary penetration
- Demonstrated at ENEA and Sandia
- Considerable vendor experience



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Joule heating demonstration and analyses

Resistance Heat Tracing

Description

- Heat exchangers, pumps, nitrate salt piping, nitrate salt valves, and Therminol piping: Mineral insulated cables
- Zone selection based on geometry; i.e., 1 heat exchanger would be a zone, as would a valve bonnet
- Redundant cables provided in each zone
- Storage tanks: Immersion heaters

Suppliers

- Chromalox
- > Other competitive

Resistance Heat Tracing - Continued

Pipe, valve body, and valve bonnet installation



Resistance Heat Tracing - Continued



End of zone installation

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High temperature pumps



Salt heat transfer systems

Initial Fill of Nitrate Salt



Two Tank Thermal Storage

- Description
 - > Vertical, cylindrical tanks with self-supporting roofs
 - > Cold tank: SA 516 Grade 70 carbon steel
 - Hot tank: SA 387 Grade 91 low alloy steel for temperatures < 480 °C; SA 240 Grade 347 stabilized stainless steel for temperatures above
 - Mineral wool wall insulation; calcium silicate roof insulation
 - Foamglass and refractory brick foundation; passive air cooling

Two Tank Thermal Storage - Continued

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Two Tank Thermal Storage - Continued

Two Tank Thermal Storage - Continued

- Floor ring header with spargers
 - Limit stratification
 - Provide uniform source temperatures for steam generator and collector field
- Tank agitation
 - Fluid recirculation
 - Mechanical mixer

Steam Generator

Description

- > Forced recirculation, with separate steam drum
- Separate superheater, reheater, evaporator, and preheater shells
- > U-tube with straight shell and longitudinal baffle
- Nitrate salt on the shell sides, water or steam on the tube sides
- Startup feedwater heater

Observations

- Steam generator will operate more hours at no-load or low-load conditions than full-load conditions
- Thorough mixing must be maintained on both nitrate salt and water/steam sides at all loads
- Coupled Rankine cycle / steam generator model for part-load conditions is a necessary element
- Daily startup and routine operation was (eventually) demonstrated at Solar Two central receiver project

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Freeze Recovery in Steam Generator

- Nitrate salt is on the shell side in all heat exchangers
- Binary salt softens and melts over a narrow temperature range
- Geometry for melting salt on the shell side more favorable than on the tube side
- Solar Two superheater thawed once with no apparent damage

Multiple sources of energy for freeze recovery

- Electric heat tracing on shells and channels
- Electric immersion heaters in steam drum; circulate saturated water from drum, to evaporator, to preheater, and return
- Send saturated steam from drum through superheater or reheater; exhaust to condenser

Nitrate Salt Valves

Description

- Gate valves for flow isolation, draining, and venting
- > Electric or pneumatic operators
- Bellows stem seals, with backup combination of Teflon washers and graphite impregnated stainless steel braid packing
- Catalog items only; specialty valves neither required nor desired
- Globe valves are not desired; flow control is provided by pump variable speed drive

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Nitrate salt valves

Instrumentation

- Description
 - > Temperature: Thermocouples in thermowells
 - Heat trace control: Surface thermocouples or resistance temperature devices
 - Pressure: Impedance coil; transmitters with remote diaphragms are not suitable
 - **Flow rate: Venturi, with differential impedance coil**
 - Tank level: Capacitance, based on dielectric properties of fluid

Instrumentation - Continued

Design Parameters and Constraints

- Conventional capillary fluids are unsuitable, but NaK alternate requires heat tracing, and suppliers are limited
- Vortex shedding flow meters are reliable, but not available for large pipe sizes (measuring a portion of the flow may be possible), or for temperatures above 400 °C
- Impedance transducers must be kept above melting point of salt, or kept dry; salt freezing on the diaphragm ruins the transducer

Instrumentation - Continued

Note: Dimensions of air/salt chamber selected to ensure nitrate salt level does not reach rear vent tube entrance at design salt flow rate and pressure.

Ball Joint Development

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Demonstration Program

ENEA

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Development Program

- Performance models and economic analyses
- Salt analysis
- Ball joint development
- Component and system tests
 - > Joule heating
 - Freeze/thaw demonstrations
 - Loop operation and maintenance
- Collector optimization

Performance and Economic Analyses

- Comprehensive study last conducted by Flabeg, Kearney & Associates, NREL, Sandia, and Nexant in 2002
 - Higher temperatures were beneficial only in conjunction with thermal storage; otherwise, increase in Rankine efficiency was offset by overnight thermal losses and the cost of heat tracing
 - A low emissivity coating for the heat collection elements was necessary

Performance and Economic Analyses

- Recent data on prototype heat collection element emissivities, low melting point salts, and costs for multiple, large Therminol plants at a common site
- Confirm projected energy cost reductions for salt projects, and define applicable ranges of plant size and storage capacity

Salt Development

- Sandia formulation
- Thermodynamic properties: Melting point, density, specific heat, thermal conductivity, and viscosity
- Corrosion rates for carbon, low alloy, and stainless steels
- Eutectic stability
- Costs: Capital, melting, and maintenance

- Therminol: Iron compression seals, a braided graphite packing, and a sealing chamber filled with graphite flakes
- In salt, graphite loss by oxidation negligible at 350 °C, appreciable at 400 °C, rapid at 500 °C
- Sandia tests
 - No suitable metal seals found
 - > Boron nitride powder a possibility to replace graphite

Ball Joint Development - Continued

- Internally insulated design, which maintains the graphite temperature below 300 °C, may be possible
- Alternate approaches
 - Flex hoses, with mesh liners to reduce pressure losses
 - Collector designs with fixed heat collection elements

Component and System Tests

Joule heating

- High current, low voltages, long distances
- IEEE restrictions on maximum voltage
- Considerable vendor experience

Joule heating

- Tests with full-size collector loop
- Current and voltage distributions over time
- Preheat and freeze recovery

Freeze / thaw experiments

- Heat collection element
 - Repeated freeze/thaw cycles to tube rupture
 - Demonstrate the ability to withstand a lifetime of cycles (30?) due to plant electric outages with simultaneous loss of fluid circulation and heat tracing
 - Assess supplemental insulation for tubes with lost vacuum or lost envelope

Freeze / thaw experiments - Continued

- Heat collection element Continued
 - Consider receiver tube material and tube fabrication process

	Annealed		
Type	elongation, %		
301	60		
304	55		
321	45		
347	45		

Freeze / thaw experiments - Continued

- Collector loop
 - Inlet line, solar collector assemblies, ball joints, crossover pipe, outlet line, and isolation valves
 - Replicate geometry, thermal losses through insulation, voids during freezing, Joule/resistance heating boundaries, and various receiver conditions (intact, lost vacuum, and lost envelope)

Collector loop maintenance

- Therminol
 - Maintenance truck with vacuum tank
 - > Air removed from loop prior to refilling
- Salt
 - Maintenance truck with heated vacuum tank
 - Cleaning procedures for weld zones
 - > Air removed from loop prior to preheating

Collector loop maintenance -Continued

- Portable 300 kVA generator and 480 V / 80 V transformer on maintenance truck for Joule heating
- Permanent low voltage cables
- 3 trucks: 48 hours to preheat 1,000,000 m² field

Collector loop demonstration

- Lowest cost approach is to convert one loop to (binary) salt at a plant with indirect thermal storage
- Add cold salt pump, Joule heating, resistance heating, salt valves, and loop fill / drain equipment
- > Outlet temperatures up to limits of selective surface
- Verify thermal performance, ball joint seals, freeze protection energy demands, and maintenance procedures

Collector Optimization

Collector tailored for salt

- Concentration ratio
- Receiver tube diameter
- > High temperature selective surface
- Fixed receiver / rotating structure