

NREL Trough Meeting 2007

Molten Salt Systems other Applications link to Solar Power Plants

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Topics

- Heat transfer and media
- Molten salt and its applications
- Melamine
- Aluminium oxide (alumina)
- Sodium hydroxide (caustic soda)
- Special applications
- Experience with salt
- Solar power plants

Indirect Heat Transfer

- The process heating unit generates the heat for the process
- This heat transfer is indirect, i.e. an intermediat thermal heat carrier is required
 - Available heat transfer carriers are: – Water (high system pressure at rather low temperature) – Water-Gylcol mixtures (for low temperature applications)
 - Gases
 - Mineral oils
 - Synthetic thermal fluids
 - Molten inorganic salts
 - Molten metals

Heat Transfer Media

Temperature range of various media in degrees Celsius



Process Heat Transfer Systems with Molten Salt



- 1 fired heater with burner
- 2 air preheater
- 3 combustion air fan
- 4 stack

- 5 circulation pump
- 6 storage tank
- 7 heat consumer (process)

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What is Molten Salt ?

- Molten salts used for indirect heat transfer are in general synthetic salts, so-called Hitec salt
- Available in tertiary or binary mixtures
- Eutectic mixture of 53 wt.% potassium nitrate (KNO₃), 40 wt.% sodium nitrite (NaNO₂) and 7 wt.% sodium nitrate (NaNO₃) or 45.5 wt.% potassium nitrate (KNO₃) and 54.5 wt.% sodium nitrite (NaNO₂)
- White solid product with a melting temperature of approx. 142°C-145°C (288°F-293°F)
- Impurities, i.e. chlorine, sulphur, magnesium, etc. and insolubles are very low

Applications for Molten Salt

- Temperature limitation of synthetic thermal fluids approx. 410°C (770°F), max. allowable filmtemperature 430°C (806°F) (Dowtherm A, Therminol VP-1, etc.)
 - For process temperatures above ≈ 400°C (752°F), molten salt has to be used
- Production of Melamine
- Production of Aluminium oxides (and aluminium)
- High concentration of Sodium hydroxide (caustic soda)
- Special applications

- Endothermic reaction in molten salt heated reactor: 6CO(NH₂)₂ -> C₃N₆H₆ + 6NH₃ + 3CO₂ Urea -> Melamine + Ammonia + Carbon Dioxide
- Over 95% of global output (≈ 1'100 tonnes per year) is used to make thermosetting resins for use in laminates, protective and paper coatings, moulding compounds and textile finishes
 - Applications in automotive, appliance, dinnerware, furniture and wood panelling industries. Melamine crystal or salts for flame retardant or moisture-resistance applications
- Major process licensors are: DSM (The Netherlands), AMI (Austria), ETCE (Italy)
- Molten salt temperature approx. 470°C

(2 molten salt systems, 2 x 7'600 kW, 470°C)



(2 molten salt systems, 1 x 32'000 kW, 1 x 26'000 kW, 465°C)



(2 molten salt systems, 2 x 9'000 kW, 465°C)



Molten Salt for Aluminium Oxides

 Aluminium oxide, also known as alumina, is the main component of bauxite, the principal ore of aluminium. The bauxite ore consists of impure Al₂O₃, Fe₂O₃ and SiO₂. The endothermic reaction takes place in the molten salt heated reactors (i.e. tube digestor) as shown in the following equation: Al₂O₃ + 3H₂O + 2NaOH -> 2NaAl(OH)₄

The Fe₂O₃ does not dissolve in the base. The SiO₂ dissolves as silicate Si(OH)₆²⁻. Upon filtering, Fe₂O₃ is removed and Al(OH)₃ precipitates. The silicate remains in solution. 2Al(OH)₃ + heat \rightarrow Al₂O₃ + 3H₂O The formed Al₂O₃ is alumina

• Molten salt temperature approx. 430-440°C

Molten Salt for Aluminium Oxides

- The largest manufacturers in the world are: Alcoa, Alcan, Rusal, Chinalco
- Annual world production of alumina is approx. 65 million tonnes, over 90% of which is used in the manufacture of aluminium metal. Major uses for aluminium hydroxide include the manufacture of water treatment chemicals such as aluminium sulphate, poly aluminium chloride and sodium aluminate. Large tonnages are also used in the manufacture of zeolites, coating titania pigments and as a fire retardant/smoke suppressant. The major uses of speciality aluminium oxides are in refractories, ceramics, polishing and abrasive applications



Molten Salt for Caustic Soda

 Sodium hydroxide is produced (along with chlorine and hydrogen) via the chloralkali process. The sodium hydroxide builds up at the cathode, where water is reduced to hydrogen gas and hydroxide ion:

 $2Na^+ + 2H_2O + 2e^- \rightarrow H_2 + 2NaOH$

Concentration of liquid caustic soda; endothermic reaction takes place in the molten salt heated double wall high concentrator

 Concentrated caustic soda is available in 50% aqueous solution or >99.5% as white solid in pellets, flakes, granulates

Molten salt temperature approx. 450°C

Molten Salt for Caustic Soda

- The largest process licensors for the (high) concentration of caustic soda in the world are: Bertrams Chemical Plants, SET, Chinese process licensors (copying machines ...;-))
- Annual world production of caustic soda is approx. 50 million tonnes and is the principal strong base used in the chemical industry. In bulk it is most often handled as an aqueous solution. It is used for chemical reactions and also for the neutralization of acidic materials

Molten Salt for Caustic Soda



Molten Salt System 1 v 14/000 USA Soda

(1 molten salt system, 1 x 11'000 kW, 450°C)



Molten Salt for Special Applications

- Production of natural fertilizers, i.e. nitrates
- Ore which contains nitrates are leached
- These nitrates are dried, crushed, melted, insolubles removed, reheated and prilled
- These nitrates are used as fertilizer or as "solar salt"
- Available as individual components or premix
- Melting temperature of individual components are different than premixed prills

Molten Salt for Special Applications heater (Picture from SQM, Coya Sur, Chile)



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Molten Salt for Special Applications better Solution Solu



"Lessons learned" with Molten Salt

- Design of the system and equipment must consider experience with salt, i.e. salt creeps, freezes, dissolves graphite, salt has a high density, salt ages when in contact with oxygen, even low impurties and possible insolubles have to be considered (corrosion, abrasion)
 - Adequate preheating and heat tracing of salt wetted parts (equipment, piping) is required
- Pipe routing and piping engineering is not "standard"
- The entire system should be drainable by gravity
- Salt is not salt ! (although quite some companies think the contrary is true)

Salt is not Salt

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(impurities, CI (from 0.03 – 0.48%); insolubles, i.e, sand, "rocks", even other (from 0.02 – 0.1%))



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Link to Solar Power Plants

- Latest development on Solar Power Plants is the thermal storage of "heat", by using solar salts
- Bertrams Heatec has more than 60 years experience in dealing with molten salt
 - Experience means the theoritical expertise, improved by the lessons learned during commissioning, including feedback of endusers during operation of their plant(s)
- Continuous improvement on design based on this experience

Solar Power Plants with TES (Thermal Energy Storage)

The solar energy is caught by a heat transfer fluid (HTF), Therminol VP1, Dowtherm A, or equivalent, circulating in a closed loop. The HTF is heated by the solar radiation up to 393°C (740°F), produces superheated steam in a shell and tube heat exchanger train and comes back to the solar radiation receivers at 293°C (560°F). To extend the operation beyond sunshine hours, a thermal energy storage system, consisting of 2 molten salt storage tanks is integrated in the solar plant. The solar energy collected by the solar field during the day is partly used for thermal storage, i.e. charging of one tank at approx. 384°C (723°F)

Solar Power Plants with TES (Thermal Energy Storage)

To discharge this heat during the night, the salt is pumped from the hot storage tank, through a shell and tube heat exchanger train, to the cold storage tank and will be cooled down to approx. 292°C (558°F). In this configuration, the HTF coming from the solar field at 393°C (740°F) is diverted to the heat exchangers, where its thermal energy passes to the salt flow arriving from the cold tank. The thermal energy transferred to the salt in the heat exchanger is accumulated in form of the hot molten salt in the hot tank. During the night or time of reduced radiation, the charging process is reversed and salt from the hot tank is pumped to the same heat exchangers, where the salt returns its thermal energy to the cold HTF

Solar Power Plants with TES



Solar Power Plants with TES

(Picture from Flagsol GmbH)



Solar Power Plants What can Bertrams Heatec offer you?

- Design, manufacturing and supply of the complete TES (Thermal Energy Storage) system, including performance quarantees
 - Design, manufacturing and supply of the Initial Nitrate Melting system, including supply and handling of the nitrates
 - Design, manufacturing and supply of the HTF (Heat Transfer Fluid) back-up heating system, including performance quarantees
- Erection supervision worldwide
- Commissioning and after sales service worldwide



Solar Power Plants Bertrams Heatec Inc.

Thank you for your attention

 For questions, inquiries, etc., please contact us: <u>www.bertrams-heatec.com</u>, <u>steven.koning@bertrams-heatec.com</u> or <u>andrew.lochbrunner@bertrams-heatec.com</u>