



Small Capacity Sulfur Recovery Units

John Watson – GTP/Merichem

2008 AIChE Midwest Regional Conference

Chicago, Illinois
September 22, 2008



Merichem Chemicals & Refinery Services LLC
Gas Technology Products
846 East Algonquin Road, Suite A310
Schweitzburg, IL 60173
(847) 285-5030 • Fax (847) 285-5068
www.gtp-merichem.com

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Agenda

- o Introduction to GTP
- o Large vs. Small Sulfur Recovery Units (SRUs)
- o Sulfur Scavengers
 - o Liquid Media
 - o Solid Media
- o Liquid Redox Systems
- o Applications
- o Future Focus

Merichem Chemicals & Refinery Services LLC
Gas Technology Products
846 East Algonquin Road, Suite A310
Schweitzburg, IL 60173
(847) 285-5030 • Fax (847) 285-5068
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Introduction to GTP --History--

1970-1992

ARI Technologies was an independently owned Chicago area company. Specialized in air pollution control systems & technologies

Developed proprietary technologies

Fluidized bed, catalytic oxidizer

Catalyst for oxidizing chlorinated hydrocarbons


Cobalt-based catalyst for the oxidation of mercaptans to disulfides

Thermal DeNO_x system for calcining kilns

Iron-based, liquid redox system for the oxidation of H₂S

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Schweitzburg, IL 60173
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Introduction to GTP --History--

1992 -1996
ARI Technologies bought by Wheelabrator Technologies (WT) and joins Wheelabrator Clean Air Systems

1996-1999
US Filter buys Clean Air Systems – forms Gas Technology Products from ARI


1999-2001
Vivendi buys all of USFilter

2001-Present
Merichem buys GTP from Vivendi

38 years – Lots of owners – Same Technology and Core People
Remains a Chicago Area Company

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Gas Technology Products
646 East Algonquin Road, Suite A100
Schaumburg, IL 60195
(847) 285-5000 - Fax (847) 285-3000
www.gtp-world.com

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Large vs. Small Sulfur Recovery Units (SRUs)

- o Claus Process – Industry Standard / Large
 - o 20 to 1000+ TPD of Sulfur Recovery
- o Scavengers – Very small scale disposable
 - o Solid Media
 - o Liquid Media
- o Liquid Redox – Small scale regenerable
 - o 200 kg – 25+ TPD of Sulfur Recovery

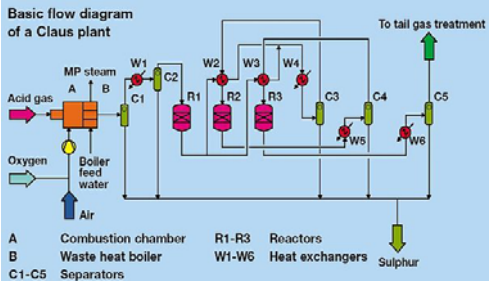
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Large SRU – Claus Process


Basic flow diagram of a Claus plant



A Combustion chamber
B Waste heat boiler
C1-C5 Separators
R1-R3 Reactors
W1-W6 Heat exchangers
Sulphur

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Schaumburg, IL 60195
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Large SRU – Claus Process

- o $\text{H}_2\text{S} (\text{g}) + 1/2 \text{O}_2 (\text{g}) = \text{H}_2\text{O} + \text{S}^{\circ}$
- o Lowest OPEX per ton of Sulfur
- o Requires removal of H_2S from HC stream
- o Can require Acid Gas Enrichment
- o Equilibrium limited – Requires Tail Gas Treating to meet modern guidelines
- o Condensed liquid sulfur – retains trace H_2S
- o Limited turn-down capability
- o Limited ability to accept feed instability

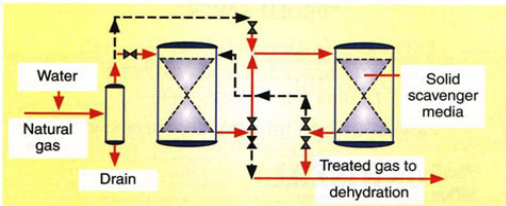
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Gas Technology Products
646 East Alhambra Road, Suite A100
Schaeffsburg, IL 60173
(847) 285-5000 • Fax (847) 285-3006
www.gpp-merrichem.com

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Very Small SRUs Solid Scavengers

Dual Vessel Lead-Lag Solid Scavenger System



Merrichem Chemicals & Refinery Services LLC
Gas Technology Products
646 East Alhambra Road, Suite A100
Schaeffsburg, IL 60173
(847) 285-5000 • Fax (847) 285-3006
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Very Small SRUs - Scavengers

- o **Original Solid Scavenger (1875)– Iron Sponge**
 - o Hydrated ferric-oxide on wood chips
 - o Reacts with H_2S to form iron sulfide
 - o Spent media potentially pyrophoric – keep wet
- o **Modern Solid Scavengers (Sulfur-Rite®)**
 - o Iron oxide on ceramic base
 - o Reacts with H_2S to form iron pyrite
 - o Not equilibrium limited
 - o High turndown – flexible operation
 - o Can remove H_2S from virtually any gas
 - o Spent media usually non-hazardous – landfilled
 - o OPEX relatively high – fresh media – \$4/#sulfur

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Gas Technology Products
646 East Alhambra Road, Suite A100
Schaeffsburg, IL 60173
(847) 285-5000 • Fax (847) 285-3006
www.gpp-merrichem.com

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Very Small SRUs – Liquid Scavengers

- o Caustic Treating – “Original” Liquid Scavenger
 - o Reversible reaction – H₂S release possible
 - o Expensive – disposal of sulfidic caustic difficult
- o “Flexible” flowschemes for liquid scavengers
 - o “Bubble” beds - batch
 - o Continuous injection
- o Modern scavengers (The Eliminator®)
 - o Some spent media provides corrosion protection
 - o Not equilibrium limited
 - o High turndown – flexible operation
 - o Can remove H₂S from virtually any gas
 - o High OPEX - \$10/#sulfur for fresh media

Mericum Chemicals & Refinery Services LLC
Gas Technology Products
646 East Alhambra Road, Suite A100
Schaeffberg, IL 60173
(847) 285-3000 - Fax (847) 285-3008
www.gpp-merichem.com

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Small SRUs – Liquid Redox (LO-CAT®) How it Works

Aqueous-based, ambient temperature process
 Converts H₂S to elemental sulfur
 Employs a “Chelated-Iron” catalyst
 Reactions are not equilibrium limited
 Removal efficiencies of 99.9+% are obtained in one step
 100% turndown
 Can process any gas stream containing H₂S – fuel gas,
 acid gas, SWS gas, biogas, etc.
 Lower OPEX - \$0.15/#sulfur

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646 East Alhambra Road, Suite A100
Schaeffberg, IL 60173
(847) 285-3000 - Fax (847) 285-3008
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Introduction to Liquid Redox How it Works

Chelates are organic compounds, which increase the solubility of metal ions in water.

- Chelates can increase the solubility of iron from 4 ppm to 5 wt%

“Chelated Iron” is employed as a catalyst to accomplish the modified, Claus reaction:

$$\text{H}_2\text{S (g)} + 1/2 \text{O}_2 \text{ (g)} \xrightarrow{\text{Fe}} \text{H}_2\text{O} + \text{S}^0$$

Non-equilibrium limited Sulfur as a solid
Iron is the catalyst

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646 East Alhambra Road, Suite A100
Schaeffberg, IL 60173
(847) 285-3000 - Fax (847) 285-3008
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Introduction to Liquid Redox
How it Works

Overall Reaction

$$\text{H}_2\text{S (g)} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{S (aq)}$$

$$\text{H}_2\text{S (aq)} \rightleftharpoons \text{HS}^- + \text{H}^+$$

$$\text{HS}^- + 2\text{Fe}^{+++} \rightleftharpoons \text{S}^0 + 2\text{Fe}^{++} + \text{H}^+$$

$$\frac{1}{2} \text{O}_2 \text{ (g)} + \text{H}_2\text{O} \rightleftharpoons \frac{1}{2} \text{O}_2 \text{ (aq)}$$

$$\frac{1}{2} \text{O}_2 \text{ (aq)} + 2\text{Fe}^{++} + \text{H}_2\text{O (l)} \rightleftharpoons 2\text{Fe}^{+++} + 2\text{OH}^-$$

$$\text{H}_2\text{S (g)} + \frac{1}{2} \text{O}_2 \text{ (g)} \rightleftharpoons \text{H}_2\text{O} + \text{S}^0$$

Rate limiting steps → $\text{H}_2\text{S (g)} + \text{H}_2\text{O}$
Iron is a catalytic reagent → Fe
Reaction is not equilibrium limited → S^0

Sulfur is formed as a solid

Merichem Chemicals & Refinery Services LLC
 Gas Technology Products
 846 East Aljurgan Road, Suite A100
 Schenectady, NY 12303
 (847) 285-5000 • Fax (847) 285-5008
 www.gtp-merichem.com

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Liquid Redox
Basic Process Configurations

Conventional Processing Scheme

- Utilized when processing
 - Combustible gas streams - Syngas, Fuel Gas, Natural Gas, Associated Gas.
 - Treated gas streams to be recovered that cannot be contaminated with air.

Autocirculation Processing Scheme

- Utilized when processing
 - non-combustible gas streams - Amine Acid Gas, Sour Water Stripper off-gas
 - Treated gas streams which are typically vented to the atmosphere.

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 Schenectady, NY 12303
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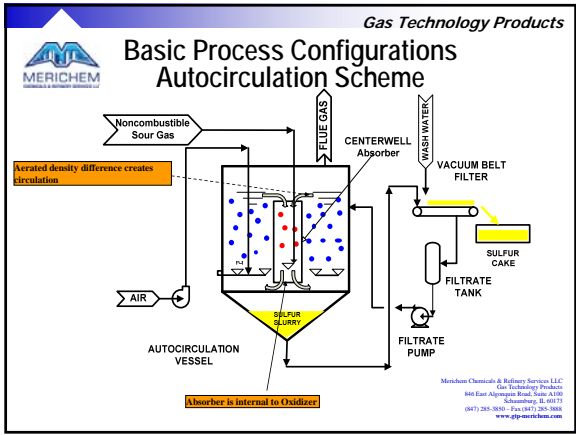
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Basic Process Configurations
Conventional Scheme

Any kind of non-plugging absorber can be employed


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Liquid Redox - Chemical Additives

Chemical additives have 5 basic functions

- Replenishment of chelate loss due to degradation
- Replenishment of chelated iron due to physical losses from unit
- Prevention of biological activity (birth control pill)
- Surfactant to improve sulfur settling rates.
- Alkaline material to control pH @ ~ 8.5
 - NaOH - Non-CO₂ systems
 - KOH - CO₂ Systems
 - NH₃ - All systems
- Cost = \$125 - \$200/ton of sulfur

Merrichem Chemicals & Refinery Services LLC
Gas Technology Products
846 East Algonquin Road, Suite A100
Schwanenburg, IL 60175
(847) 285-5000 - Fax (847) 285-5008
www.gtp-merrichem.com

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Liquid Redox - Sulfur Disposal

Produced as a solid
No dissolved H₂S in sulfur

Methods of removal:


- Bag filter - 35% sulfur cake (simple gravity filtration)
- Vacuum belt filter - 65% sulfur cake
- Pressure filter - 80+% sulfur cake
- Molten sulfur - 99.9% pure

As purity increases:

- Operating costs decrease
- Capital costs increase

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Gas Technology Products
846 East Algonquin Road, Suite A100
Schwanenburg, IL 60175
(847) 285-5000 - Fax (847) 285-5008
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Liquid Redox - Bag Filter



Merrichem Chemicals & Refinery Services LLC
Gas Technology Products
846 East Algonquin Road, Suite A100
Schwanenburg, IL 60175
(847) 285-5000 - Fax (847) 285-5008
www.gtp-merrichem.com

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Liquid Redox – Belt Filter



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MERICHEM Chemicals & Refinery Services LLC
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 646 East Alton Road, Suite A100
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Liquid Redox -Sulfur Disposal

Solid sulfur is advantageous for agricultural use

- Good soil absorption
 - 8 micron average particle size
 - Process surfactant enhances hydrophilicity
- Can be applied to soil as produced by liquid redox

Contains micronutrients

- Chelated Iron, thiosulfate are present in sulfur cake

Excellent fungicide when applied directly on foliage

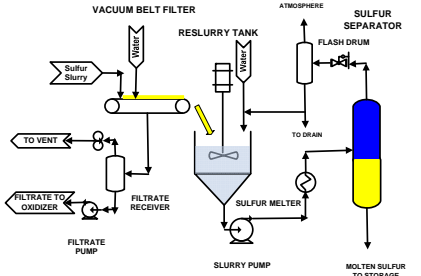
Experience = 25,000+ TPY of sulfur from Liquid Redox is used in agricultural direct soil applications

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Liquid Redox Sulfur Melter



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Liquid Redox Molten Sulfur Quality

Sulfur	99.86 wt%
Carbon	0.075 wt%
Ash	0.009 wt%
Moisture	0.093 wt%
As	< 0.1 ppmw
Se	< 0.1 ppmw
Te	< 0.1 ppmw

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Schauversburg, IL 60173
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Traditional Markets for Small Capacity SRUs

- Oil & Gas Production
- Refining
- Chemical Processing
- WTP / WWTP
- Iron & Steel Production
- Food & Beverage Grade CO₂
- Geothermal Power

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Developing Markets for Small Capacity SRUs

- Floating Oil Production Vessels
- Gasification
 - Traditional HC
 - Waste
- Carbon Sequestration

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Summary

“CLAUS family” will continue to be dominant S producer

Small Sulfur Recovery Units
 not equilibrium limited
 reliable, flexible operations
 high turndown
 can treat almost any gas

Liquid Redox
 produces solid, H₂S free sulfur
 with potential agricultural use
 lowest OPEX small SRU

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Thank You



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