Reactive stripping in a rotating packed bed for the production of hypochlorous acid

Reported at BHR Group PI conferences in 1999 and 2001 by Dave Trent, Dan Tirtowidjojo and George Quarderer and:
One of the 20 PI cases reported in the review issued 2003

Henk van den Berg ***PIN NL 17 June 2010***

How this research project was started

Dow wanted to have low-chlorides hypochlorous acid HOCl to replace Cl_2

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Looking for a production process in industry + literature

Selected: stripping of HOCl from the brine produced from reaction of Cl_2 and aqueous caustic soda

Process properties:

- Looked simple and low capital
- Inexpensive raw materials
- Fast kinetics, low vapor pressure of HOCl and undesired decomposition reaction

Process chemistry

Reaction of chlorine and caustic soda in 2 steps:

$2NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O$

$NaOCl + Cl_2 + H_2O \rightarrow 2HOCl + NaCl$ (solution <5kmol/m3)

HOCl and NaOCl are in equilibrium, to NaOCl at high pH, at pH 3-5 HOCl is dominant (2nd reaction)

Hypochlorite is ionic, HOCl is not →can be stripped at low pH

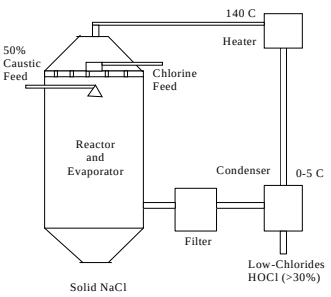
But: HClO in the presence of OCl^- and Cl^- is very unstable

$2HOCl + OCl^- \rightarrow ClO_3^- + 2HCl$

Maximum rate at pH~7.4, this must be traversed as NaOH reacts with Cl_2 to HOCl (conversion in seconds)

Vapor phase reaction: $2\ HOCl \rightarrow Cl_2O + H_2O$ (already at 1 molar) and explosion limit Cl_2O ~23%

Olin Corporation's process for low-chlorides HOCL



HOCl yields 65-80% on NACl

But:

- Solid salt product
- Energy consumption
- High gas recycle
- 50% NaOH expensive
- High pressure (65-70 bar) for spray atomization in Cl_2
- Close to explosion limit Cl_2O

Process concepts

Developments in Dow before RPB –Rotating Packed Bed:

- Understanding that HOCl had to pass quickly through the decomposition pH zone
- HOCl reasonable stable in the vapor phase, can be absorbed in water = low-chlorides HOCl
- Absorb Cl_2 gas in diluted NaOH, countercurrently
  → no precipitation of NaCl
  → HOCl formed in caustic and evaporation with water
  → reasonable yield - 75-80%, and energy input

But:

- Small liquid drops (<200 micron) entrained in gas
- Large gas flow → large diameter towers
- Small spray nozzles prone to plugging, salt formation

Process concepts

Gas-side mass transfer limitation

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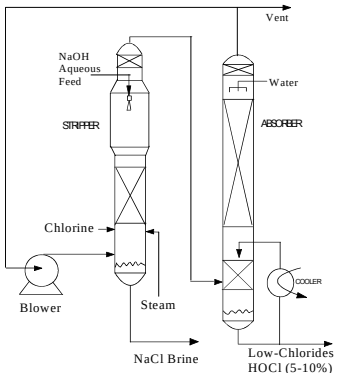
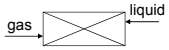
limited room for improvement in packed tower



Process intensification

George Quaderer suggested RPB – rotating packed bed:
centrifugal forces move liquids through porous packing,
gas moves countercurrently

Many issues:



- Construction
- Shorter contact times to lower losses??
- Operation parameters
- Scale-up
- No understanding of RPB mechanism, contact times, mass transfer

→ **Pilot RPB build and tests done**

Rotor: axial height 25 mm, outside diameter 406 mm

Process intensification – Rotating Packed Bed

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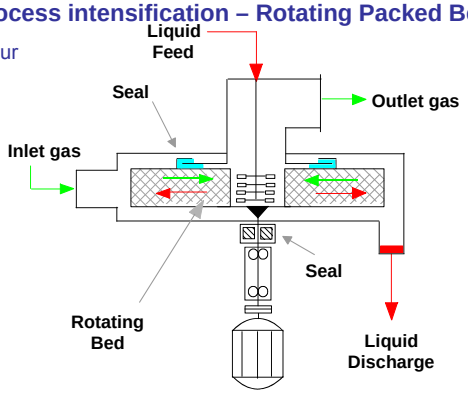

Process intensification

No good V/L data for HOCl over brine

Pilot plant variables:

- Packing – glass beads, flat plates, **wire gauze** → packing geometry, surface area, porosity
- G and L side mass transfer resistance
- V/L ratio to be 20+ for HOCL yields 90% required
- RPM – no effect of G-force > 20
- Packing support
- Liquid distribution – full cone spray nozzles preferred
- Average HTU 4.2 cm, can be reduced to 1.8 cm

Results used for scale-up

RPB – industrial application

System

- Absorption of Cl_2 + reaction – liquid site controlled, stripping HOCL is gas-side mass transfer controlled

Characteristics:

- Short residence time, time scale adequate for reaction and mass transfer
- Mechanical design
- New in application

Results:

- Lower ΔP than expected
- HTU was nearly doubled compared to pilot → 8 cm
- High gas side mass transfer coefficient $k_g a \sim 50\ s^{-1}$
- HOCL yields > 90%

RPB – industrial application

HOCl absorption tower and RPBs

Operation for almost 10 years!

Development path:

The need to improve
Exploring new idea
Development of pilot
Pilot tests
Understanding fundamentals
Scale-up
First a conventional column built
RPB has taken over

No9 Trent+/Dow - reactive stripping in RPB

- **Goal: efficient HOCl production**
- **Existing: stripping of HOCl from brine of Cl2 and NaOH**
- **New: application of rotating packed bed**
  - **quickly move through decomposition zone and maximize rate of stripping HOCl to reduce CLO3-**
  - **minimize rate of decomposition to Cl2O**
- **RPB - a new technology; no result of systematic analysis or process synthesis**
- **Results: improved HOCl yield, lower costs**