CHLOR - ALKALI 2

1994

REACTIVE CHEMICALS REVIEW

BRINE AREA

BRINE TREATING
CHEMICAL REACTIONS

$Ca + Na_2CO_3$ ---> $CaCO_3 + 2\ Na$

$Mg + 2\ NaOH$ ---> $Mg(OH)_2 + 2\ Na$

$2\ NH_4Cl + 2\ NaOCL$ ---> $N_2 + 3\ NaCl + 3\ H_2O + 2\ HCl$

TANNINS + NaOCl ---> INSOLUBLE SOLIDS

$2\ NaOH + Cl_2$ ---> $NaOCl + NaCl + H_2O$

$2\ NaOH + CO_2$ ---> $Na_2CO_3 + H_2O$

pH > 10

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NOTE: As per the reactive chemical audit of 1994, the following action item response has been entered on 1-5-95. The action item # is RC-10. Follow up by Jeff Harrison.

In the Brine Treating area, T-101B (Carb. Tower) utilizes the above reaction:

$$2\ NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O$$

pH > 10

to form Sodium Carbonate. Sodium Carbonate is used in the mix tanks to treat Calcium. However, the above reaction requires a pH > 10. In the event the pH is low (7-10), the possibility exists for the following to form (Bicarbonate):

$$OH^- + CO_2 \longrightarrow HCO_3^-$$

pH 7-10

This an unwanted reaction from the standing that the efficiency of Calcium removal becomes lower. Requiring twice as much Bicarbonate than Carbonate to treat the Calcium in the mix tanks. See the following reactions:

<u>Carbonate and Calcium</u>

$$CO_3^{--} + Ca^{++} \longrightarrow CaCO_3$$

<u>Calcium and Bicarbonate</u>

$$2\ HCO_3^- + Ca^{++} \longrightarrow Ca(HCO_3)_2$$

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Therefore, the undesired result is the efficiency reduction. The potential for Hydrogen gas formation in the Bicarbonate reaction is not likely.

Lines of Defense

To prevent the Bicarbonate from forming, the Carbonate tower runs with a pH control scheme and grab samples are analyzed 3 times per shift.

Reaction Chemistry for MDEA in Raw Brine Entering the Chlor-alkali Process

The likely reaction pathways for MDEA in brine are as follows:

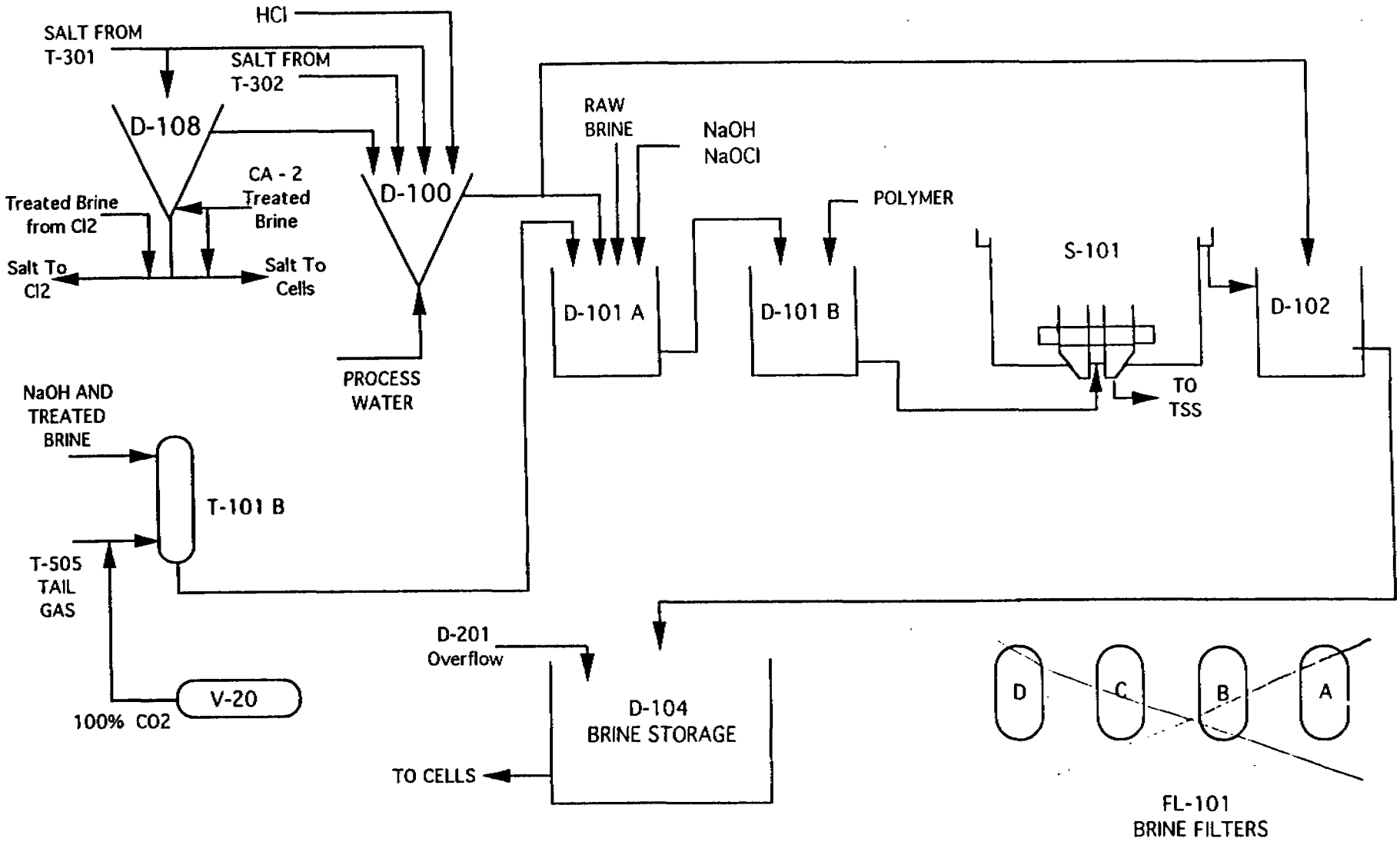
Reaction 1	$CH_3N(CH_2\,CH_2OH)_2 + 2HOCl \rightarrow ClN(CH_2\,CH_2OH)_2 + HCHO + H_2O + HCl$
	then
Reaction 2	$ClN(CH_2\,CH_2OH)_2 \rightarrow NH_2CH_2CH_2OH + HCHO + HCl,$
	then
Reaction 3	$NH_2CH_2CH_2OH + 2HOCl \rightarrow NH_2Cl + 2HCHO + HCl$
	then
Reaction 4a	$2NH_2Cl + 2H_2O \rightarrow N_2 + 2HCl + 2HOCl + 2H^+$
	or
Reaction 4b	$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$
	or
Reaction 4c	$NH_2Cl + 2HOCl \rightarrow NCl3 + 2H_2O$

The selected reaction pathway from among Reactions 4a-c is highly dependent on molar ratio of hypochlorus acid to MEA and pH. High pH (≥12) promotes reaction 1. Reaction 4c should be assumed for reactive chemical planning purposes, though reactions 4a-c are likely to be competing.

LINES OF DEFENSE

1. Grand Bayou Operations has written agreements with the owners of the gas fractionation plant where the MDEA is stored to report significant releases of MDEA to Dow.
2. Maximum allowable quantities have been established with the owners of the gas fraction plant for on-site storage of MDEA.
3. Extreme dilution of an MDEA spill with ground water used for mining would mitigate any immediate danger from excessive nitrogen trichloride formation.
4. Raw brine is monitored for ammonia content weekly.
5. Brine mining wells can be quarantined to control or prevent processing of contaminated brine.
6. Any MDEA release large enough to have a significant impact on raw brine would trigger and environmental notification.
7. Nitrogen trichloride is monitored in the taffy pots weekly.

BRINE AREA



BRINE
RAW MATERIALS

BRINE:

Ca	350 PPM
Mg	10 PPM
NaCl	300 GPL

RESATURATED BRINE:

NaCl	350 GPL
NaOH	1 - 5 GPL

CARBONATE:

NaOH	3 - 6 GPL
Na_2CO_3	60 - 80 GPL

HCl:

15 - 18% Dilute from 35% with Condensate

NaOH: 10%

BETZ 90820

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BRINE
PRODUCTS

TREATED BRINE:

Total Hardness (Ca^{+2}) 2 - 5 PPM

NaOH	1.5 - 4 GPL
Na_2CO_3	2 - 2.5 GPL
NaOCl	60 -80 PPM
NH_3	< 1 PPM
NaCl	> 300 GPL

CLARIFIER UNDERFLOW:

H_2O	70.5 %
NaCl	23.7 %
$CaCO_3$	4.8 %
$Mg(OH)_2$	0.5 %
Na_2CO_3	0.2 %
NaOH	0.1 %
SOLIDS	0.1 %
FLOC	0.01 %