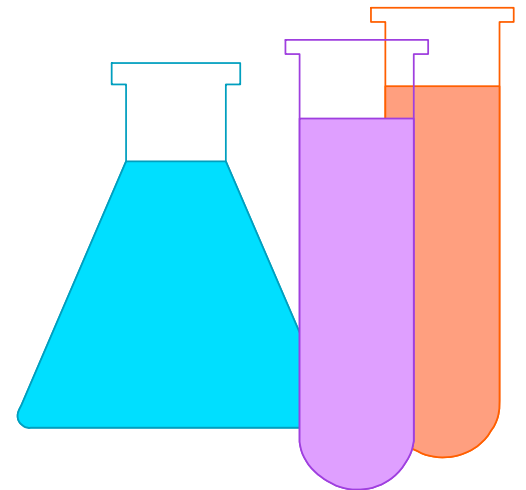


Chlorine Dioxide Generation Chemistry

Dennis Froats
ERCO Worldwide Technical Service

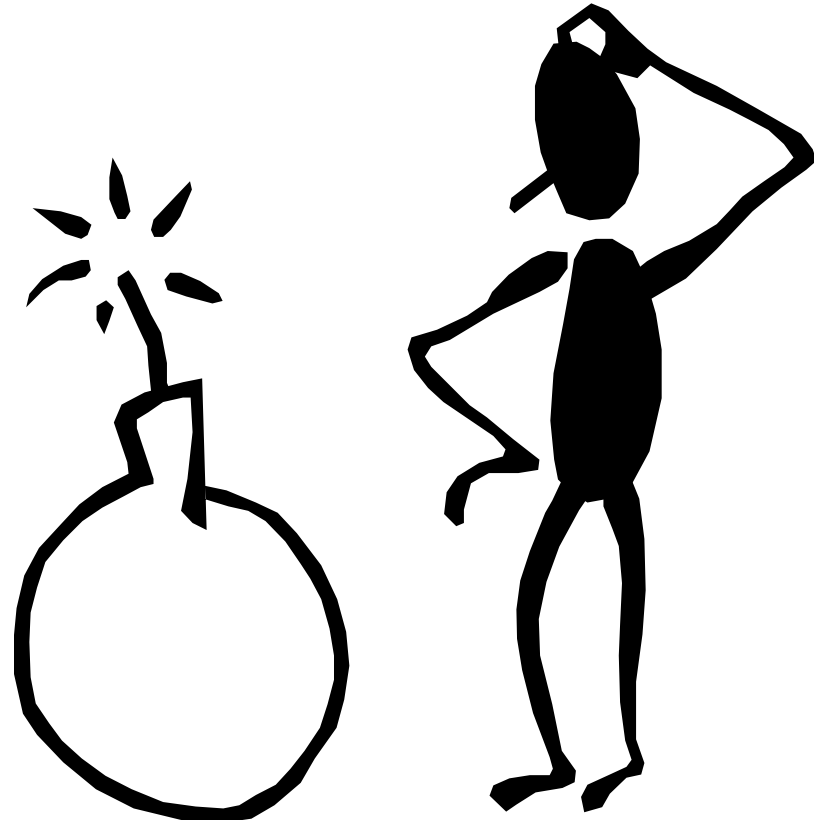


What is Chlorine Dioxide?

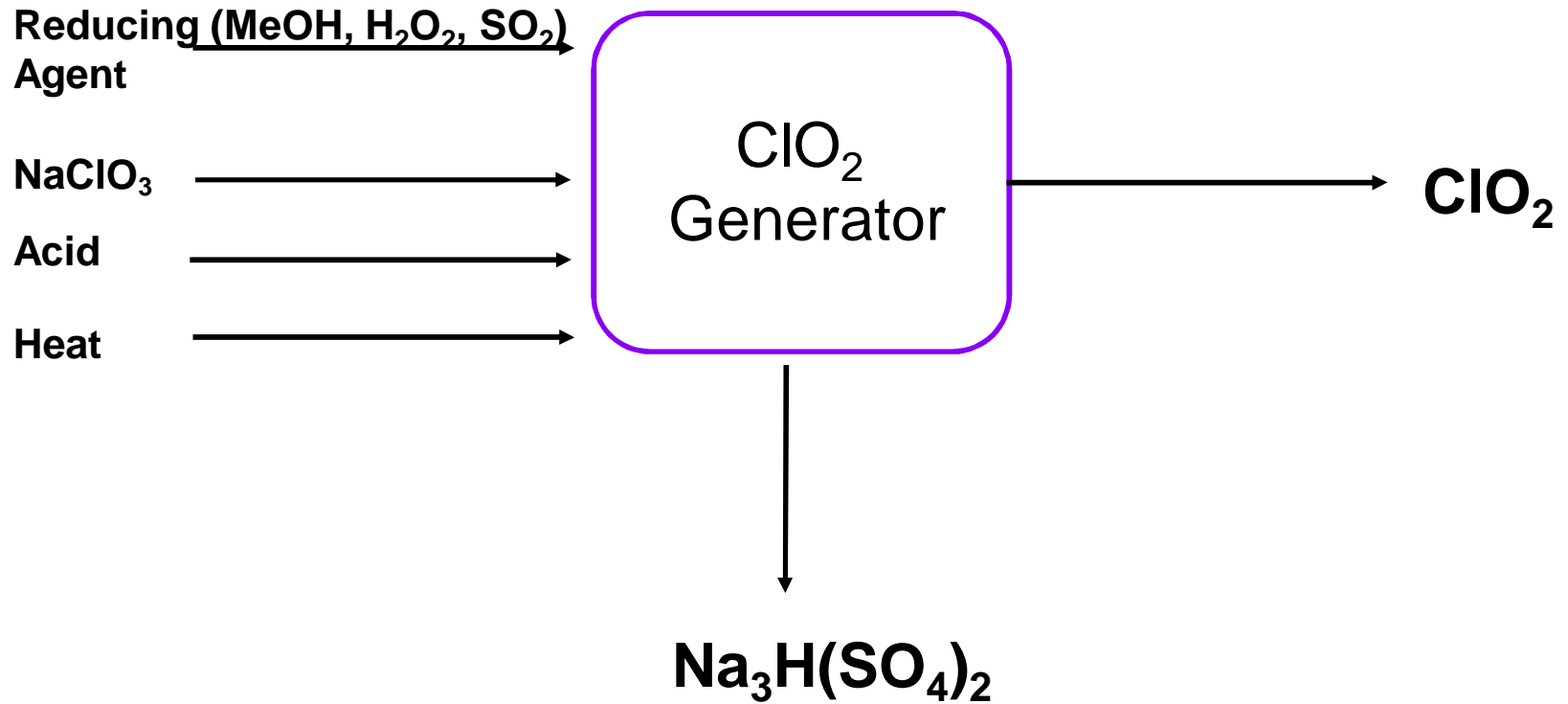
- ClO_2 is a valuable bleaching agent for pulp.
- It can bleach pulp to a high brightness while maintaining pulp strength & viscosity.

What is Chlorine Dioxide?

- ClO_2 gas will decompose violently under certain conditions.
- It must be produced at the mill near the point of application.
- It must be treated with respect.



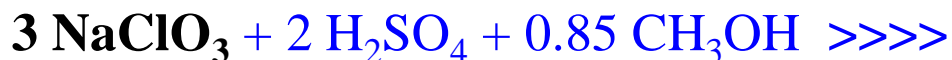
Process Flow Diagram



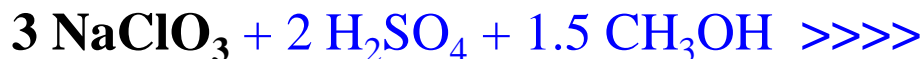
Chemical Reactions



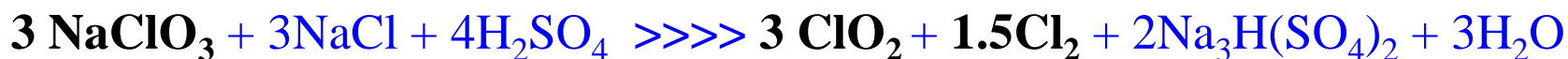
Reaction 1 (Most Desirable)



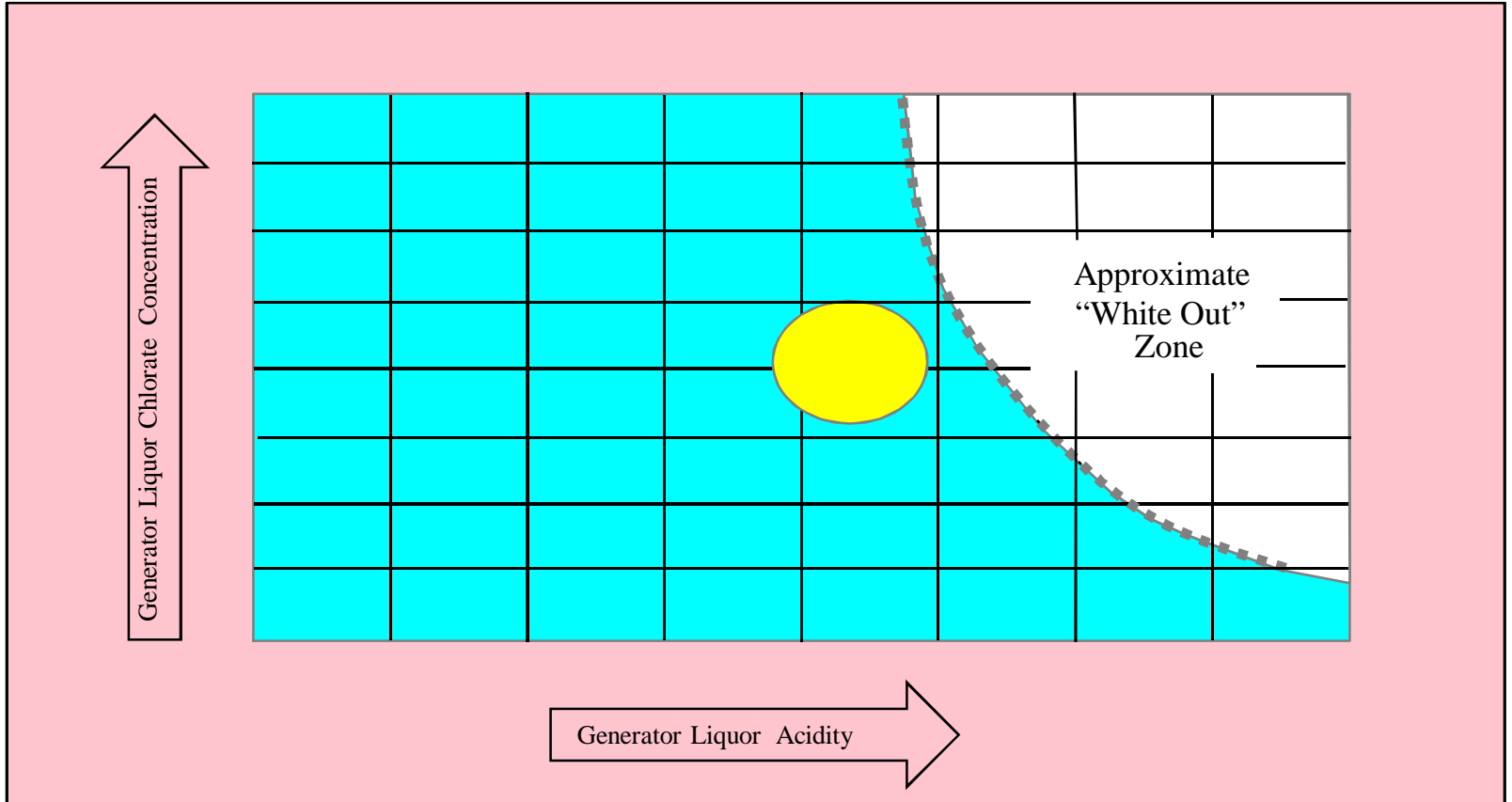
Reaction 2 (Less Desirable)



Reaction 3 (Unavoidable)

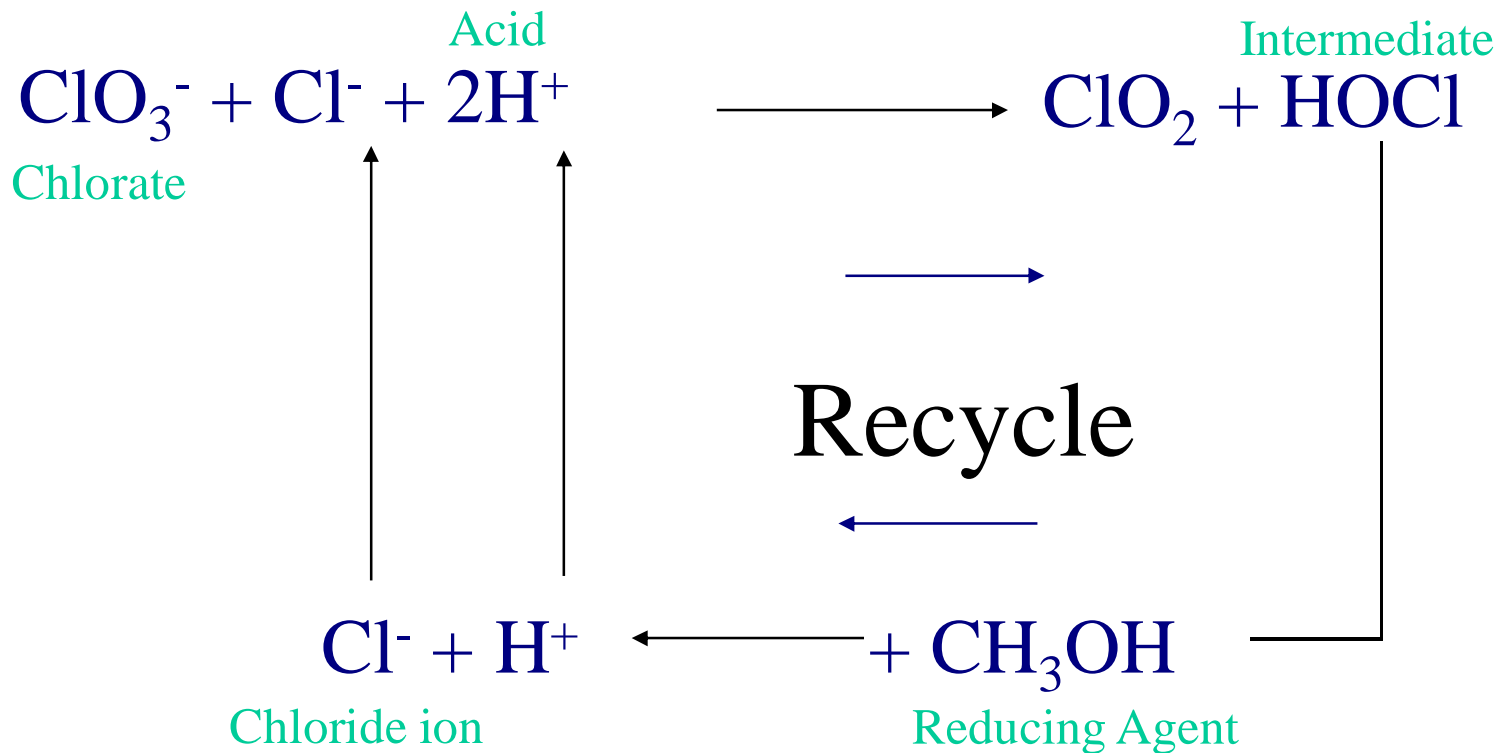


Generator Liquor Conditions

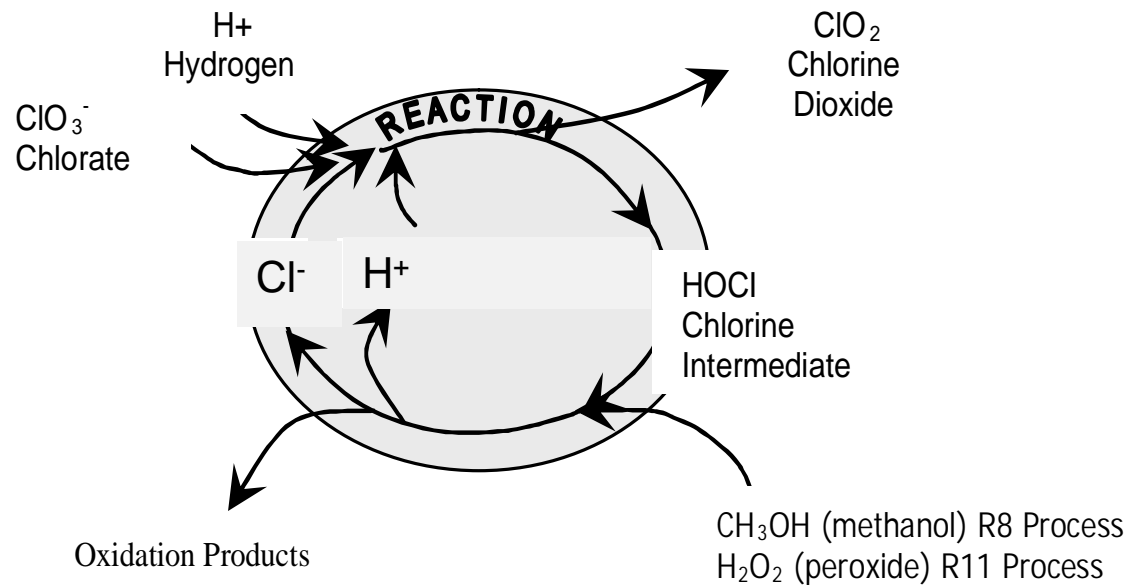


Reaction Mechanism

Chlorate Reduction in Acid Environment



Reaction Cycle



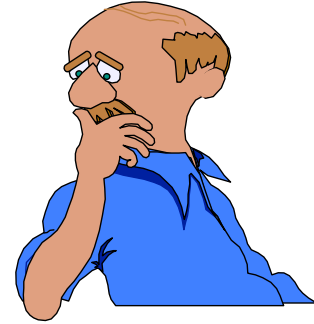


What is a “White-Out”?

A white-out is the cessation of chlorine dioxide production due to the depletion of chloride in the generator, which typically occurs at high generator liquor acidity.

Production of chlorine dioxide will stop even though there is a flow of all the feed chemicals into the generator. (Reducing Agent, Chlorate, & Acid)

How to recognize a “white-out”



- ClO_2 analyzer reading drops quickly to zero (0) gpl.
- The generator liquor is a milky “greyish” color. The ClO_2 , which imparts the yellow/green color, is absent.
- The generator liquor temperature generally higher than normal due to higher acidity.
- Chlorine is formed, consuming all the chloride present in the generator.
- Typically there is a high generator pressure when MeOH is flowing or restarted (ejectors are overloaded with chlorine) and the liquor remains milky grey even after the methanol has been flowing for some time.

How to recover from a “white-out”

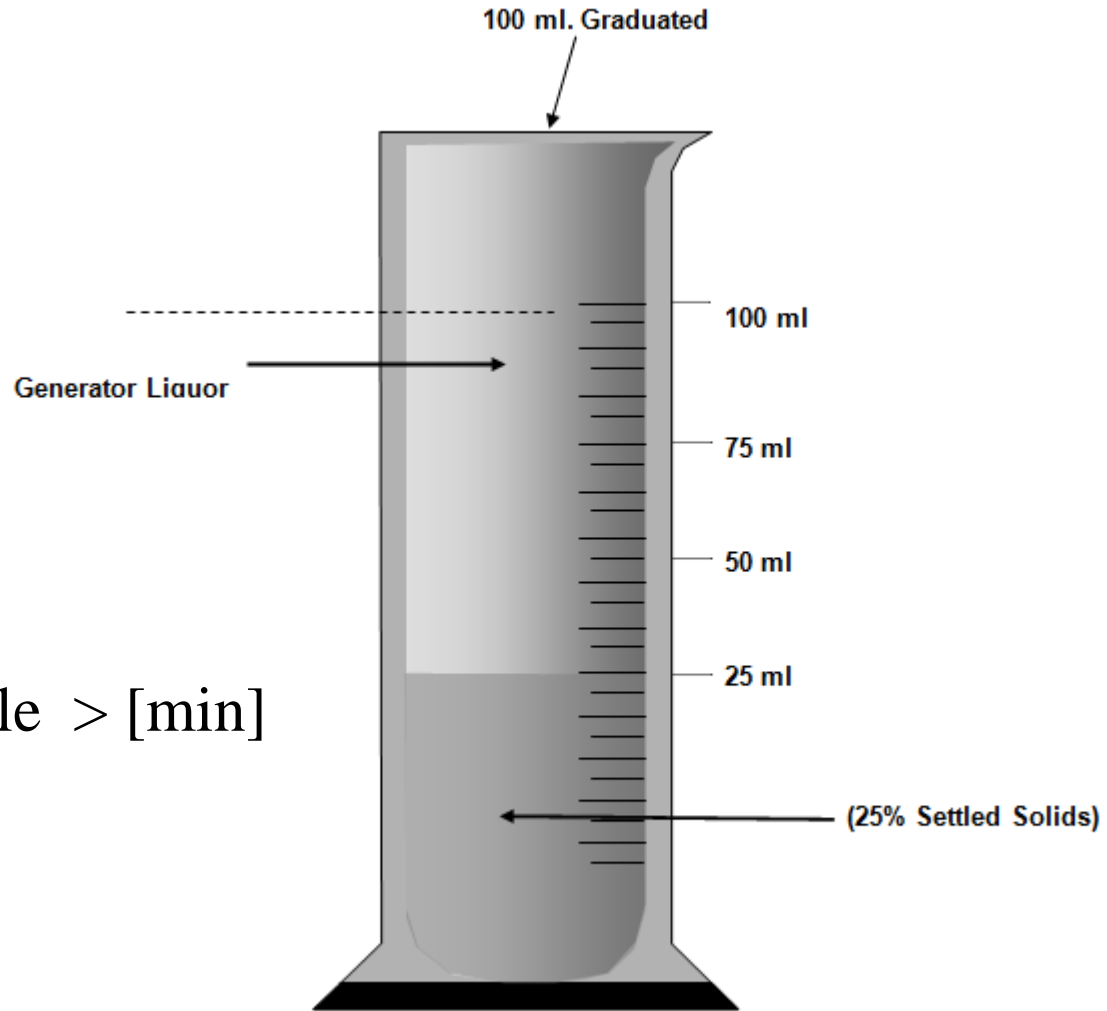
- Test generator liquor. Is white-out due to high acid, chlorate, or both?
- If generator has not tripped - shut off acid feed.
 - Stop chlorate feed only if necessary.
- Dilute generator liquor with water.
 - Add water until the liquor temperature is approximately 1°C lower than the normal operating temperature.
- Adjust flow of chilled water to absorption tower and start ClO₂ production by restarting methanol (MeOH) flow.
- Test liquor concentrations again and restart acid feed at correct flow.

Low Acidity White-Out

A White-Out can also occur when starting up the generator with a fresh chemical batch.

Liquor Acidity Test

[max] > acidity sample > [min]

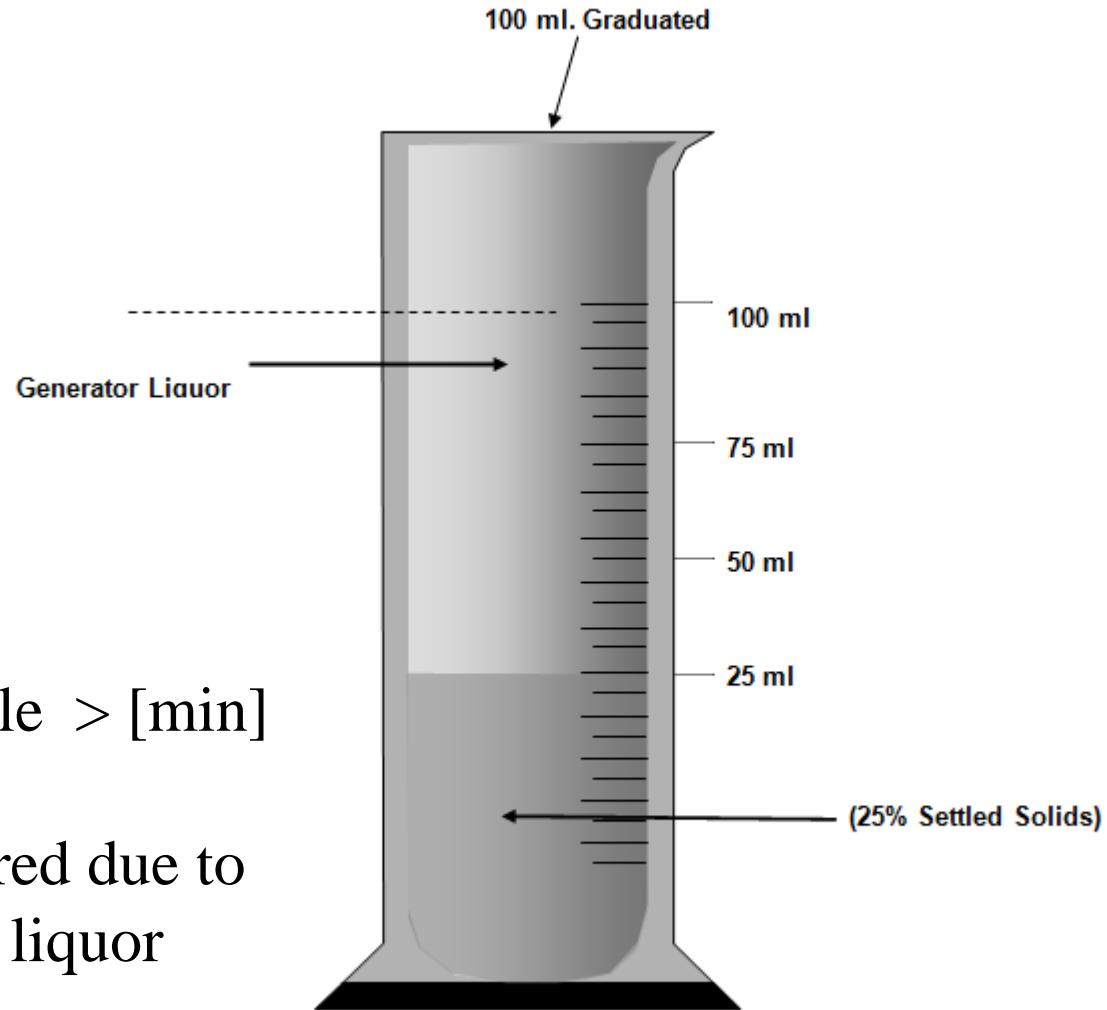


Liquor Acidity Test

[max] > acidity sample > [min]

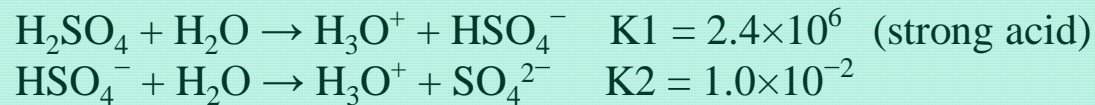
> 70% acidity measured due to dissolved bisulfate in liquor

$\text{Na}_3\text{H}(\text{SO}_4)_2$ solid



Low Acidity White-Out

In this case, a measure known as the Free Acidity is important.



Free acidity is the measure of the concentration of the first proton from the sulphuric acid, which is available for the reaction to produce ClO_2 .

Free acidity does not include bisulfate (HSO_4^-) acidity

Total acidity = acid test = free acidity + bisulfate acidity

How to Avoid a Low Acidity White-Out

Keep the Free Acidity constant at the appropriate value until the saltcake saturation point has been reached (solids appear in liquor).

Follow the recipe in the operators manual.

ClO₂ Chemistry - Summary

- There always needs to be traces of chloride in the generator to sustain the reaction (amount is a function of the reducing agent).
- Reaction 1 is the most efficient reaction.
- Acid is the greatest contributor to reaction efficiency.
- Too much acid (or chlorate) can cause “white-outs”.
- Follow operator’s manual recipe for fresh chemical batch startups.