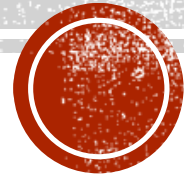


**IsoFLO<sup>TM</sup>**  
**WHITE LIQUOR OXIDATION  
REACTOR**

**NORAM**



**PAPTAC BLEACHING COMMITTEE  
MEETING AT DOMTAR DRYDEN -  
SPRING 2020**

**Rohan Bandekar**  
*[rbandekar@noram-eng.com](mailto:rbandekar@noram-eng.com)*

# INTRODUCTION

## ■ White Liquor

- Mainly NaOH and Na<sub>2</sub>S
- Also contains Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>

## ■ Inexpensive source of NaOH

- Purification of Flue gases
- Oxygen Delignification
- Caustic Extraction in Kraft Pulp Bleaching

# INTRODUCTION

## Why Oxidize White Liquor?

- ❖ Reduces/Eliminates the formation of hydrogen sulfide when the liquor pH drops below 10
- ❖  $\text{Na}_2\text{S}$  negatively affects pulp quality (brightness and viscosity) when used in  $\text{O}_2$  Delignification and Bleach Plant Extraction Stages
- ❖ Using oxidized white liquor as a source of alkali is often necessary to preserve the mill's chemical balance without the need for purchased chemicals

# INTRODUCTION

## ▪ Partial Oxidation of White Liquor to Thiosulphate

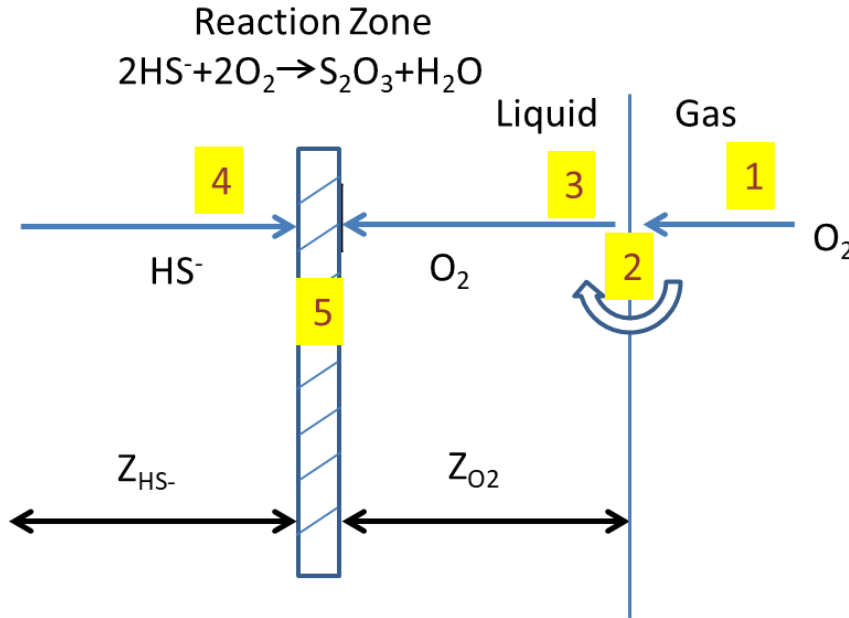


- $\text{Na}_2\text{S} + \text{H}_2\text{O} \rightarrow \text{NaHS} + \text{NaOH}$  (hydrolysis)
- $2\text{NaHS} + 2\text{O}_2 \rightarrow \text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O}$  (heat)

## ▪ $\text{Na}_2\text{S}_2\text{O}_3$ production

- 1<sup>st</sup> order reaction with respect to Sulphide
- Faster reaction rate compared to  $\text{SO}_4$  production
- Limited by mass transfer initially and later on by chemical kinetics
- Exothermic
- Equilibrium reaction (i.e., reversible to some degree as opposed to FOWL to  $\text{SO}_4$ )

# KINETIC MODEL



## Rate of Reaction Resistances

1. Diffusion of O<sub>2</sub> in the gas phase through air or water vapor
2. Solubility of Oxygen
3. Diffusion of O<sub>2</sub> from phase boundary to reaction zone
4. Diffusion of HS<sup>-</sup> to reaction zone
5. Chemical Kinetics governing the reaction zone

# BUBBLE COLUMN REACTOR

## ▪ Operation:

- WL enters 1<sup>st</sup> stage through a tube at the origin and undergoes reaction as it is contacted with sparged air bubbles, rising from the bottom of the vessel.
- WL enters outer annular region (2<sup>nd</sup> stage) and flows around it reaching the baffle from where it underflows to 3<sup>rd</sup> stage before exiting.

## ▪ Reaction takes place in 3 stages:

- Inner cylindrical compartment is used as 1<sup>st</sup> stage.
- Outer compartment is used for the second and third stages. The outer compartment is baffled to divide it into half.
- **Retention Time: 2-3 hours** (atmospheric pressure along with relatively low interfacial area leads to high required residence times)

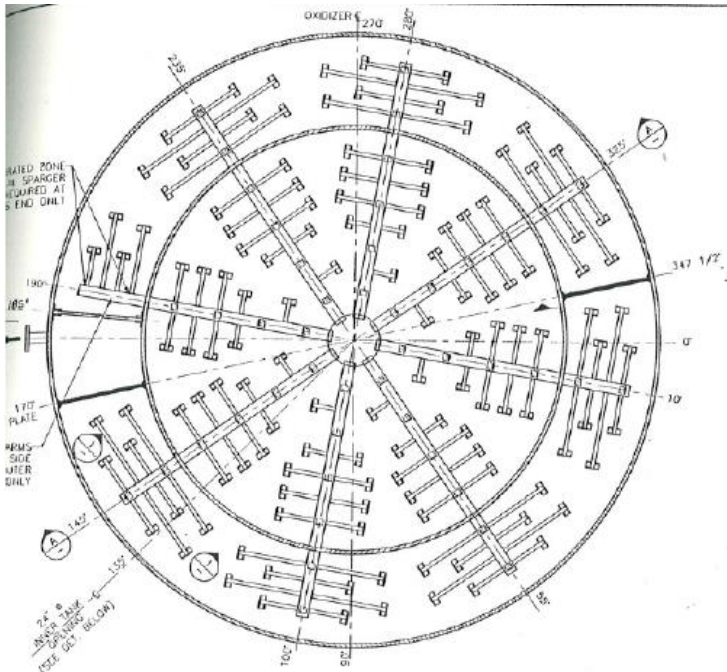
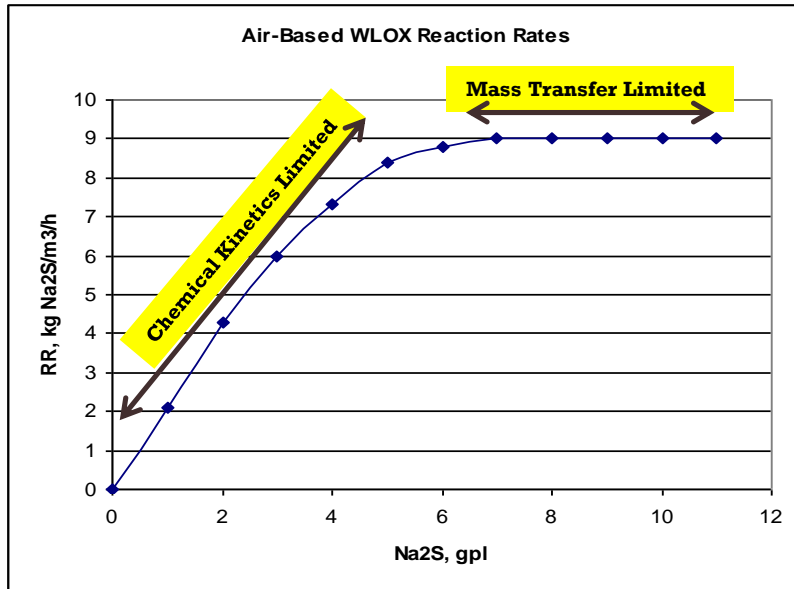


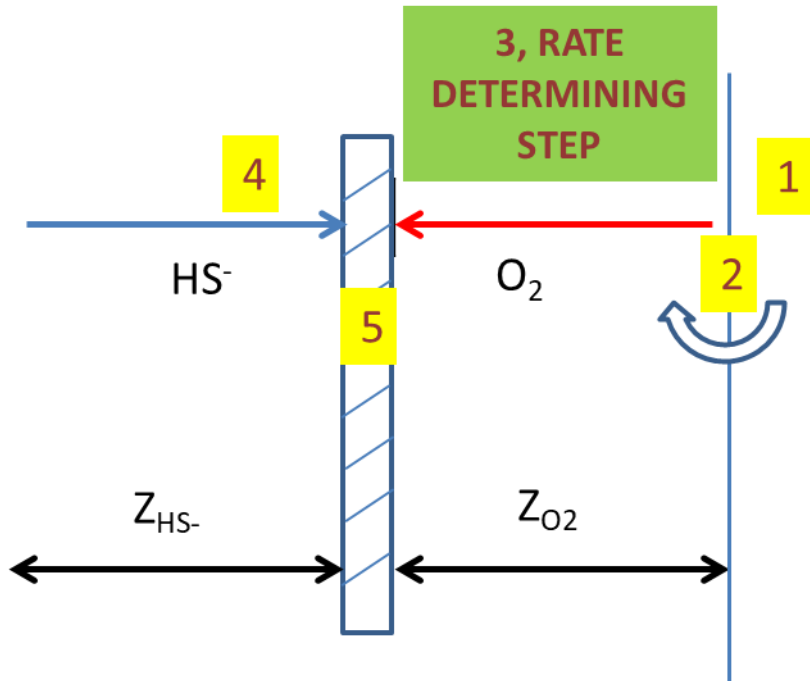
Figure 1 WLOX Reactor Cross-sectional View

# KINETICS RATE OF WLOX BUBBLE COLUMN REACTOR



- The reaction is oxygen limited when sulfide is highly concentrated
- The reaction is sulfide limited when the sulfide concentration is low

# HOW TO IMPROVE OVERALL RATE OF REACTION?



## MASS TRANSFER:

- Increase the rate of diffusion of  $O_2$  from phase boundary to reaction zone by reducing the distance from phase boundary to reaction zone.
  - Use a reactor that can provide a thin liquid film (Packed bed or Fluidized bed reactor)
- Increase interfacial area by decreasing average bubble size

## CHEMICAL REACTION:

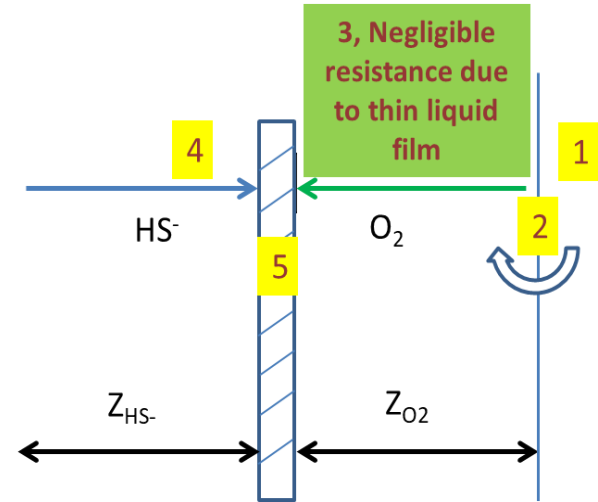
- Increase the rate by using a catalyst (weak black liquor, lime mud, any other)
- Increase the reaction rate by increasing the temperature.
- Utilize plugflow conditions to maximize concentration gradient and thus increase reaction rate at a given temperature

# PACKED BED REACTOR

- Provides higher surface area per unit volume than a bubble column reactor
- Low /negligible diffusion resistance due to formation of thin liquid film which is continuously renewed
- Reaction totally governed by chemical kinetics with rate being a function of partial pressure and solubility of oxygen, concentration of sulfide ions and temperature

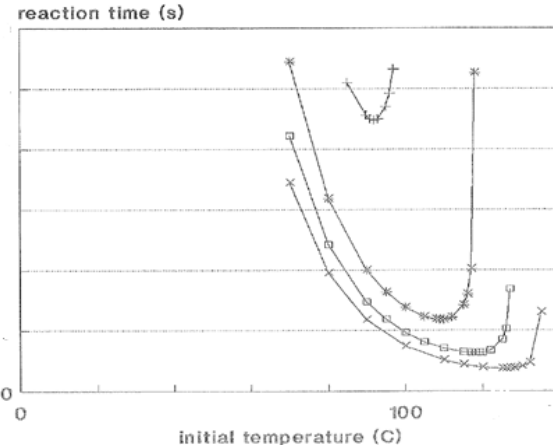
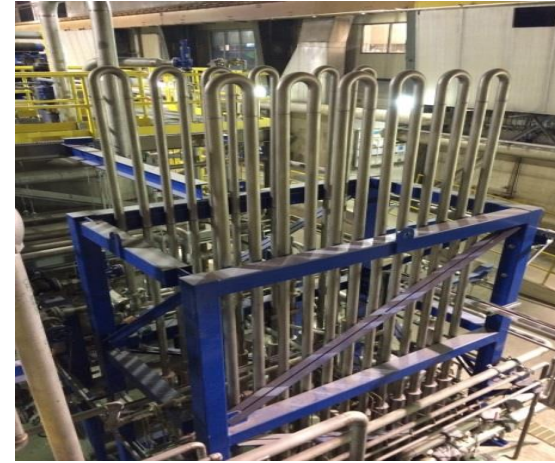
$$\frac{dCHS^-}{dt} = -Ae^{\frac{EA}{RT}} C_{HS^-}^n C_{O_2}^m$$

- Tremendous reduction in residence time compared to air-based bubble column reactor.
- At elevated temperature instantaneous brown-black thin scale (Fe, Mn, Mg, Si, C, O) was observed during pilot runs.



# PIPELINE REACTOR

- Oxygen is mixed with white liquor at an operating pressure determined by available oxygen.
- A temperature rise due to exothermic reaction affects reaction rate as oxygen mass transfer rate decreases as temperature increases
- Lower capital cost for pipeline reactor would be partially offset by higher operating costs due to need of oxygen in pipeline reactor
- Rapid scaling is known to occur in current oxidizers in higher temperature zones, such as discharge area, which necessitates frequent acid washing



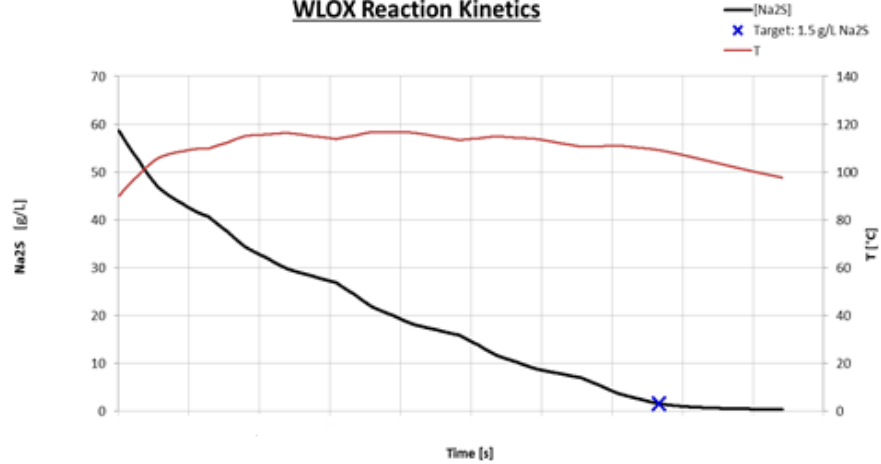
# ISOFLO™ OXIDIZER

- Standard vertically oriented U-tube exchanger, with tube passes interconnected and sealed via a proprietary channel head.
- Oxygen is injected into the Oxidizer in multiple locations
- The oxidized white liquor is cooled by a recirculating flow on the shell side of the oxidizer.
- Mill water is added to the cooling loop to control the oxidized white liquor outlet temperature from the oxidizer.
- Oxidized white liquor can be recirculated to provide turndown and maintain steady conditions in the reactor.

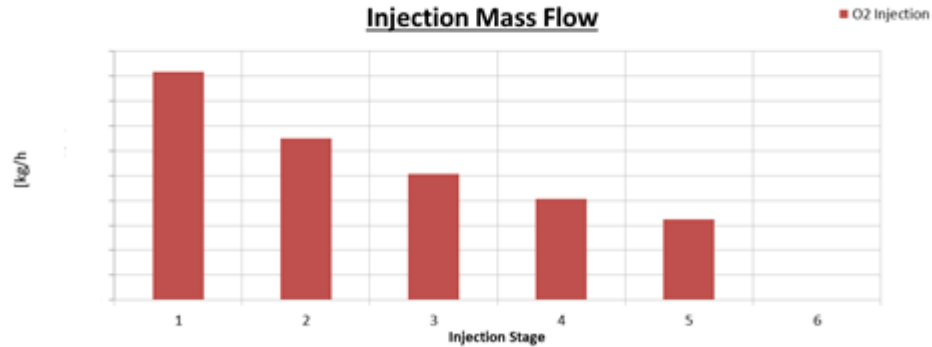


# ISOFLU™ REACTOR PERFORMANCE

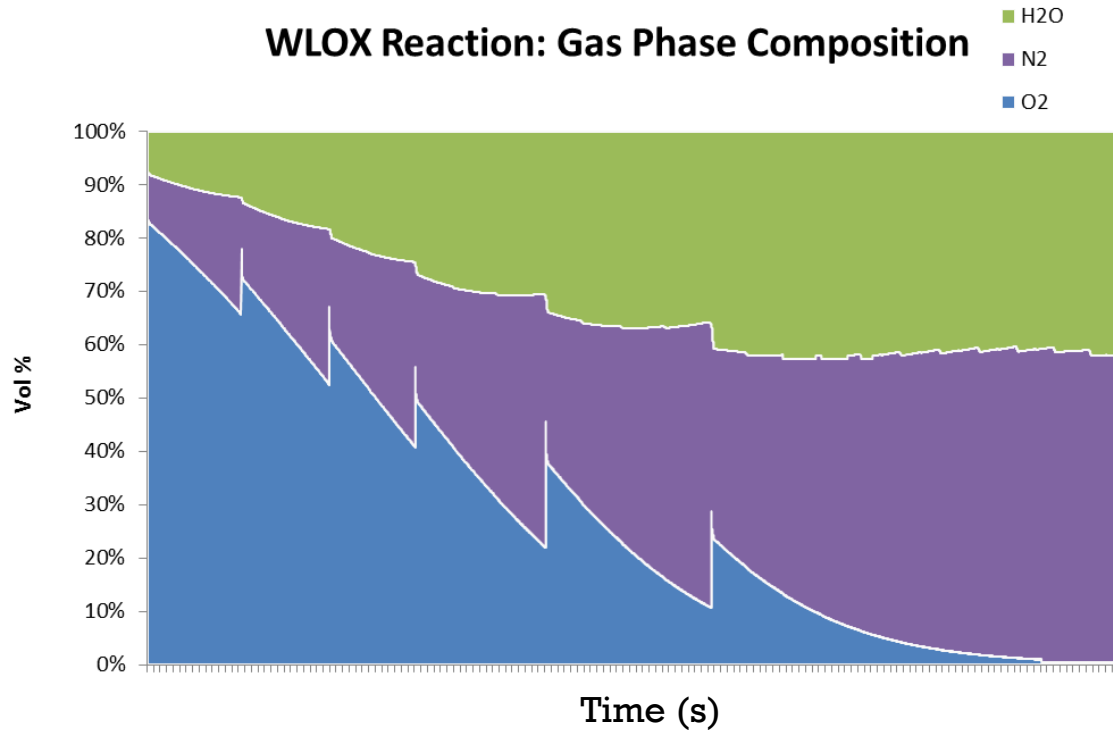
## WLOX Reaction Kinetics



## Injection Mass Flow



# IsoFlo™ Reactor Performance



# SUMMARY OF ISO FLO™ OXIDIZER

- Plug flow minimizes volume and maximizes efficiency.
- Plug flow configuration results in very low O<sub>2</sub> venting and maximum O<sub>2</sub> utilization
- Integrated heat recovery and temperature control. No need for external cooler.
- Controlled operation below stress corrosion cracking limits - increased safety, reliability, and equipment life
- High temperature decreases oxygen solubility. Controlled operation results in low O<sub>2</sub> consumption
- Controlled temperature at high turbulence will minimize rapid scaling at high temperature

# SUMMARY OF ISOFLU™ OXIDIZER

- Control the outlet temperature of cooling water to mill desired temperature
- Vertical Orientation, Small Footprint
- Infinite turndown
- No by-passing, channeling, or back-mixing issues as seen in a Bubble Column, Packed Bed, or Agitated reactors
- Provision for easy mechanical cleaning if required
- Can also be used to oxidize black liquor if mill is recovery boiler bottlenecked and increase pulp production by ~3-5%.

# QUESTIONS?

