Review of degradation and corrosion inhibition for chemical absorption

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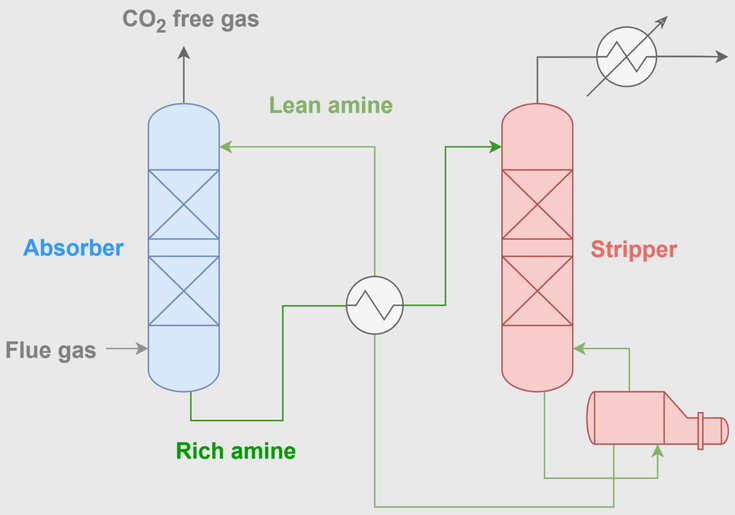
Introduction



Oxidative degradation:

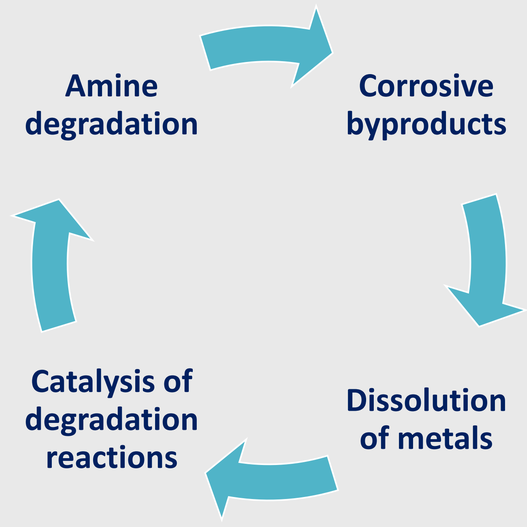
- Caused by oxidizing agents in the flue gas (O_2, SO_x, NO_x)
- Primarily takes place in the **Absorber**

Thermal degradation:

- Caused by exposure to high temperature (~100-130°C)
- Takes place in the **Stripper**

Corrosion:

- Some degradation products induce corrosion of the metal equipment
- Metals like Fe, Cu and V act as catalysts towards amine degradation



Inhibitor Evaluation

An ideal inhibitor for amine-based absorption needs to effectively prevent amine oxidation, while being thermally stable, non-corrosive and non-toxic. More than 40 different compounds have been tested in the literature, as potential inhibitors, however, no single additive or blend fulfils all criteria. The table below compares selected inhibitors reviewed in this work.

Categories

Fe^{2+} **Chelating agents**: Chemically bond with dissolved metals mitigating their catalytic effect on degradation.

$O_2/ROO^{\cdot}$ **Oxygen/radical scavengers:** React competitively with dissolved oxygen or free radical intermediates preventing amine oxidation.

Heat stable salts (HSS): Decrease O_2 solubility in the aqueous solvent by increasing the ionic strength of water. Stable salt accumulation is generally indicative of degradation, however the addition of certain stable salts (e.g. KI) can significantly reduce amine loss.

Oxidation passivators: Adsorb onto the metal surface forming a protective film layer that prevents corrosion.

Inhibitor	Mechanism	Oxidative degradation mitigation	Corrosion mitigation	Thermal stability	Toxicity
Potassium Iodide (KI) [1-6]	Scavenger/ stable salt				
1,3-diaminopropane-*N*,*N*,*N*,*N* -tetraacetic acid (PDTA) [11]	Chelating agent				
ethylenediaminetetraacetic acid (EDTA) [1, 8, 9]	Chelating agent				
etidronic acid (HEDP) [1, 13, 14]	Chelating agent				
diethylenetriamine pentaacetic acid (DTPA) [1, 14]	Chelating agent				
2,5-dimercapto-1,3,4-thiadiazole (DMTD) [1, 14]	Scavenger/ chelating agent				
Carbohydrazide [11, 13]	O_2 scavenger				
Sodium metavanadate ($NaVO_3$) [11, 12]	Oxidation passivator				
Sodium sulfite (Na_2SO_3) [7, 8]	O_2 scavenger				
Bicine [8-10]	Radical scavenger				
Formaldehyde [8]	O_2 scavenger				

Degradation mitigation: *excellent oxidation inhibition, moderate oxidation inhibition, increased degradation*
Corrosion mitigation: *corrosion reduction, negligible effect, increased corrosion*
Solvent thermal stability at stripper conditions: *Increased stability at stripper conditions, negligible effect, increased thermal degradation or inhibitor decomposition*
Toxicity: $LD_{50} >> LD_{50\ MEA}$, $LD_{50} \approx LD_{50MEA}$, $LD_{50} << LD_{50\ MEA}$

Conclusions

- KI, HEDP, DTPA and DMTD are the best oxidation inhibitors, reducing amine oxidation by more than 90% in isolated absorber conditions.
- HEDP inhibition is drastically decreased when added to an already thermally degraded amine solution, while DTPA and DMTD gradually lose their effectiveness over time.
- KI is the only reviewed additive that is not consumed while inhibiting oxidation, making it potentially a promising inhibitor.
- Oxidative degradation inhibitors seem to have stability issues at high temperatures, and therefore inhibitor testing at process-relevant conditions is highly important.
- Some degradation products (e.g. bicine) and expected oxidation intermediates (e.g. formaldehyde) may provide inhibition, indicating that amine oxidation could be partially self-limiting.

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Future work

- More work towards identifying and testing potential inhibitors **under process-relevant conditions** is needed. Laboratory work to help explain the complex relationships between the additives and process parameters, could allow for the development of more effective inhibitors.
- It has been proposed that the decrease in inhibition can be attributed to metal ion concentration increase during temperature cycling. Therefore, further testing of **degradation-corrosion inhibitor blends** could prove valuable.

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