
Question 42: Are you adding hydroxyl generating compounds (methanol or other alcohols) to the chlorination zone of the continuous catalytic regeneration section of their reforming unit? What are the observed results of this procedure?

Michael Windham (UOP)

Whether or not methanol or another hydroxyl is injected into the oxy-Chlorination zone is based on the design of the regenerator. UOP designed units do not inject hydroxyls into the oxy-Chlorination zone, UOP recommends you contact the process Licensor before making any alternations to the Regeneration Tower flows or controls.

There are two primary objectives of the oxy-Chlorination: metals dispersion and obtaining the target chloride on catalyst. When methanol is injected into the oxy-Chlorination, a higher organic chloride rate is required to obtain the target chloride on catalyst; consequently, a higher chloride agent injection rate is required.

Injecting methanol into the oxy-Chlorination zone was originally patented by UOP in 1971, but not used commercially. UOP designs the burn zone to have a high Cl/Cl₂ concentration, resulting in minimal metal agglomeration in the burn zone. Consequently, because of minimal metal agglomeration, water injection into the oxy-Chlorination was not required. The minimal metal agglomeration in UOP's burn zone is exemplified by high H₂/Pt with fresh catalyst in black burn operation (i.e., no oxychlorination).

Operational issues with injecting water are less flexibility in optimizing chloride on catalyst from the regenerator, since two targets are trying to be achieved. A higher chloride on catalyst may result in higher cracking and lower yields. _____

Olivier Le-Coz (Axens)

The relevance or necessity of injecting alcohols in the oxy-chlorination zone depends on the conditions in the upstream burning zone of the regenerator and how this zone is designed. The facility to inject alcohols in the oxy-chlorination zone is foreseen in Axens design. Even without the dedicated line, it is still possible to inject alcohols by diluting them with the chlorinating agent and use the dedicated injection line provided the pump capacity is sufficient.

In Axens design water or hydroxyl generating compounds injection to this zone allows better controlling of the Delta chloride which is achieved in the regenerator of the CCR. Sufficient chlorine injection in the oxy-chlorination zone is essential to ensure good Platinum re-dispersion, but the total resulting chloride content on the alumina support must not exceed an optimum value. Too high chloride would enhance the catalyst acidity too much resulting in increased activity but non optimal selectivity towards reformate

product. The chloride content on the catalyst depends on the equilibrium between water and HCl bonding on the catalyst support which is related to the ratio between water and HCl in the gas phase surrounding the catalyst. Injection of water or alcohol in the oxy-chlorination zone allows better control of this optimum ratio.

Erik Myers (Valero) This is more of a licensor specific item. We have one such unit and the unit operates well with the prescribed use of methanol in the chlorination zone.

Brad Palmer (ConocoPhillips)

ConocoPhillips does not add hydroxyl generating compounds to our CCR chlorination zone nor to the feed. There is enough moisture in the recycle streams to keep a good water/chloride balance on the catalyst. Adjusting the PERC injection rate is sufficient to maintain the correct chloride levels.

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2011