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SOx reduction additive for UFCCs

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The use of an additive to reduce SO_x emissions in Fluid Catalytic Cracking (FCC) units is a reliable and cost-effective strategy that enables refiners to comply with increasingly stringent environmental regulations while enhancing unit profitability by processing more challenging high-sulfur feeds.

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Risks of SO_x emissions: Sulfur oxides (most abundant species: SO_2 and SO_3 – so called SO_x) are considered air pollutants due to their detrimental effects on both the environment and human health. In industry, SO_3 can also react with water vapors from flue gas forming sulfuric acid (H_2SO_4), which is corrosive and can cause significant damage to equipment. [1]

Source of sulfur: The feed processed in FCC units often contains heteroatoms, including sulfur. The sulfur content in the feed can vary from 0.1% to 4% by weight. [2]

Distribution of sulfur in products: Depending on the origin of the oil and operating conditions, the distribution of sulfur among the products varies approximately as presented in Figure 1. Typically, 3 to 10% of the sulfur in a UFCCs feed ends up as sulfur contained in the spent catalyst coke and is responsible for the SO_x emissions in the unit's combustion gases. When the spent catalyst is regenerated, sulfur is oxidized to SO_2, SO_3, and other sulfur species. In this process, it is essential to ensure that SO_x emissions comply with current environmental standards and regulations.

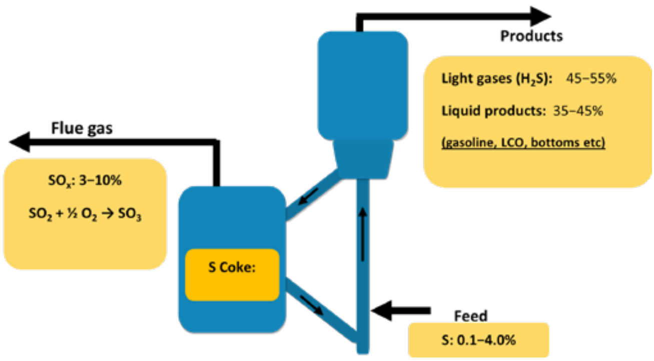

Figure 1: Distribution of sulfur in UFCC products. [2]

Solutions for reducing sulfur emissions

Some main measures can be implemented at UFCC to reduce emissions, such as:

- Feed selection and/or pre-treatment (mainly hydrotreatment) to reduce the sulfur in the feed;
- Hardware solutions that remove SO_x from flue gas (for example: flue gas wet gas scrubbers);
- SO_x reduction additives.

Hardware modifications usually involve a large capital investment. In this context, the use of additives may be the fastest and most feasible solution for a FCC unit.

Sulfur capture and release mechanism

Additive mechanism	Development of product	Magnesium role in the additive
• Designed to capture the oxidized sulfur compounds present in the regenerator and release them in the riser; • Sulfur leaves the FCC unit as hydrogen sulfide (H_2S), along with the cracked products in the reactor effluent; • H_2S is easily processed in the gas plant downstream of the UFCC.	• **1970's** - catalysts based on MgO, Al_2O_3, $MgAl_2O_4$ (spinel), La_2O_3 and CeO_2 for FCC operations. • ***1980's - Ketjen*** pioneered and patented the use of hydrotalcite-based additive, ($Mg_6Al_2OH_{16}$), an anionic layered clay, which increased the Mg/Al ratio from 1:2 to 3:1 compared to other technologies.[3] • **Importance of the Mg/Al ratio:** Ketjen's product offers the highest amounts of Mg available in the market and, consequently, a highest reduction in SO_x emissions.	• Magnesium acts as a capture agent by forming magnesium sulfate in the regenerator. • The reducing environment of the riser releases sulfur from the magnesium sulfate, effectively regenerates the particle and makes it available to capture sulfur again in the next pass through the FCC unit.

Chemical reactions involved

The chemical reactions involving the additive occur throughout the catalyst cycle, as illustrated in Figure 2 below:

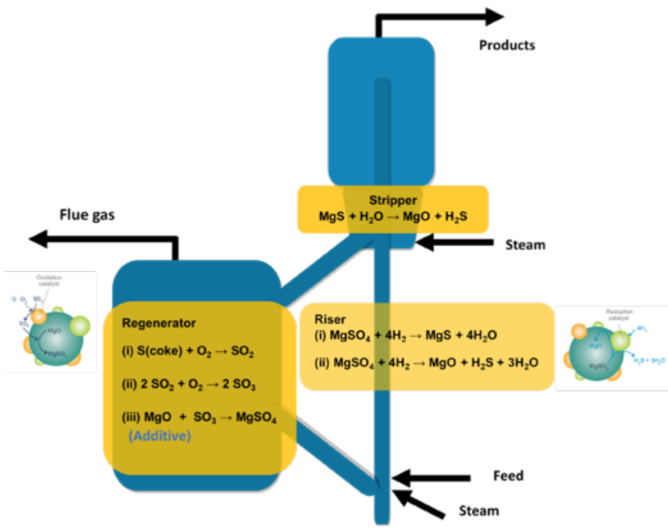

Figure 2: The sulfur capture (left) and release (right) reactions occurring during the use of SOx reduction additives. [3]

Regenerator: The SO_3 is chemisorbed onto the additive, forming magnesium sulfate ($MgSO_4$). Once this occurs, it circulates with the catalyst, and the compound moves to the riser section. The SO_x reduction additive is more effective at capturing SO_3 than SO_2, making it more beneficial for use in full combustion units. However, there are also additives developed for partial combustion units.

Riser: : In the reducing environment of the riser, H_2S release reactions occur, regenerating part of the additive.

Stripper: In the presence of steam, the remaining additive is regenerated with the release of H_2S.

Typical application of the SOx reducing additive

Additive injection rates: The percentage of additive typically ranges from 1% to 10% of the inventory. This concentration varies depending on the UFCC model design and, to a large extent, on the sulfur concentration in the feed. Units processing low-sulfur feeds may use less than 1% additive.

Reduction of SO_x emissions: The effectiveness of the additive's action may depend on factors such as higher partial pressures of SO_x and O_2, efficiency in the stripper and good distribution of catalyst and air in the regenerator. Field studies indicate that additives can generally reduce SO_x emissions by 50% to 80% in full combustion units and by 30% to 50% in partial combustion units, depending on operating conditions.

$DURASO_x$ additive from FCC S.A. - Ketjen

Operating efficiency:

- The $DURASO_x$ additive is the result of development work focused on creating SO_x reducing additives with the highest friction resistance on the market without compromising performance. In addition to being more resistant to particulate loss, the binding process used in $DURASO_x$ enables more active sites to be incorporated into each particle of the additive. The higher Mg/Al 3:1 ratio of this additive increases SO_x capture efficiency.

$DURASO_x$ is recommended for the following types of UFCC [3]:

- Full combustion operation;
- Loss-sensitive units with turbines and expanders;
- Opacity compliance issues due to the use of soft SO_x reduction additives;
- UFCCs operating under a conduct adjustment agreement with the environmental protection agency;
- Performance-oriented FCC units.

Reinforcing the importance of its application in industrial processes focused on greater sustainability and efficiency, the $DURASO_x$ additive from FCC S.A./Ketjen offers several benefits. It provides higher efficiency in SO_x removal with the same amount of additive compared to conventional additives, minimizes catalytic activity loss due to dilution effects and provides enhanced attrition resistance.

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About FCC S.A.

FCC S.A is a leading-edge technology company, with headquarters in Rio de Janeiro, comprising the Petrobras S.A. and Ketjen companies. Being the sole manufacturer of catalytic cracking catalysts and additives for petroleum refining in the South-American market, its consumer customers are the refineries of the Petrobras Systems, as well as the petroleum refineries of South-American countries.

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